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# 1 **Chemical modelling of Delayed Ettringite Formation for assessment of** 2 **affected concrete structures**

3

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## 7 **Abstract**

8 Delayed Ettringite Formation (DEF) modelling is addressed in the context of structural analysis. First,  
9 a chemical model is specified to simulate the effects of the heating of concrete in terms of reactions  
10 involving sulfates, aluminates and alkalis. It can be decomposed into: dissolution of primary  
11 sulfoaluminates at high temperature, fixation of aluminates in hydrogarnet or carboaluminates, and  
12 formation of delayed ettringite at low temperature. The influences of alkalis, temperature and water  
13 saturation on these reactions are taken into account. The main result of this model is the amount of  
14 delayed ettringite. The parameters of the proposed chemical model are fitted on a large number of  
15 experiments taken from the literature. The chemical model is then coupled with a nonlinear  
16 mechanical model based on poro-mechanics modelling. An application of chemo-mechanical  
17 coupling shows the features and benefits of such modelling to help practitioners in the management  
18 of structures affected by DEF.

19 Keywords: DEF, concrete, finite element, modelling

20

## 22 Introduction

23 Unexpected combinations of cement composition and curing conditions can lead to Delayed  
24 Ettringite Formation (DEF). This well-known deleterious chemical reaction takes place in the cement  
25 matrix often several years or decades after the concrete has been heated sufficiently to dissolve  
26 primary sulfoaluminate hydrates. The main causes of excessive heating can be either the exothermic  
27 reactions of cement hydration (which can occur particularly in massive structures like dams, large  
28 foundations, columns or beams), or overheating during the production of precast concrete elements.  
29 Since recommendations became available concerning the prevention of this problem (limits on the  
30 maximum temperature during hydration and of the amount of sulfates and alkali in cement),  
31 concrete structures can be built without apprehension [21]. However, the aptitude of DEF-affected  
32 structures has to be assessed to manage potential repairs or replacement. Various tools are available  
33 to help practitioners in this choice: follow-up of cracking to observe damage induced by the DEF,  
34 laboratory analysis, and residual swelling tests on core samples are the most used [28]. These  
35 experimental techniques are performed at a given moment and location. The question of the residual  
36 strength of the whole structure, and the future evolution of damage in the structure can only be  
37 addressed by combining these techniques with modelling. Unfortunately, DEF depends on many  
38 parameters (cement chemistry, interaction with aggregates, possibility of alkali leaching, concrete  
39 porosity, strength, concrete mechanical behaviour, maximum temperature reached, duration of the  
40 hot periods, water saturation, stress and strain states, and damage), so designing a DEF model  
41 applicable at the structure scale remains a challenge. Some models based on thermodynamic  
42 considerations are already able to explain the different reactions leading to DEF [19,36]. They are  
43 highly nonlinear, as several coupled equations have to be solved simultaneously, and are thus  
44 difficult to use in the context of structural analysis in an industrial situation where several thousands  
45 of chemical and structural computation have to be performed simultaneously at each node of finite  
46 element meshes and at each step of stepwise analysis. From a mechanical point of view, efficient  
47 nonlinear models exist to analyse structural behaviour affected by swelling problems  
48 [10,23,25,37,38] but they are not yet able to consider all the chemical particularities of DEF. The  
49 purpose of this work is to propose a simplified chemical model answering the need for structural  
50 modelling. It has to be simple enough to be coupled with a nonlinear mechanical model  
51 implementable in a finite element code. The paper starts with the chemical model assumptions and  
52 equations, and this model is then fitted on a large number of experiments from the literature. Finally,  
53 the chemical model coupled with the nonlinear mechanical model based on poro-mechanics

54 considerations is used to analyse the development of DEF expansion and cracking in a concrete  
 55 cylinder. The features and the interest of a coupled chemo-mechanics approach to managing  
 56 concrete structures affected by DEF is thus illustrated.

## 57 1 Principles and notations

58 In this model, the mineralogy of concrete is idealized in main phases noted  $E_1$  and  $M_1$  respectively for  
 59 the number of moles of primary ettringite and of primary monosulfate per unit of concrete volume.  
 60 These primary hydrates correspond to the theoretical amount that would be created in standard  
 61 conditions (ambient temperature, high humidity, complete hydration of cement). Their initial values  
 62 can be computed from the amount of cement, the chemistry of which is usually supplied by the  
 63 cement manufacturer. The number of moles of delayed ettringite is noted  $E_2$ . It corresponds to the  
 64 amount of delayed products created after a thermal cycle causing a dissolution of primary species.  
 65 Assessing these products is the aim of the present chemical model. Sulfates and aluminates adsorbed  
 66 in C-S-H during the heating period are considered to be available for DEF if the required  
 67 environmental conditions occur. They are noted  $\bar{S}$  and  $\bar{A}$  in the mass balance equations. The  
 68 correspondence between the variables, the chemical notations and the usual cementitious  
 69 abbreviations is given in Table 1.

70 **Table 1 : Notation correspondence between model abbreviation, cementitious notation and general chemistry notation**

Name / Notation (mole)	Model	Cementitious	General Chemistry Notation
Anhydrous phases			
Tricalcium Aluminate	$C_3A$	$C_3A$	$(CaO)_3(Al_2O_3)$
Ferrite	$C_4AF$	$C_4AF$	$(CaO)_4(Al_2O_3)(Fe_2O_3)$
Equivalent Tricalcium Aluminate	$C_3A^{eq}$	$C_3A + 2C_4AF$	$(CaO)_3(Al_2O_3) + 2(CaO)_4(Al_2O_3)(Fe_2O_3)$
Gypsum	$C\bar{S}$	$C\bar{S}$	$(CaO)(SO_3)$
Water	H	H	$H_2O$
Equivalent Alkali	$Na_2O^{eq}$	$Na_2O^{eq}$	$Na_2O + 0.658 K_2O^{(1)}$
Hydrates and ions (free or absorbed)			
Ettringite	$E_1,$ $E_2$	$(C_3A)(C\bar{S})_3H_{32}$	$(CaO)_6(Al_2O_3)(SO_3)_3 \cdot 32H_2O$
Monosulfate	$M_1$	$C_4A\bar{S}H_{12}$	$(CaO)_4(Al_2O_3)(SO_3) \cdot 12H_2O$
Available Sulfates	$\bar{S}$	$\bar{S} + C\bar{S}$	$SO_4^{2-} + Ca SO_4$
Iron	F	F	$Fe_2O_3$

Aluminium	A	A	$Al_2O_3$
Available Aluminates	$\tilde{A}$	$A + C_3AH_6$	$(Al(OH)_4^-)_{1/2} + (CaO)_3(Al_2O_3)(H_2O)_6$
Hydrogarnet	G	$C_3AS_yH_{4(3-y)}$	$Ca_3(Al_xFe_{1-x})_2(SiO_4)_y(OH)_{4(3-y)}$
Calcium Silicate Hydrates	CSH	C-S-H	$(CaO)_{1.65}(SiO_2)(H_2O)_{2.45}$
Mass Balance Variables			
Total aluminate	$A_c$	Total A	$Al_2O_3$
Total sulfate	$S_c$	Total $\bar{S}$	$SO_3$
Equivalent number of moles of alkali	$Na_{eq}$	$Na_{eq}$	$Na^+ + K^{+(3)}$
Alkali concentration in saturated porosity	(Na)	$\frac{Na_{eq}}{\phi \cdot S_r + k^{(2)} \cdot CSH}$	$[Na^+] + [K^+]$
Ferrite fraction	$\rho_F$	$\rho_F = \frac{F}{A + F}$	-

71 (1) if the calculus is performed with the mass instead of the moles number

72 (2) The coefficient k (0.077 l/mol) concerns alkali fixation in C-S-H. It is calculated according to  
73 [24],but this coefficient can also be taken equal to 0 if the heating takes place at early age.

74 (3) In moles number

75 Table 2 : Physical Data

Data	Notation	Definition
Temperature	T	Absolute temperature
Concrete porosity	$\emptyset$	Void volume per volume unit of concrete
Free water volume	W	Volume of free water per unit volume of concrete
Saturation rate	$S_r$	$W/\emptyset$

76

77 The total number of moles of sulfates in a unit volume of concrete is noted  $S_c$  and the total number  
78 of moles of aluminates,  $A_c$ . According to [1], due to the solid–liquid equilibrium, the ionic  
79 concentrations of aluminates and sulfates are about 100 times smaller than the concentration of  
80 calcium or alkali. Therefore these two species are rapidly bound by the production of new phases  
81 and their mass transfer can be neglected at the scale of the structure. The mass balances imply that  
82 equations (1) and (2) are constantly verified.

$$83 \quad A_c = E_1 + E_2 + M_1 + G + \tilde{A} \quad (1)$$

$$84 \quad S_c = 3(E_1 + E_2) + M_1 + \tilde{S} \quad (2)$$

85 with  $G$ , the hydrogarnet (Table 1) that can be formed at high temperature [16].

86 Alkalis do not act directly in the two reactions but they strongly interfere with other ionic species in  
87 thermodynamic equilibrium (fixation of  $S$  in C-S-H [18], affect portlandite equilibrium and thus  
88 calcium concentration [36]). Only the alkalis are assumed to be significantly mobile at structure scale.  
89 They can be fixed reversibly by C-S-H, be leached out of concrete or be consumed in alkali-silica  
90 reaction. Their initial concentration in the concrete pore solution thus depends on the saturation  
91 degree ( $Sr$ ) (defined in Table 2) and the amount of C-S-H per unit volume of concrete (Table 1).

92 The main chemical phenomena considered in this model are:

- 93 • Progressive dissolution or delayed formation of Primary Aluminous hydrates ( $E_1$  and  $M_1$ )  
94 when the temperature exceeds a threshold of dissolution noted  $T_{th,d}$ . The ionic species,  
95 products of the dissolution, are stored in different forms of aluminate (carboaluminates in  
96 the case of lime aggregates or lime additions [42]), or hydrogarnet if the temperature is  
97 greater than another threshold  $T_{th,f}$  [16,36], or can be reversibly bound in the cement  
98 matrix. The aluminate available for DEF is noted  $\tilde{A}$ . The sulfates that are reversibly absorbed  
99 in the cement matrix and are available for DEF are noted  $\tilde{S}$ .  $\tilde{A}$  and  $\tilde{S}$  are the main state  
100 variables of the model.
- 101 • Conversion of a proportion of available aluminates  $\tilde{A}$  into hydrogarnet ( $G$ ) if the temperature  
102 stays above the threshold value of fixation  $T_{th,f}$ , for long enough [16].
- 103 • Conversion of available aluminates  $\tilde{A}$  or  $M_1$  and available sulfates  $\tilde{S}$  into secondary ettringite  
104 ( $E_2$ ) when the temperature drops below the threshold of dissolution  $T_{th,d}$ . If some residual  
105 monosulfate  $M_1$  subsists after the heating period, it can be combined with available sulfates  
106  $\tilde{S}$  and converted into secondary ettringite [45]. When  $M_1$  is used up, the formation of  
107 delayed ettringite also consumes  $\tilde{A}$ .

108 Three main impacts on the chemical phenomena have to be quantified in modelling:

- 109 • Alkali concentration ( $Na$ ) acts on the temperature threshold of dissolution  $T_{th,d}$  and on the  
110 kinetics of dissolution and precipitation of hydrates [5,26,34].
- 111 • Temperature ( $T$ ) activates the diffusion into the unit volume of concrete and activates  
112 chemical reactions [27].
- 113 • The Water Saturation ratio of the concrete porosity ( $Sr$ ) can limit the kinetics of DEF  
114 precipitation when the temperature is lower than  $T_{th,d}$  [43], but it does not limit the  
115 dissolution of primary sulfoaluminates at high temperature because water released by  
116 ettringite is assumed to allow ions to migrate toward the adsorption sites (specifically C-S-H).

117 Two other parameters of influence are listed below but are not yet considered in the model  
118 because of the lack of experimental results:

- 119 • Ferrite fraction,  $\rho_F$  (Table 1) which could delay the DEF and modify the kinetics towards the  
120 end of the reaction [33].
- 121 • Sulfate sorption capability in C-S-H, which could limit the amount of sulfate available for DEF  
122 due to a supersaturation in sulfate during the heating period [17].

123 These last two parameters could have an important impact in cases of blended cement [33]. In fact,  
124 in such cements, the ferrite fraction,  $\rho_F$ , can be greater than in classic clinker, and the additions can  
125 decrease the calcium / silica ratio in C-S-H, which modifies the sulfate sorption capability of the C-S-  
126 H. For the sake of simplicity, this limitation is not considered in the present model, where all the  
127 sulfates can be absorbed in C-S-H if the heating period is long enough. Concerning the action of the  
128 ferrite fraction, it is not explicitly considered but is assumed to be included in the parameters  
129 controlling the kinetics of the DEF.

130 In the present work, the model is specified in the form of differential equations so as to be able to  
131 follow the variable evolutions of environmental conditions (temperature,  $T$ , water saturation rate,  
132  $S_r$ , and alkali concentration ( $Na$ )). A differential equation can easily be implemented in any finite  
133 element code to compute the amount of DEF, with a time finite difference method for instance. If  
134 the environmental conditions are piecewise constant, an analytical solution of the model can be  
135 found and used. The analytical solution is especially convenient for fitting the model with  
136 spreadsheet software.

137 Once the chemical model is solved, the amount of DEF is known and can be used in a poro-  
138 mechanical model able to compute the structural effects of expansion [23] [22]. This mechanical  
139 aspect of the modelling can be decoupled from the chemical ones since the pressure induced by the  
140 DEF remains lower than the thermodynamic pressure needed to stop the chemical reaction.  
141 According to [11] cited in [2], the crystallization pressure is proportional to the logarithm of the  
142 activity product. The activity product can be very high in the concrete porosity since the available  
143 species involved in the DEF are supplied by an amount of cement that is large relative to the volume  
144 of free water. As concrete can crack at low pressure due to its low tensile strength, the mechanical  
145 pressure is considered never to be sufficient to limit the DEF in this simplified model. In addition, due  
146 to the concrete pore microstructure, not all the DEF participates in expansion [19]. This is also  
147 considered in the proposed poro-mechanical model [22,23].

148 **2 Chemical Model Formulation**

149 **2.1 State variables and initial conditions for the chemical problem**

150 For any simulation of DEF, the process begins with the determination of the initial conditions for the  
 151 different state variables of the model. The state variables are the ones corresponding to the set  
 152 called “Hydrates and Ions (free or absorbed)” in Table 1. Their determination results from the  
 153 compatibility between anhydrous phases and hydrates. To simplify the model, ferrites and  
 154 aluminates are first merged in an equivalent moles number of  $C_3A$  noted  $C_3A^{eq}$ :

155 
$$C_3A^{eq} = C_3A + 2C_4AF = A + F \quad (3)$$

156 Then the total number of moles of aluminates  $A_c$  and sulfate  $S_c$  provided by the cement are  
 157 computed:

158 
$$A_c = C_3A^{eq} \quad (4)$$

159 
$$S_c = \bar{S} \quad (5)$$

160 with  $\bar{S}$  the sulfate contained in the initial gypsum (Table 1).

161 According to the molar ratio of sulfate / aluminate, the different state variables are initialized as  
 162 follows. These relations can be easily retrieved using the stoichiometry of the hydration reactions. If  
 163 the ratio is greater than 3, primary ettringite can be created:

164 
$$\text{If } \left(\frac{S_c}{A_c}\right) > 3 \Rightarrow \begin{cases} E_1 = A_c \\ M_1 = 0 \\ \tilde{A} = 0 \\ \tilde{S} = S_c - E_1 \\ G = 0 \\ E_2 = 0 \end{cases} \quad (6)$$

165 If the sulfate / aluminate ratio is between 1 and 3, mono- and tri-sulfoaluminates coexist:

166 
$$\text{If } 1 \leq \left(\frac{S_c}{A_c}\right) \leq 3 \Rightarrow \begin{cases} E_1 = \frac{S_c - A_c}{2} \\ M_1 = \frac{3A_c - S_c}{2} \\ \tilde{A} = 0 \\ \tilde{S} = 0 \\ G = 0 \\ E_2 = 0 \end{cases} \quad (7)$$

167 If the sulfate/aluminate ratio is lower than 1, only monosulfate exists and residual aluminates are  
 168 stored in variable  $\tilde{A}$ :

$$169 \quad \text{If } \left(\frac{S_c}{A_c}\right) < 1 \Rightarrow \begin{cases} E_1 = 0 \\ M_1 = S_c \\ \tilde{A} = A_c - M_1 \\ \tilde{S} = 0 \\ G = 0 \\ E_2 = 0 \end{cases} \quad (8)$$

## 170 2.2 Mass balance equations

171 Two cases have to be envisioned:

- 172 • The temperature is greater than or equal to the dissolution threshold,  $T_{th,d}$ . This leads to  
173 dissolution of the primary hydrates ( $E_1, M_1$ ) (or avoids their formation if the heating cycle  
174 takes place at early age) to produce free forms of aluminates ( $\tilde{A}$ ) available to form  
175 carboaluminates in presence of lime, or hydrogarnet if the temperature is kept higher than  
176 the fixation threshold,  $T_{th,f}$ , for long enough.
- 177 • If the temperature is lower than the dissolution threshold,  $T_{th,d}$ , the free aluminates ( $\tilde{A}$ ),  
178 sulfates ( $\tilde{S}$ ) and the monosulfate ( $M_1$ ) can be combined to produce DEF.

### 179 2.2.1 Chemical reactions at temperatures higher than the dissolution threshold $T_{th,d}$

180 When the temperature allows the dissolution of sulfoaluminates, ettringites - whether they are in a  
181 primary or a secondary form ( $E_1$  and  $E_2$ ) - and the monosulfate  $M_1$  are destabilized [13–15],  
182 (equation set 9):

$$183 \quad \begin{cases} \frac{\partial E_1}{\partial t} = -\frac{E_1}{\tau_d} \\ \frac{\partial M_1}{\partial t} = -\frac{M_1}{\tau_d} \\ \frac{\partial E_2}{\partial t} = -\frac{E_2}{\tau_d} \end{cases} \quad (9)$$

184 with  $\tau_d$  the characteristic time for the dissolution processes. The dissolution of the three species is  
185 not instantaneous. The characteristic time translates the progressivity of the dissolution processes  
186 associated with the diffusion and sorption of released ions. A single characteristic time is used for  
187 sake of simplicity. As illustrated below, the results obtained with this simplification are in good  
188 accordance with experimental results. Even if the different sulfo-aluminates hydrates have different  
189 sensitivity towards the temperature rising, the diffusion of dissolved species and their fixation are  
190 certainly slower than the thermodynamic destabilization. Thus, it is not necessary to use different  
191 characteristic times for the different sulfo-aluminate hydrates. The species released by the  
192 dissolution lead to an increase of free aluminates ( $\tilde{A}$ ) and sulfates ( $\tilde{S}$ ). The sulfates are assumed to be  
193 reversibly bound in cement hydrates [17]. They remain available for the DEF:

194 
$$\frac{\partial \tilde{S}}{\partial t} = -3 \left( \frac{\partial E_1}{\partial t} + \frac{\partial E_2}{\partial t} \right) - \left( \frac{\partial M_1}{\partial t} \right) \quad (10)$$

195 At high temperature ( $T > T_{th,f}$ ) the free aluminates ( $\tilde{A}$ ) can be converted to hydrogarnet ( $G$ )  
 196 [16,36], or carboaluminates in presence of limes. The kinetics of the production of hydrogarnet and  
 197 carboaluminates depends on the amount of aluminate released from primary hydrates: the greater  
 198 the amount of aluminate released, the greater the production of hydrogarnet or carboaluminate. The  
 199 dependence is given by equation (11):

200 
$$\frac{\partial G}{\partial t} = \frac{\tilde{A}}{\tau_f} \quad (11)$$

201 with  $\tau_f$  the characteristic time for the fixation of aluminates in hydrogarnets or carboaluminates. Due  
 202 to this reaction, the mass balance equation of free aluminates ( $\tilde{A}$ ) has to consider this possibility:

203 
$$\frac{\partial \tilde{A}}{\partial t} = - \left( \frac{\partial E_1}{\partial t} + \frac{\partial E_2}{\partial t} + \frac{\partial M_1}{\partial t} \right) - \frac{\tilde{A}}{\tau_f} \quad (12)$$

204 Using the mass balance equations (1) and (2) in (12) leads to the following differential equations:

205 
$$\begin{cases} \frac{\partial \tilde{A}}{\partial t} = \frac{A_c - G - \tilde{A}}{\tau_d} - \frac{\tilde{A}}{\tau_f} \\ \frac{\partial G}{\partial t} = \frac{\tilde{A}}{\tau_f} \end{cases} \quad (13)$$

206 If the characteristic times  $\tau_d$  and  $\tau_f$  remain constant during a period  $\Delta t = t - t_0$ , and the threshold  
 207 temperatures both exceeded, the two differential equations (13) can be merged into one:

208 
$$\frac{\partial^2 \tilde{A}}{\partial t^2} + \left( \frac{1}{\tau_d} + \frac{1}{\tau_f} \right) \frac{\partial \tilde{A}}{\partial t} + \frac{\tilde{A}}{\tau_d \tau_f} = 0 \quad (14)$$

209 This last equation admits an analytical solution given in the appendix. This solution can be used to fit  
 210 the model from an experimental result obtained with a thermal cycle presenting a substantial  
 211 temperature plateau or, in a finite element context, to improve the numerical accuracy for a time  
 212 step  $\Delta t$ , during which the environmental conditions can be considered as fixed.

### 213 **2.2.2 Chemical reaction at temperature lower than the dissolution threshold $T_{th,d}$**

214 The aluminates  $\tilde{A}$  and sulfates  $\tilde{S}$  available for DEF depend on the duration of the heating period. They  
 215 are computed during the hot period using the equation set presented above. When the heating  
 216 period ends, concrete returns to the ambient temperature  $T < T_{th,d}$ . The dissolution of  
 217 sulfoaluminates and the formation of hydrogarnet are then no longer possible, but DEF can occur.  
 218 The DEF is also modelled by a differential equation able to consider variations of environmental  
 219 conditions. As shown in [36], the DEF kinetics is mainly controlled by the release of sulfates bound in

220 the cement matrix, so in the present simplified modelling this phenomenon is assumed to control  
 221 totally the precipitation kinetic:

$$222 \quad \frac{\partial E_2}{\partial t} = \frac{\tilde{S}}{\tau_p} \quad (16)$$

223  $\tau_p$  is the characteristic time to control the precipitation kinetics. It depends on the water saturation  
 224 rate  $S_r$ , which allows the different chemical species to move towards one another by diffusion under  
 225 the influence of the chemical affinity of the reaction. It also depends on the alkali concentration  
 226 ( $Na$ ), which favours the retention of sulfates in C-S-H, delaying their release into the pore solution  
 227 according to the model of Salgues et al [36], and possibly on the ferrite fraction,  $\rho_F$ , because  
 228 ettringite containing Fe is generally created more slowly than that with Al [33].

229 If monosulfates  $M_1$  subsist after the hot period, sulfates can be combined with them to form delayed  
 230 ettringite [45]. As  $M_1$  already contains one mole of aluminate and one mole of sulfates, the evolution  
 231 of the state variables is then:

$$232 \quad \begin{cases} \frac{\partial M_1}{\partial t} = -\frac{\partial E_2}{\partial t} \\ \frac{\partial \tilde{S}}{\partial t} = -2\frac{\partial E_2}{\partial t} \\ \frac{\partial \tilde{A}}{\partial t} = 0 \end{cases} \quad (17)$$

233 Once all the monosulfates  $M_1$  have been consumed by reactions (17), if some  $\tilde{S}$  subsist, the DEF  
 234 continues to consume  $\tilde{A}$  as follows:

$$235 \quad \begin{cases} \frac{\partial M_1}{\partial t} = 0 \\ \frac{\partial \tilde{S}}{\partial t} = -3\frac{\partial E_2}{\partial t} \\ \frac{\partial \tilde{A}}{\partial t} = -\frac{\partial E_2}{\partial t} \end{cases} \quad (18)$$

236 The delayed ettringite formation stops when no more sulfates or aluminates remain.

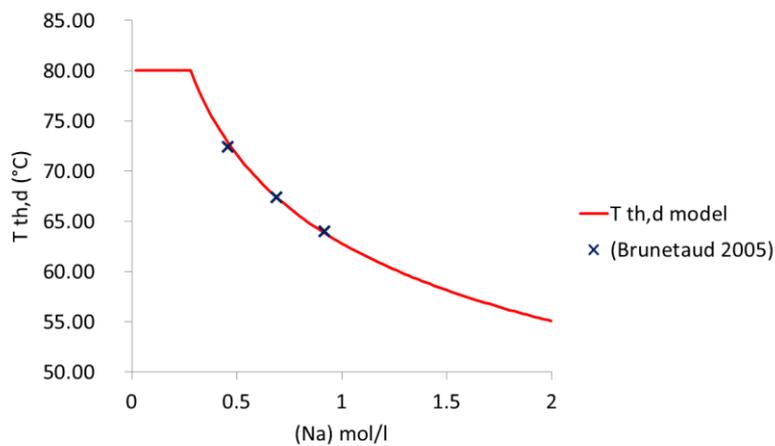
### 237 **2.3 Assessment of the destabilization threshold temperature $T_{th,d}$**

238 The destabilization of ettringite at high temperature can be ideally modelled in a thermodynamic  
 239 context using a Van't Hoff equation, which gives the evolution of the solubility constant [13] versus  
 240 temperature as in the model presented in [36]. Such thermodynamic modelling needs to solve the  
 241 mass balance equations simultaneously for all chemical species involved in the equilibrium  
 242 equations. The resulting numerical problem becomes too computer-time consuming to be used in a  
 243 finite element context also involving numerous other nonlinear problems (creep, plasticity, damage,  
 244 poro-mechanics, and reinforcements). So, a simplification is proposed, which can be used in a

245 context of coupling with non-linear mechanical problems in order to consider the dependence of the  
 246 threshold temperature on the chemical context. Kchakech [26] proposed an empirical law deduced  
 247 from Brunetaud's experimental results [5] and based on the dependence on the alkali concentration.  
 248 This law is adapted here to have a normalisation parameter,  $Na_k$  in equation (19). It allows having a  
 249 relationship form independent of the unit system used. More, the parameter is also used as  
 250 threshold value, in order to avoid obtaining too high temperature for low alkali concentration:

$$251 \quad T_{th,d} = T_0 + \begin{cases} T_{th,ref} & Na < Na_k \\ T_{th,ref} \left(\frac{Na_k}{Na}\right)^n & Na \geq Na_k \end{cases} \quad (19)$$

252 The fitting of equation (19) on results supplied by Brunetaud [5] corresponds to  $T_{th,ref} = 80^\circ C$  for  
 253  $Na_k = 0.28 \text{ mol/l}$  and  $n = 0.19$ . It is illustrated in Figure 1. In equation (19), the threshold  
 254 temperature can be changed from degrees Celsius to Kelvin for further applications with  $T_0 =$   
 255  $273.15 K$ .



256

257 **Figure 1 : Temperature threshold evolution, model fitted on Brunetaud's results**

258 In Figure 1, experimental results come from Brunetaud's experimental observations [4,5]. As these  
 259 results come from a single author, the law proposed by Kchakech [26] could be affected by the  
 260 cement composition and should be verified experimentally for alkali contents outside this fitting  
 261 range.

## 262 2.4 Influence of environmental conditions on reaction kinetics

263 The characteristic times ( $\tau_d, \tau_f, \tau_p$ ) used in the mass balance equations (9, 11, 16) to control the  
 264 reaction kinetics depend on environmental conditions: temperature (T), moisture (H) and chemical  
 265 conditions (C). Although the lack of data remains the main problem in clarifying this part of the  
 266 model, evolution laws are needed so that the different environmental conditions of real structures

267 can be considered. Their fitting is addressed in the section dedicated to the model application. To  
 268 consider the THC (Thermo-Hydro-Chemical) effects systematically, each characteristic time of the  
 269 model is modified by three coefficients as follows:

- 270 • The characteristic time  $\tau_d$  used in the equation of dissolution of primary sulfoaluminates (9)  
 271 is modified by coefficients  $C_d^T$ ,  $C_d^H$ ,  $C_d^C$ :

$$272 \quad \frac{1}{\tau_d} = \frac{1}{\tau_d^{ref}} C_d^T C_d^H C_d^C \quad (20)$$

- 273 • The characteristic time  $\tau_f$  controlling the uptake of aluminate (equation 11) is modified as  
 274 follows:

$$275 \quad \frac{1}{\tau_f} = \frac{1}{\tau_f^{ref}} C_f^T C_f^H C_f^C \quad (21)$$

- 276 • The characteristic time  $\tau_p$  controlling the precipitation of secondary ettringite at low  
 277 temperature (equation 16) is modified in a similar way:

$$278 \quad \frac{1}{\tau_p} = \frac{1}{\tau_p^{ref}} C_p^T C_p^H C_p^C \quad (22)$$

279 These nine coefficients C require a very large experimental plan if they are to be fitted accurately.  
 280 Nevertheless, the theoretical knowledge of some phenomena highlighted by thermodynamic  
 281 considerations such as Arrhenius thermal activation of diffusion for  $C_d^T$  [27], chemical equilibrium  
 282 conditions for  $C_d^C$  [14,15]. Experimental observations can also be used, such as absence of swelling  
 283 below a given saturation rate for  $C_p^H$  [44] or above a given alkali concentration [5] for  $C_p^C$ . All these  
 284 information can guide the choice of reasonable laws which can then be fitted from the experimental  
 285 results available in the literature. Note that the characteristic times above also depend on other  
 286 physical phenomena like concrete porosity or thermal damage, but these influences are considered  
 287 as factors that affect the concrete permanently, so they are somehow already included in the  
 288 reference values of characteristic times.

#### 289 2.4.1 Influence of the temperature on the kinetics

290 Temperature impacts chemical reactions by the activation of micro diffusion processes. This effect  
 291 can be considered with an Arrhenius law [27]. A loss of chemical affinity of DEF also has to be  
 292 considered when the temperature is close to the dissolution threshold  $T_{th,d}$ . It could be modelled by  
 293 the Van't Hoff law if all the ionic species involved in the DEF were considered in the model [13], as is  
 294 the case in [36] for instance. In the present model, for the sake of simplicity, only sulfates, aluminates  
 295 and alkali are considered. It is then no longer possible to use the Van't Hoff law directly. The thermal

296 effects are simplified by combining the Arrhenius and Van't Hoff laws in a single approximation. The  
 297 best fit concerning the dissolution and fixation processes (when  $T > T_{th,d}$ ) were obtained with the  
 298 following laws:

$$299 \quad C_d^T = \exp\left(-\frac{Ea_d}{R}\left(\frac{1}{T} - \frac{1}{T_{th,d}}\right)\right) - 1 \geq 0 \quad (23)$$

$$300 \quad C_f^T = \exp\left(-\frac{Ea_f}{R}\left(\frac{1}{T} - \frac{1}{T_{th,f}}\right)\right) - 1 \geq 0 \quad (24)$$

301 with  $Ea_d$  and  $Ea_f$  the activation energy of dissolution and fixation mechanisms **respectively**.

302 Experiments modelled in the sections below show that  $T_{th,f}$  is independent of the alkali content, and  
 303 a value close to 70°C seems acceptable to explain the absence of a pessimum effect of heating  
 304 duration for specimens heated to 65°C, while, according to Kchakech [26] specimens heated to 71°C  
 305 present a very low pessimum effect, **and that this pessimum effect is more pronounced at higher**  
 306 **temperature**.

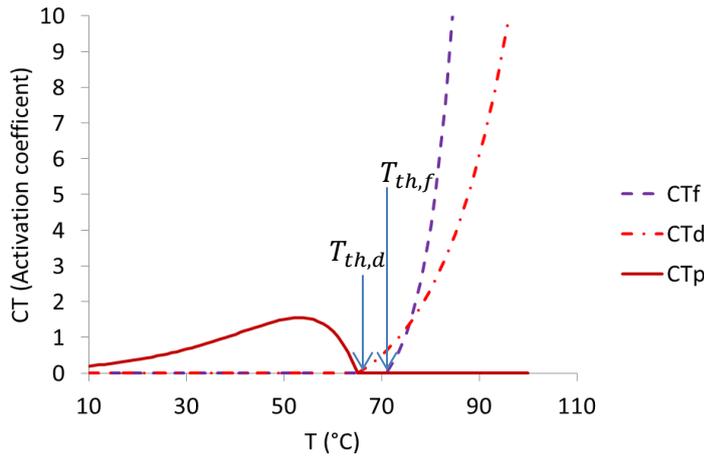
307 When the temperature is lower than the dissolution threshold ( $T < T_{th,d}$ ), only the DEF is active. The  
 308 dependence of the DEF kinetics on the temperature is then driven by the Arrhenius law on  
 309 precipitation mechanisms.

$$310 \quad C_p^T = \exp\left(-\frac{Ea_p}{R}\left(\frac{1}{T} - \frac{1}{T_p^{ref}}\right)\right) \frac{C_d^T(T)}{C_d^T(T_p^{ref})} \quad (25)$$

311 with  $Ea_p$  the activation energy of precipitation. To facilitate the calibration of this parameter, the  
 312 reference temperature  $T_p^{ref}$  can be chosen independently of  $T_{th,d}$ , which is why the normalization  
 313 term  $C_d^T(T_p^{ref})$  appears in equation (25). **As the literature supplies contradictory tests results for**  
 314 **specimens stored at different temperatures during the DEF, the calibration of activation energy  $Ea_p$**   
 315 **is not yet feasible: in [19], the specimen does not swell at 38°C, while in[29], this same temperature**  
 316 **allows to accelerate swelling. Therefore, a value close to the one usually used in hydration models**  
 317 **( $Ea_p \approx 44\text{kJ/Mol}$ ) is adopted to illustrate the method chosen to consider effect of temperature on**  
 318 **DEF kinetics [6]. It will have to be readjusted as soon as adequate experimental results will be**  
 319 **available**.

320 **The evolutions of thermal coefficients are illustrated in Figure 2 for a dissolution threshold chosen**  
 321 **equal to  $T_{th,d} = 65^\circ\text{C}$ . This value is chosen arbitrarily among the different values possible in Figure 1.**  
 322 **It could be obtained for instance using a high alkali concentration during heating of about 0.8 mol/l**

323 according to equation 19 fitted on Brunetaud's experimental results [5], in low alkali cement this  
 324 temperature is greater as illustrated in Figure 1. The three kinetics: dissolution of primary  
 325 sulfoaluminates ( $C_d^T$  in Figure 2), fixation of aluminates ( $C_f^T$ ), and precipitation of secondary  
 326 sulfoaluminates ( $C_p^T$ ) are null at the point corresponding to this threshold temperature. For the  
 327 modelling presented in this figure, precipitation of sulfoaluminates stops for temperatures higher  
 328 than 65°C and dissolution begins above this temperature (Figure 2), while the aluminate fixation  
 329 starts for temperatures higher than 70°C.



330

331 **Figure 2 : Thermal activation coefficients versus temperature for dissolution of primary sulfoaluminate hydrates (CTd),**  
 332 **fixation of aluminate in hydrogarnet at high temperature (CTf) or precipitation of secondary ettringite (CTp) (example for**  
 333 **a threshold dissolution temperature of 65°C corresponding to a high alkali content (0.8 mo/l), and a threshold fixation**  
 334 **temperature of 70°C Eap=44 kJ/mol, Ead 80 kJ/mol and Eaf=180 kJ/mol)**

### 335 2.4.2 Influence of alkali on kinetics

336 At given temperature and humidity, a high alkali concentration promotes the sorption of sulfates in  
 337 the cement matrix [18,34] and consequently accelerates the dissolution of primary sulfoaluminates.  
 338 This effect is considered in the model by reducing the characteristic time of dissolution  $\tau_d$  with the  
 339 coefficient  $C_d^C$ :

$$340 \quad C_d^C = \left( \frac{Na}{Na_k} \right) \quad (26)$$

341 with  $Na_k = 0.28 \text{ mol/l}$ , the alkali concentration in the saturated porosity already used as  
 342 normalization parameter in equation (19).

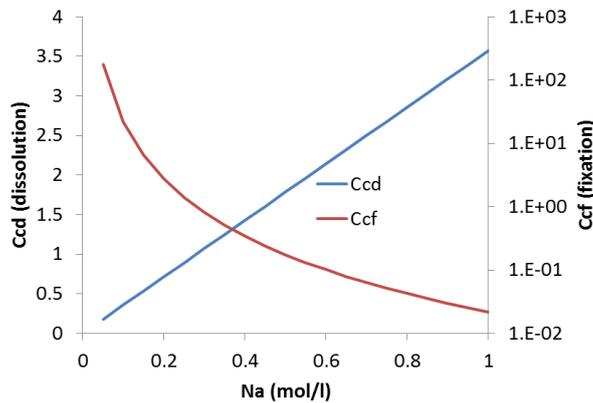
343 The analysis of Kchakech's results [26] by this model shows that the kinetics of aluminate fixation  
 344 (considered with  $C_f^C$  in equation 21) has to be modified according to the alkali content. It has to

345 evolve inversely to the alkali concentration and faster than  $C_d^C$ , which is why the fitting parameter  $m$   
 346 in equation (27) must be set equal to 3 to adjust the model to experimental results:

$$347 \quad C_f^C = \left( \frac{Na_k}{Na} \right)^m \quad (27)$$

348 The evolutions of these coefficients are illustrated in Figure 3. The modification of the kinetics of  
 349 these two phenomena with alkali content was already observed by Martin and Kchakech [26] and  
 350 considered in their phenomenological models. Only the shape of the laws have been modified to  
 351 obtain a calibration of the present model with all the experiments considered just below. Finally,  
 352 Figure 3 sums up the effects of alkali on the kinetics involved in sulfoaluminate dissolution. The larger  
 353 the initial alkali concentration:

- 354 - the faster the sulfoaluminate dissolution; it can be modelled by a linear relationship,
- 355 - the slower the aluminate fixation, with a nonlinear equation.



356

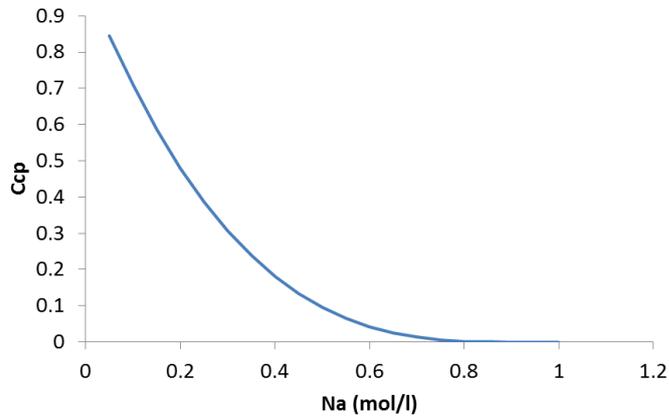
357 **Figure 3: Effect of alkali concentration on dissolution and fixation kinetics during heating period ( $Na_k=0.28 \text{ mol/l}$ ,  $m=3$ )**

358 Due to their influence on the sorption of sulfates, alkalis have an effect during DEF at low  
 359 temperature that is the inverse of that during dissolution at high temperature. As illustrated in the  
 360 application section below, a high concentration reduces the kinetics of DEF [18]. This is modelled by  
 361 equation (28):

$$362 \quad C_p^C = \begin{cases} \left(1 - \frac{Na}{Na^{bl}}\right)^m, & \text{if } Na < Na^{bl} \\ 0, & \text{if } Na \geq Na^{bl} \end{cases} \quad (28)$$

363 The evolution of the kinetic coefficient is illustrated in Figure 4 with  $Na^{bl} = 0.92 \text{ mol/l}$  and  $m = 3$   
 364 (fitted on Famy's results illustrated in Figure 9): the larger the alkali concentration, the slower the  
 365 DEF. The value of  $Na^{bl}$  depends on the concrete mix, a  $Na^{bl}$  twofold the initial alkali concentration  
 366 matches well enough with experimental results considered in this work. The curve in Figure 4

367 explains why DEF tests are faster in storage conditions allowing alkali leaching (since the DEF kinetic  
 368 increases with the low alkali concentrations).



369

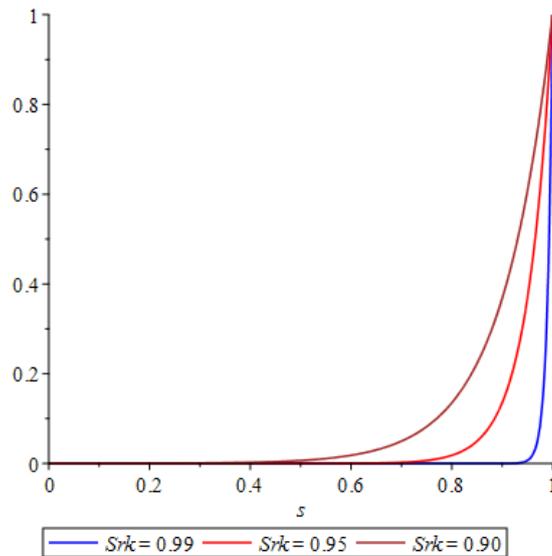
370 **Figure 4 : Evolution of  $C_p^C$  versus alkali concentration ( $Na_{bi}=0.92mol/l, m=3$ )**

371 **2.4.3 Influence of water saturation on kinetics**

372 Sulfoaluminates are assumed to be able to dissolve whatever the saturation rate. However, they  
 373 need water to precipitate because ions have to move by diffusion in the pore solution to create local  
 374 stoichiometric conditions of ettringite precipitation; moreover water is a reactant. For the sake of  
 375 simplicity, the dissolution and fixation phenomena are possible whatever the saturation ( $C_d^H$  and  $C_f^H$   
 376 are set equal to one). Only  $C_p^H$ , used in equation (23), which controls the precipitation rate, presents  
 377 any great dependence on the saturation. According to [43], the DEF kinetics is measurable in  
 378 laboratory conditions and with an acceptable experiment duration (about 3 years) only close to the  
 379 saturation condition, leading to relationship (29) for  $C_p^H$ . As soon as the porosity is no longer  
 380 saturated, the diffusion of ions rapidly becomes difficult and the kinetics of precipitation decreases  
 381 drastically. This leads to a highly nonlinear equation:

382 
$$C_p^H = \exp\left(-\frac{1-S_r}{1-S_r^k}\right) \tag{29}$$

383 The evolution of  $C_p^H$  is illustrated in Figure 5 for three different values of the fitting parameter  $S_r^k$ .



384

385

Figure 5 : Effect of water saturation on precipitation kinetics of sulfoaluminates

386

If the saturation degree is equal to  $S_r k$ , the kinetics of precipitation is reduced by 60% compared to its

387

value in the saturated condition (Figure 5). A value of  $S_r k$  greater than or equal to 95% is needed to

388

explain the observations of [43]. In his PhD thesis, Al Shamaa shows that specimens stored at 98% RH

389

have a water mass intake four times slower than at 100% RH. This phenomenon can be explained by

390

a DEF kinetics four times slower at 98% than at 100%, corresponding approximately to a  $S_r k$  of 95%. It

391

is obvious that this great nonlinearity of the DEF kinetics versus the saturation ratio  $S_r$  could be

392

problematic for the prediction of DEF in non-saturated structures, for which the determination of  $S_r$ ,

393

remains a challenge in itself.

394

## 2.5 Calibration and application of the chemical model

395

### 2.5.1 Materials

396

In this section, five materials are studied with the chemical model presented above These materials

397

(Table 3) were chosen because their compositions, heating conditions and conservation conditions

398

are well-described in the corresponding publications [4,18,26,29]. For all these materials, expansions

399

were measured until stabilization. Different heating conditions were used, and the chemical model

400

parameters could be calibrated by considering the dissolution and fixation phenomena [5,26]. With

401

these five materials, the cement composition or alkali content present large enough variations to fit

402

the alkali effects considered in the model. The conservation conditions were also evaluated in terms

403

of alkali leaching possibility through literature data [18], in order to fit the effect of the alkali

404

concentration in the pore solution on DEF kinetics. Among these materials, four are concrete and one

405

is a mortar (the material studied by Famy).

406 In these applications the alkali concentration in the pore solution was computed assuming that part  
 407 of the alkali ( $Na^B$ ) was bound in the C-S-H:

$$408 \quad Na^B = k.CSH.(Na) \quad (30)$$

409 Using the mass balance of alkali (31) then leads to a conventional alkali concentration in pore water  
 410 (32):

$$411 \quad \phi.Sr.(Na) + k.CSH.(Na) = 2 Na_2O_{eq} \quad (31)$$

412 In (31), according to [36],  $k \sim 0.077 \text{ l/mol}$ . The moles number of C-S-H for clinker can be assessed  
 413 using the moles number of silicate divided by its stoichiometric coefficient in C-S-H (1.65 for plain  
 414 clinker cements), and multiplied by the hydration rate [7].

$$415 \quad (Na) = \frac{2 Na_2O_{eq}}{\phi.Sr+k.CSH} \quad (32)$$

416 Equation (32) is given for further applications of the model. However, for the following analysis, the  
 417 alkali concentration was either given by the authors (these materials are the ones, with superscript  
 418 (1) in Table 3), or for the others, it was imposed through an alkali supply during the concrete mix.  
 419 More, for some of them, the heating cycles are applied at very early age. In this case, the alkali are  
 420 not yet bounded in C-S-H during the primary ettringite destabilisation at high temperature, so the  
 421 alkali concentrations can be assessed, neglecting the term  $k.CSH$  comparatively to  $\phi.Sr$ , (superscript  
 422 (2) in Table 3). Concerning the saturation rate  $Sr$ , as all specimens were stored in water, it is taken  
 423 equal to one. In Table 3, the oxides are given in % of cement mass.

424 **Table 3: Materials used to calibrate the model from [4,18,26,29]**

Author/ Material	Cement (kg/m <sup>3</sup> )	$\phi$ (%)	CSH (mol/m <sup>3</sup> )	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	SO <sub>3</sub> (%)	Ac Mol/m <sup>3</sup>	Sc Mol/m <sup>3</sup>	Sc/Ac -	(Na) Mole/l
Brunetaud <sup>(3)</sup>	400	14	884	4.1	3.75	3.36	255	168	0.66	0.92 <sup>(1)</sup> 0.69 <sup>(1)</sup> 0.46 <sup>(1)</sup>
Kchakech R0 <sup>(3)</sup>	410	15.2	1078	3.33	3.83	2.61	232	134	0.58	0.38 <sup>(1)</sup>
Kchakech R1 <sup>(3)</sup>	410	15.2	974	4.3	3.8	3.46	270	177	0.66	0.84 <sup>(1)</sup>
Famy <sup>(2)</sup>	500	25	1274	5.4	2.2	3.9	333	244	0.73	0.53 <sup>(1)</sup>
Martin <sup>(3)</sup>	410	14.6	974	4.3	3.8	3.46	270	177	0.66	0.91 <sup>(1)</sup>

425 (1) Alkali computed from initial conditions, neglecting the fixation in C-S-H at early age, and  
 426 assuming a water saturation of the porosity

427 (2) Mortar

428 (3) Concrete

429 The parameters necessary to determine the dissolution of primary sulfoaluminates and the fixation  
430 of aluminate at high temperature (listed in Table 5) are fitted on the final expansion (asymptotic  
431 values of swelling) measured for the concrete studied in these five experiments given in Table 4. For  
432 the sake of simplicity, and to avoid resorting to the mechanical part of the model presented in the  
433 next section, the final expansion is assumed to be proportional to the delayed ettringite amount,  
434 which depends on the conditions during the heating period (duration and temperature of the  
435 heating, alkali concentration during this period). The volume change of the specimen is taken to be  
436 isotropic as observed in [3] and DEF volume is assumed to be totally reported in the swelling to a first  
437 approximation. The volume change is thus assumed to be 3 times the measured axial expansion. So,  
438 during this simplified calibration, the DEF volume obtained by the chemical modelling is divided by 3  
439 compared to the free uniaxial swelling measured during the experiment. Thus a DEF volume of 6% is  
440 assumed to correspond to an isotropic volumetric swelling of 6%, which is equivalent to a specimen  
441 change of length of 2% in each direction. This assumption is only made for the calibration of the  
442 parameters of the chemical model as the combination with mechanical considerations would lead to  
443 complex calibration for all these five experiments. In real structure conditions, the poro-mechanical  
444 modelling takes account of the interaction with concrete microstructure and mechanical properties,  
445 and computed expansions will not always be proportional to the ettringite amount as explained  
446 below.

447 **Table 4 : Environmental conditions and final swellings**

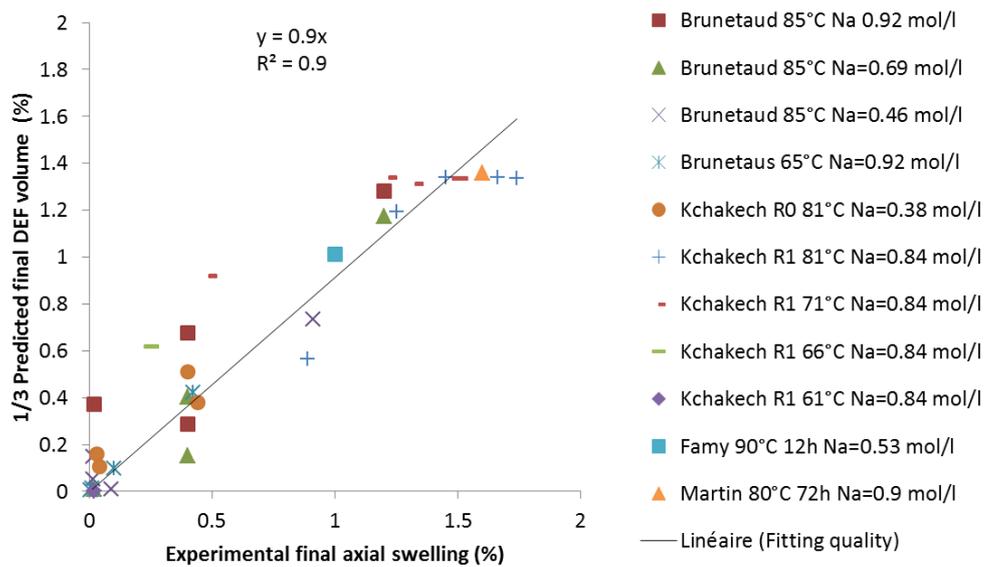
Author, heating temperature, heating duration (plateau only)	Experimental final expansion (specimen relative length change %)		
<i>Alkali concentration (Na) for Brunetaud's tests</i>	<i>0.92 mol/l</i>	<i>0.69 mol/l</i>	<i>0.46 mol/m</i>
Brunetaud 85°C 2h	0.40	0.40	0.014
Brunetaud 85°C 6h	0.40	0.40	0.014
Brunetaud 85°C 48h	1.20	1.20	0.91
Brunetaud 85°C 240h	0.02	0.20	0.09
Brunetaud 65°C 2h	0.01		
Brunetaud 65°C 6h	0.01		
Brunetaud 65°C 48h	0.05		
Brunetaud 65°C 240h	0.5		

Kchakech R0 81°C 25h	0.03
Kchakech R0 81°C 73h	0.44
Kchakech R0 81°C 169h	0.40
Kchakech R0 81°C 337h	0.04
Kchakech R1 81°C 25h	1.25
Kchakech R1 81°C 73h	1.74
Kchakech R1 81°C 121h	1.66
Kchakech R1 81°C 169h	1.45
Kchakech R1 81°C 337h	0.89
Kchakech R1 71°C 54h	0.49
Kchakech R1 71°C 175h	1.33
Kchakech R1 71°C 288h	1.51
Kchakech R1 71°C 341h	1.48
Kchakech R1 71°C 677h	1.22
Kchakech R1 66°C 345h	0.25
Kchakech R1 61°C 347h	0.00
Famy 90°C 12h	1.00
Martin 80°C 72h	1.60

## 448 2.5.2 Global fitting of DEF potential

449 For each material and each heating condition, the analytic solutions of equations (9, 10, 14) giving  
450 aluminates  $\tilde{A}$ , sulfates  $\tilde{S}$  and residual mono-sulfoaluminates  $M_1$  are used to compute the number of  
451 moles of reactive species able to produce ettringite in the long term. Then the maximal amounts of  
452 ettringite in the long term in saturated and alkaline leaching conditions are computed (asymptotic  
453 values of equation (17) and (18)) and used to assess the volume of delayed ettringite (by multiplying  
454 the number of moles by the molar volume of ettringite: 715 cm<sup>3</sup>/mol according to [1,20]). Figure 6  
455 shows the correlation between the third of calculated DEF volume and the experimental final  
456 swelling. All the points in Figure 6 were obtained with the single parameter set given in Table 5. Once  
457 fitted, the model is able to explain more than twenty different experiments performed with different  
458 materials, alkali contents and heating durations. The prediction capability corresponding to  
459 coefficient  $R^2$  in Figure 6 is close to 90%. The model presents a better prediction capability for large  
460 swellings than for smaller ones. Effectively, from a physical point of view, the final swelling cannot be  
461 linked to the DEF volume so easily: on the one hand, the chemistry description level proposed in this  
462 model contains many simplifications and, on the other hand, mechanical aspects play a non-  
463 negligible role in linking DEF volume and swelling [19]. In the poro-mechanical model used below, a

464 certain amount of DEF is first used to fill a part of the porosity connected to the sites of ettringite  
 465 precipitation without causing pressure, as analysed in [19]. This connected porosity thus absorbs part  
 466 of the DEF without causing expansion (like the gel of alkali-silica reaction in [35]). For DEF, it could  
 467 correspond to pores that are too large to lead to damaging pressure. As expansion does not involve  
 468 the entire DEF amount, this can also explain why the slope of the correlation line (0.9 in Figure 6) is  
 469 lower than one, and why the swelling is overestimated more often for small swellings than for large  
 470 ones.



471

472 **Figure 6 : Overview of prediction capability of the model with single parameter set (given in Table 5)**

473 **Table 5: Model parameters corresponding to the global fitting**

Parameter	Equation	Physical meaning	Fitted value	Unit
$T_{th,ref}$	(19)	Dissolution temperature at $Na_k$	80	°C
$Na_k$	(19) (27) (28)	Characteristic alkali concentration	0.28	mol/l
$n$	(19)	Exponent for the dissolution temperature low	0.18	-
$\tau_d^{ref(1)}$	(20)	Characteristic time for the dissolution (at high temperature)	65	hour
$\tau_p^{ref(1)}$	(22)	Characteristic time for the DEF	30	day
$\tau_f^{ref(1)}$	(21)	Characteristic time for the fixation of	30	hour

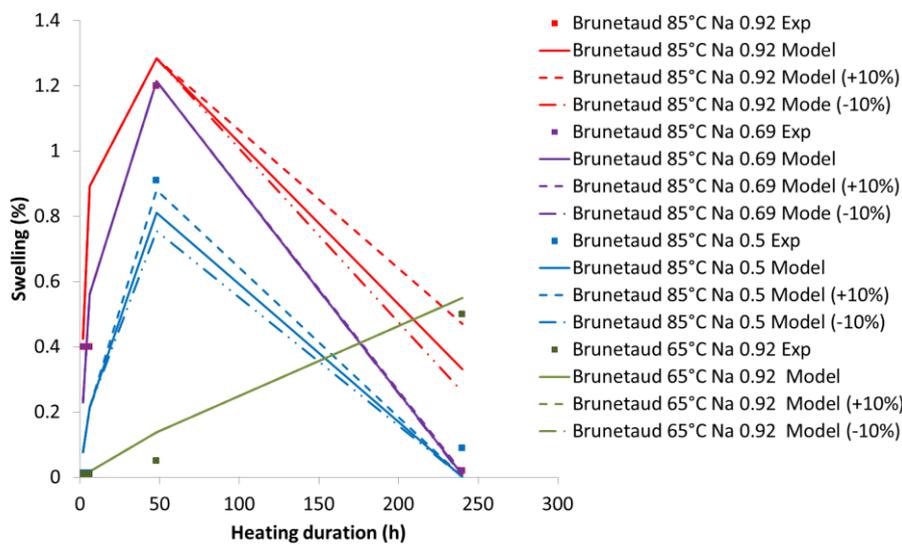
		aluminates (at high temperature)		
$T_{th,f}$	(24)	Threshold temperature for the fixation of aluminates	70	°C
$Ea_d$	(23)	Energy activation for the dissolution processes at high temperature	80,000	J/mol
$Ea_f$	(24)	Energy activation for the fixation of aluminates at high temperature	180,000	J/mol
$Ea_p$	(26)	Energy activation for the DEF	44,000	J/mol
$T_p^{ref}$	(26)	Reference temperature used to define $\tau_p^{ref}$	20	°C
$m$	(27) (28)	Exponent for the lows considering the limiting effect of Na on aluminate fixation and DEF	3	-
$Na^{bl}$	(28)	Alkali concentration above which the DEF is impeded	0.96	mol/l
$S_r^k$	(29)	Characteristic saturation rate below which the DEF is limited	0.95	-

474 (1) Characteristic times correspond to environmental condition for which the temperature,  
475 saturation rate and alkali content leads to coefficient  $C^T, C^H$  and  $C^C$  equal to the unit.

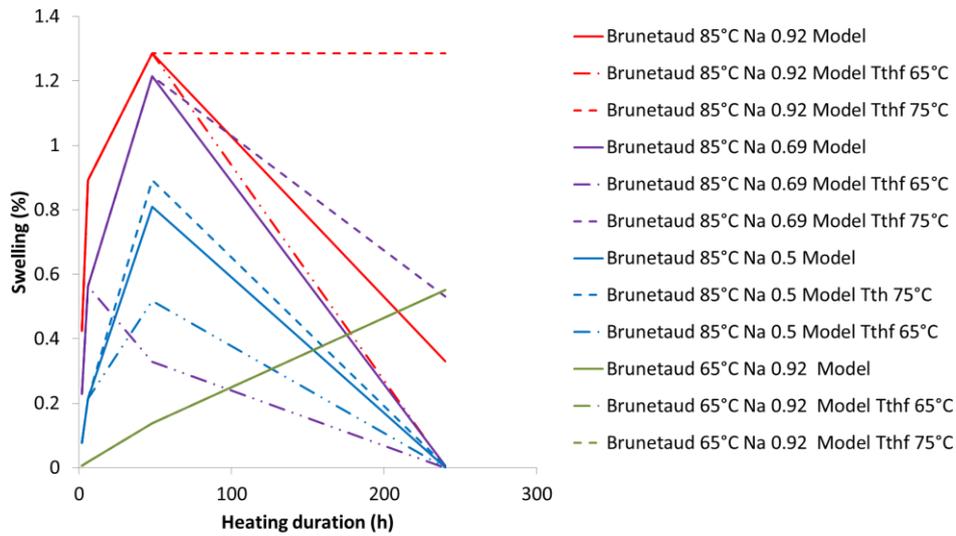
### 476 2.5.3 Effect of heating duration (analysis of Brunetaud's results)

477 To highlight the effects of heating duration and alkali content during heating, Brunetaud's  
478 experimental results are summarized in Figure 7, which shows the final swelling of specimens free of  
479 stresses versus heating duration. In this figure, the plain lines link the final swelling predicted by the  
480 model and the points represent the swelling values at the end of the experiments [5]. For initial  
481 heating cycles at 85°C, the final swellings present a maximum for a heating duration close to 50  
482 hours. The amplitude of this swelling depends on the alkali content: the higher the initial alkali  
483 content, the larger the swelling. For heating cycles at 65°C, the pessimum effect does not exist for  
484 the heating durations analysed in this experimentation. The swelling is smaller than at 85°C and  
485 appears to be proportional to the heating duration. In the model, the absence of pessimum at 65°C is  
486 explained by the impossibility of creating hydrogarnet to fix aluminates during heating below  $T_{th,f} =$   
487 70°C. At 85°C, this possibility exists and leads to progressive fixation of aluminates with the heating  
488 duration, depriving DEF of one of its constituents. Two parametric studies are now given to analyse  
489 the influence of model parameters. In Figure 7, the effects of the characteristic times (with +/-10%  
490 variation) are given. The impact of the characteristic times on final expansion is small. The maximum

491 deviation is for high duration with variation of about 20% of the final expansion for the variation of  
 492 10% of the characteristic times. In Figure 8, the reference solutions (plain lines) are compared with  
 493 two others for which the threshold temperature of fixation of Al in Hydrogarnet varies of +/-5°C.  
 494 Results show clearly the great impact of this last parameter which controls the amplitude of final  
 495 swelling for specimens with long heating. The higher the threshold temperature of fixation of Al, the  
 496 higher the final swellings, except for the heating at 65°C which is not sensible to this parameter and  
 497 presents none pessimum for the duration studied here. In the model, this is the consequence of a  
 498 heating temperature lower than the minimal temperature required to fix Al in Hydrogarnet.



499  
 500 **Figure 7 : Prediction of final swelling (lines) versus heating duration for Brunetaud's tests, compared to experimental**  
 501 **results (point) (parametric study with +/-10% on characteristic times of dissolution and fixation dotted lines)**



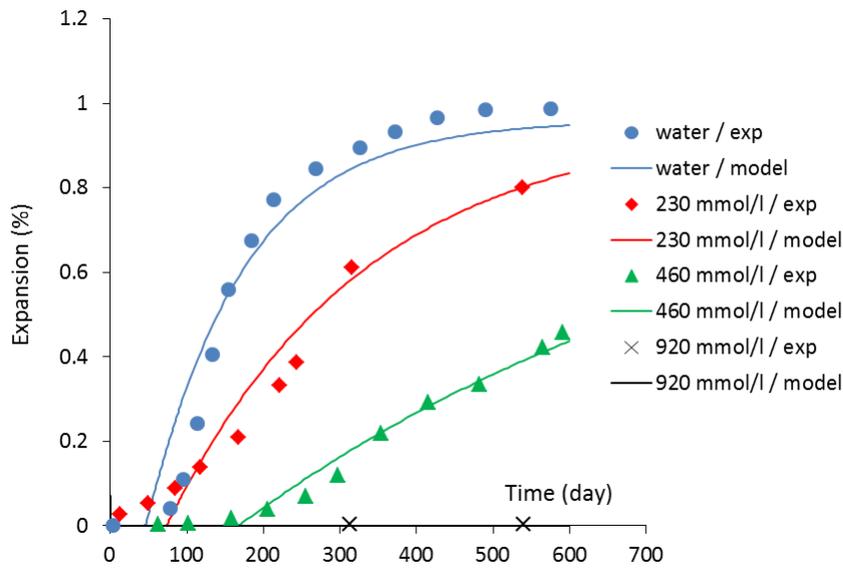
502

503 **Figure 8 : Prediction of final swelling versus heating duration for Brunetaud's mix : parametric study with +/-5°C on**  
 504 **threshold temperature of Al fixation during hot period ( $T_{th,f}$ )**

#### 505 2.5.4 Effect of alkali concentration during DEF (analysis of Famy's results)

506 To show the influence of alkali on DEF, Famy carried out a series of experiments in which the  
 507 specimens were heated in similar conditions but stored in water with different alkali concentrations  
 508 [18]. As illustrated in Figure 9, the higher the alkali concentration during DEF, the slower the DEF  
 509 kinetics. In this experiment, a concentration of 0.92 mol/l was able to prevent DEF expansion. In the  
 510 model, the slowdown of DEF kinetics is obtained by the coefficient  $C_p^C$  (equation 28), which depends  
 511 on alkali concentration as illustrated in Figure 4. The fitted parameter is  $Na_{bl}$  (given in Table 5). It is  
 512 obtained by error minimization using a classical least square method which minimizes the difference  
 513 between computed and experimental curves. The diffusion is first modelled. Calculus are performed  
 514 assuming an initial concentration of 0.53 mol/l during the heating period, and the different boundary  
 515 conditions are in accordance with the storage conditions specified by Famy [18].

516



517

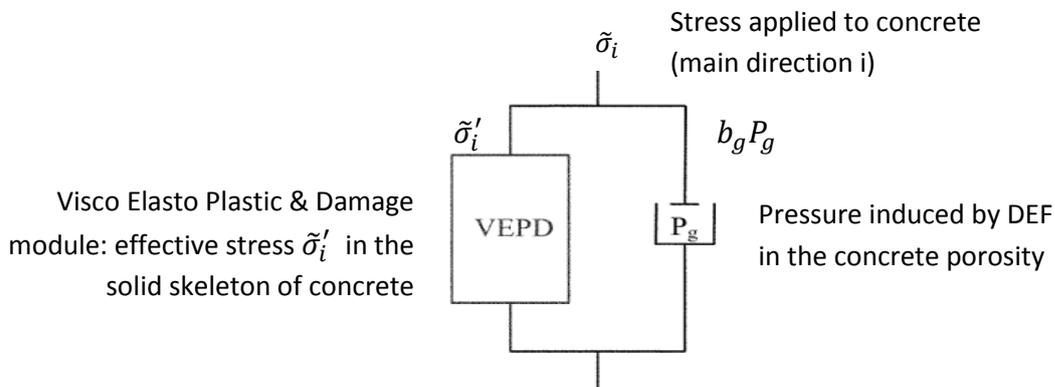
518 **Figure 9: Influence of KOH concentration in the storage bath on kinetics of DEF. Mortar was initially at 530mmol/l of**  
 519 **Na<sup>eq</sup>: comparison between model (lines) and Famy’s experimental results (symbols)**

### 520 3 Chemo-mechanical Model Formulation

521

#### 522 3.1 Poro-mechanical formulation

523 To illustrate the different features of the chemical model and its coupling with a mechanical finite  
 524 element code, the chemical model presented above was implemented with a nonlinear mechanical  
 525 model [39] already used in a close form to consider structural effects of alkali aggregate reaction  
 526 (AAR) [23]. This model is able to consider the effect of pressure ( $P_g$ ) in a part of the porosity of  
 527 concrete through equations (33) as illustrated in Figure 10.



528

529 **Figure 10 : Idealized scheme of the poro-mechanical model of concrete affected by DEF**

$$530 \quad \begin{cases} \sigma_i = (1 - D_i)\tilde{\sigma}_i \\ \tilde{\sigma}_i = \tilde{\sigma}_i' - b_g P_g \end{cases} \quad (33)$$

531 with  $b_g$  the Biot coefficient for the DEF and  $P_g$  the pressure due to DEF.

532 In equation (33),  $\sigma_i$  is the main stress,  $D_i$  is the damage induced in the main direction “i” by swelling  
 533 and external loading in the solid skeleton of the concrete,  $\tilde{\sigma}_i$  is the total stress in the undamaged part  
 534 of the concrete (stress in the matrix plus stress due to the DEF pressure),  $\tilde{\sigma}_i'$  is the effective stress in  
 535 the undamaged part of the concrete (depending only on the elastic strain in the matrix according to  
 536 equation 34):

$$537 \quad \begin{cases} \tilde{\sigma}_i' = \lambda^{tr} \bar{\bar{\epsilon}}^e + 2\mu \epsilon_i^e \\ \bar{\bar{\epsilon}}^e = \bar{\bar{\epsilon}} - \bar{\bar{\epsilon}}^c - \bar{\bar{\epsilon}}^{p,m} - \bar{\bar{\epsilon}}^{p,g} \end{cases} \quad (34)$$

538 with  $\lambda$  and  $\mu$  the Lamé elastic coefficients of undamaged concrete,  $\bar{\bar{\epsilon}}$  the mechanical strain tensor  
 539 (total strain minus thermal strain),  $\bar{\bar{\epsilon}}^c$  the creep strain tensor computed according to the model  
 540 presented in [41],  $\bar{\bar{\epsilon}}^{p,m}$  the plastic strains associated with the cracking induced by the external  
 541 loading and computed according to the model presented in [39].  $\bar{\bar{\epsilon}}^{p,g}$  is the irreversible strain  
 542 induced by the DEF and computed as explained below. Note that the creep and irreversible strains  
 543 are combined in equation (34) to compute the effective stress in the concrete matrix ( $\tilde{\sigma}_i'$ ), then  
 544 equation (33) allows the resulting stress ( $\sigma_i$ ) to be assessed, which also takes the effect of pressure  
 545  $P_g$  induced by the DEF and the effect of cracking on concrete stiffness into consideration through the  
 546 damage variable  $D_i$ . Therefore, the main benefit of the poro-mechanical formulation is to combine  
 547 all the non-linear phenomena involved in the long-term behaviour of concrete in a relatively simple  
 548 formulation. The benefits of a poro-mechanical formulation have already been underlined by other  
 549 authors [12,46].

550 In the current work, the model directly uses the volume of ettringite supplied by the chemical  
 551 equations presented above to compute a pore pressure given by equation (35):

$$552 \quad P_g = M_g \left( \phi_{DEF} - \left( \frac{\phi_{DEF}^v C_g P_g}{R_t} + b_g^{tr} (\bar{\bar{\epsilon}}^e + \bar{\bar{\epsilon}}^c + \bar{\bar{\epsilon}}^{p,m}) + tr \bar{\bar{\epsilon}}^{p,g} \right) \right) \quad (35)$$

553 In equation (35),  $M_g$  is the Biot modulus controlling the mechanical interaction between the delayed  
 554 ettringite volume  $\phi_{DEF}$  (compressibility modulus  $K_g$ ) and the surrounding matrix (compressibility  
 555 modulus  $K_m$ ). The Biot modulus can be assessed using equation (36):

$$556 \quad \frac{1}{M_g} = \frac{b_g - \phi_{DEF}}{K_m} + \frac{\phi_{DEF}}{K_g} \quad (36)$$

557 In which the Biot coefficient  $b_g$  can be assessed with equation (37) if a Mori Tanaka scheme of  
 558 homogenization [32] is used with a Poisson coefficient of the matrix of 0.2 :

$$559 \quad b_g = \frac{2\phi_{DEF}}{1+\phi_{DEF}} \quad (37)$$

560 In the Mori Tanaka method,  $\phi_{DEF}$  represents the volume of void filled by the fluid with the pressure  
 561  $P_g$ . If this pressure is equal to the crystallization pressure, as the crystallisation takes place in water  
 562  $K_g$  is equal to 2.1 GPa. In (36),  $K_m$  is the compressibility modulus of the matrix around the void filled  
 563 by the water under pressure  $P_g$ , it can be deduced of the concrete compressibility coefficient  $K_c$   
 564 using equation (38).

$$565 \quad K_m = \frac{K_c}{1-b_g} \quad (38)$$

566 Considering these assumptions, the Biot coefficient and modulus vary during the reaction due to the  
 567 variation of the volume of ettringite  $\phi_{DEF}$  given by equation (39), based on the chemical variables  
 568 supplied by equations (17) or (18):

$$569 \quad \frac{\partial \phi_{DEF}}{\partial t} = V_{AFt} \frac{\partial E_2}{\partial t} - V_{AFm} \frac{\partial M_1}{\partial t} \quad (39)$$

570 with  $V_{AFt} = 715 \text{ cm}^3/\text{mol}$  and  $V_{AFm} = 254 \text{ cm}^3/\text{mol}$  according to [1] who cites [20], the molar  
 571 volumes of ettringite and mono-sulfates. According to [45] part of the monosulfate can be replaced  
 572 by DEF in certain situations as explained in the presentation of the chemical model. In equation (35),  
 573  $\phi_{DEF}^v$  is the volume to be filled, in a specimen free of stresses, around the sites of DEF before the  
 574 pressure damages the concrete matrix [19], this volume leads to a reduction of swelling for small  
 575 values of  $\phi_{DEF}$ , compensating the overestimation of small swelling pointed out in Figure 6 for the  
 576 chemical model used alone.  $R_t$  is the tensile strength of concrete,  $C_g$  the stress concentration factor.

577 In equations (34) and (35),  $\bar{\epsilon}^{p,g}$  is the plastic strain, which represents the irreversible diffuse cracking  
 578 induced in the solid skeleton (left branch in Figure 10) by the pressure when its combination with  
 579 external loading ( $\tilde{\sigma}_i$ ) exceeds the tensile strength ( $R_t$ ) of the concrete matrix. The plastic criterion  
 580 driving this diffuse cracking due to pressure between cement paste and aggregates can be assessed  
 581 in each main direction "i" of stresses:

$$582 \quad f(P_g, \tilde{\sigma}_i) = \begin{cases} C_g P_g + \tilde{\sigma}_i - R_t & \text{if } \tilde{\sigma}_i < R_t \\ P_g & \text{if } \tilde{\sigma}_i \geq R_t \end{cases} \quad (40)$$

583 With  $C_g$  the stress concentration factor around aggregates taken to one for sake of simplicity  
 584 (spherical inclusions in a swelling matrix). For the stress state in the concrete matrix ( $\tilde{\sigma}_i \leq R_t$ ) to be

585 considered admissible,  $f(P_g, \tilde{\sigma}_i)$  has to stay lower than zero. It then controls the evolution of plastic  
 586 strain  $\bar{\varepsilon}^{p,g}$  according to the consistency conditions of plasticity: as soon as a pressure  $P_g$  leads to the  
 587 criterion (equation 37) being exceeded, a plastic increment  $d\varepsilon_i^{p,g}$  is computed to return the yield  
 588 function  $f(P_g, \tilde{\sigma}_i)$  to zero (equation's set 40):

$$589 \left\{ \begin{array}{l} \left( \frac{\partial f}{\partial P_g} \frac{\partial P_g}{\partial \varepsilon_i^{p,g}} + \frac{\partial f}{\partial \tilde{\sigma}_j} \frac{\partial \tilde{\sigma}_j}{\partial \tilde{\sigma}_k} \frac{\partial \tilde{\sigma}_k}{\partial \varepsilon_i^{p,g}} + \frac{\partial f}{\partial R_t} \frac{\partial R_t}{\partial \varepsilon_i^{p,g}} \right) d\varepsilon_i^{p,g} + f(P_g, \tilde{\sigma}_i) = 0 \\ d\varepsilon_i^{p,g} = d\lambda_i \frac{\partial f}{\partial \tilde{\sigma}_i} \end{array} \right. \quad (41)$$

590 In (41)  $d\lambda_i$  is a plastic multiplier adjusted to verify the first equation in (40). Note that, through the  
 591 formulation of (40), an external loading corresponding to a compression ( $\tilde{\sigma}_i \leq 0$ ) reduces the yield  
 592 function  $f(P_g, \tilde{\sigma}_i)$ , and then delays or prevents swelling in the corresponding direction.  
 593 Consequently, the pressure can increase in the matrix until the criterion is exceeded in another  
 594 direction. This formulation is thus able to model anisotropic swelling induced by the interaction  
 595 between the pressure induced by ettringite precipitation and non-isotropic external loading as  
 596 observed in [3]. The ability of this plastic criterion to manage anisotropic swelling has been  
 597 confirmed, for instance for a pressure induced by alkali-aggregate reaction [31]. Once the plastic  
 598 strain tensor has been updated with the increments (41), its main values are computed and used to  
 599 assess the corresponding damage variables, which take the reduction of concrete stiffness induced  
 600 by micro-cracking (equation 42) into account:

$$601 d_i = \frac{\varepsilon_i^{p,g}}{\varepsilon_0 + \varepsilon_i^{p,g}} \quad (42)$$

602 The damage then affects the Young modulus of the matrix through the equations (33-34), thus  
 603 considering the damage due to the swelling (43).

$$604 D_i = \begin{cases} 1 - \left( (1 - d_j)(1 - d_k) \right)^\alpha, & \tilde{\sigma}_i < 0 \\ d_i, & \tilde{\sigma}_i \geq 0 \end{cases} \quad (43)$$

605 In equation (43) ( $d_i, d_j, d_k$ ) are the main values of the damage induced by the DEF (equation 43  
 606 applied in the three main directions of  $\bar{\varepsilon}^{p,g}$ ),  $\alpha \approx 0.15$  according to [40], considers that micro-  
 607 cracking is less efficient to reduce the concrete stiffness in compression than in tension due to the  
 608 possible re-closure under compression of some micro-cracks filled by ettringite.

609 In equation (42),  $\varepsilon_0 \approx 0.3\%$  is a constant to link the plastic strain and the tensile damage due to the  
 610 matrix micro-cracking.  $\alpha$  and  $\varepsilon_0$  were first used in 2002 for AAR modelling by [9]. The first  
 611 calculations for DEF are performed with the same data as for alkali-aggregate reaction but future

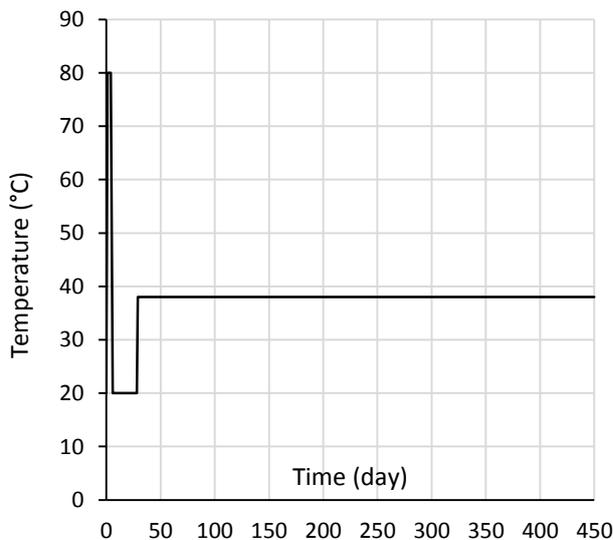
612 uses of this model to simulate other configurations [3,30] will confirm the parameters or will lead to  
 613 modifications of some of them.

### 614 3.2 Application to the alkali leaching effect on expansion (analysis of 615 Martin's results)

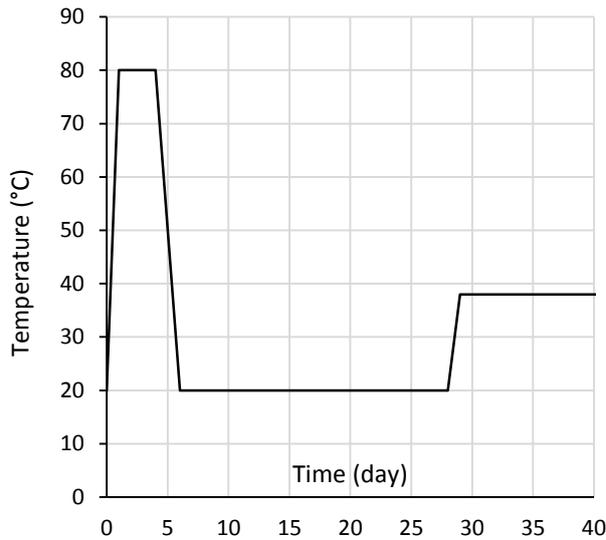
616 The case considered here is a cylindrical specimen studied by Martin [29]. The main material  
 617 characteristics are given in Table 3, they are close to the Kchakech's ones [26]. The temperature  
 618 chronology, including the heating period, is presented in Figure 11. Figure 12 provides a zoom to  
 619 show the details of the heating cycle. As the specimen is stored in tap water, alkali leaching occurs  
 620 during the storage. This leaching is considered using a diffusion equation of alkali in the saturated  
 621 porosity of the specimen, and a boundary condition for the surfaces in contact with the external  
 622 water ( $Na = 0 \text{ mol/l}$  in equation 44 is an approximation of tap water by pure water for sake of  
 623 simplicity). As the specimen and the boundary conditions present cylindrical symmetry, the finite  
 624 element model is meshed in an axisymmetric base, and only the upper half of the specimen is  
 625 modelled.

$$626 \left\{ \begin{array}{l} (\phi + k.CSH) \frac{\partial(Na)}{\partial t} = \text{div} \left( D_{Na} \overrightarrow{\text{grad}}(Na) \right), \forall M \in \Omega \\ Na(M, t = 0) = 0.91 \frac{\text{mol}}{\text{l}}, \forall M \in \Omega \\ Na(M, t) = 0. \frac{\text{mol}}{\text{l}}, \forall t, \forall M \in \delta \Omega \end{array} \right. \quad (44)$$

627 In (43), M is any point in  $\Omega$ , the volume of the specimen, and  $\delta \Omega$  is its boundary in contact with the  
 628 water of the storage bath. The initial condition  $Na=0.91 \text{ mol/l}$  corresponds to the data in the last line  
 629 of Table 3.



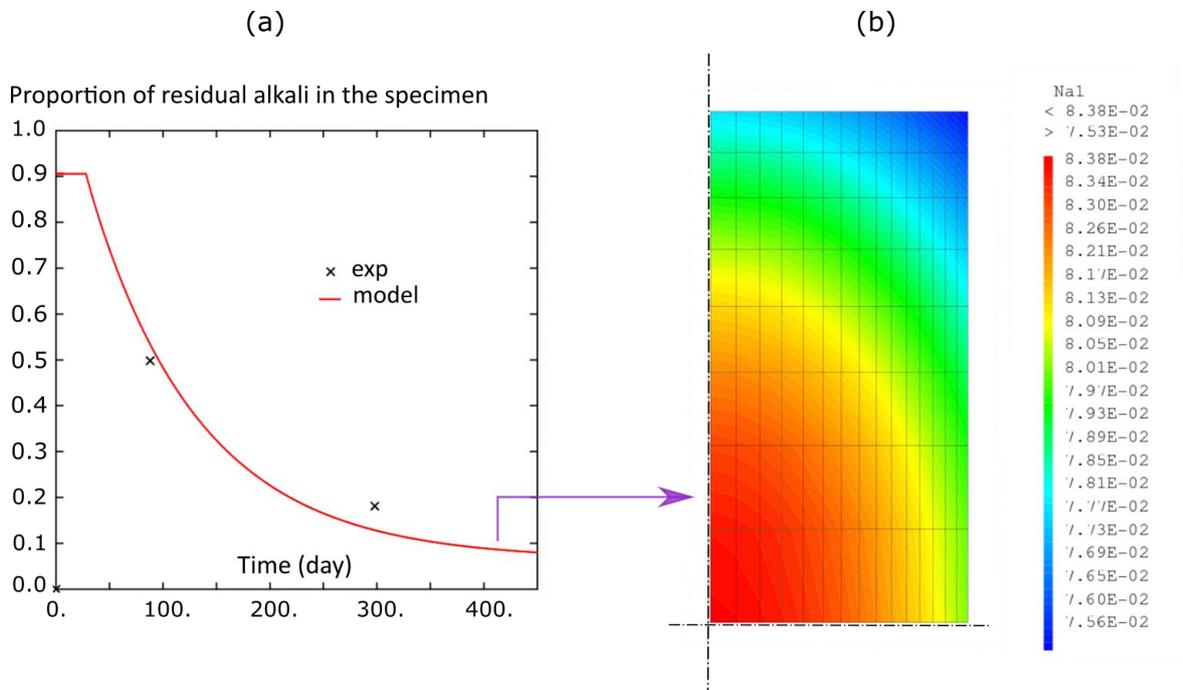
630  
 631 **Figure 11: Thermal cycle (72h at 80°C, aging at 38°C after 28 days)**



632

633 **Figure 12 : Thermal cycle, zoom on first 50 days**

634 An illustration of the alkali concentration in the pores of the concrete is supplied in Figure 13, where  
 635 the ratio of residual alkali to initial alkali is given versus time (a) with a concentration field at the end  
 636 of the simulation (b). In Figure 13(a), the two crosses correspond to measurements performed by  
 637 Martin. The diffusion coefficient,  $D_{Na} \approx 0.5 \cdot 10^{-12} \text{ s}^{-1}$ , was fitted to reproduce the leaching  
 638 kinetics.

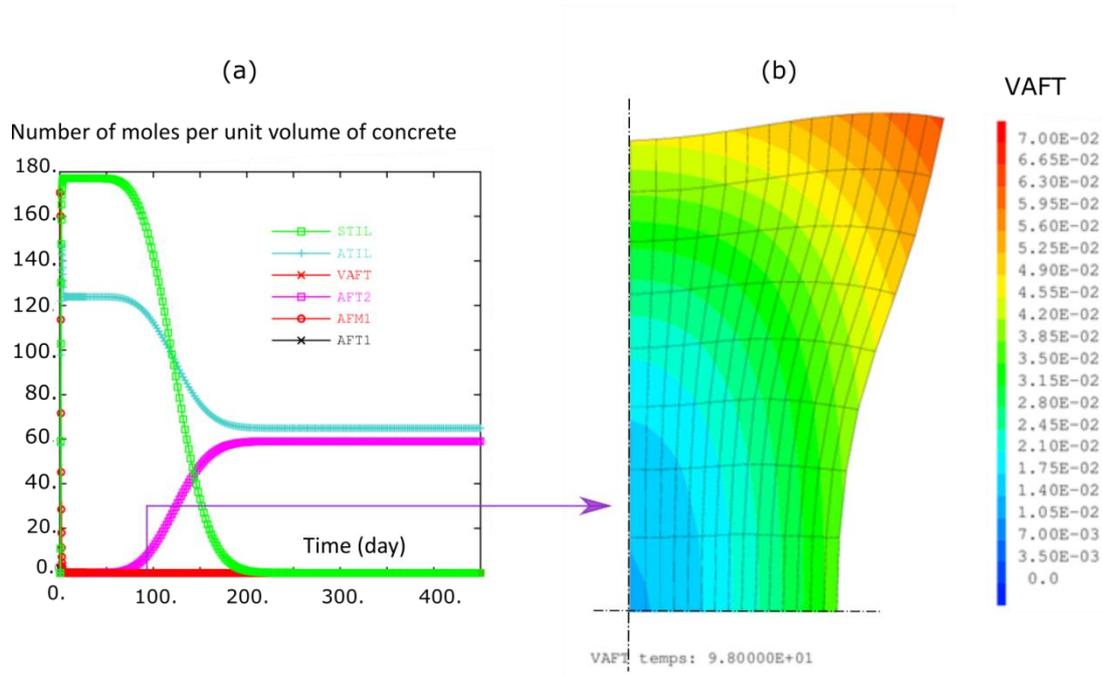


639

640 **Figure 13: Proportion of residual alkali in the specimen versus time (a), final alkali concentration plotted on the**  
 641 **axisymmetric mesh of the half upper part of the specimen (b)**

642 Once the alkali concentration is known for each time step of the stepwise analysis, the chemical  
 643 model and the poro-mechanical models described above can be used. Figure 14 (a) shows the  
 644 evolution of the state variables of the chemical model during the test. The production of secondary  
 645 Aft (AFT2 in the graph legend corresponding to E2 in the chemical equations) increases between 50  
 646 and 200 days, and the available sulfates ( $STIL = \tilde{S}$ ) and aluminates ( $ATIL = \tilde{A}$ ) decrease  
 647 simultaneously. The DEF stops after around 200 days due to lack of sulfates ( $STIL = 0$ ). Figure 14(b)  
 648 gives an illustration of the variable VAFT corresponding to  $\phi_{DEF}$  in equations (35) and (36), plotted  
 649 on the deformed mesh (amplified 100 times). The deformed mesh shows that swelling is faster in the  
 650 upper right corner of the specimen due the faster alkali leaching in this zone; which accelerates the  
 651 DEF as illustrated in Figure 4.

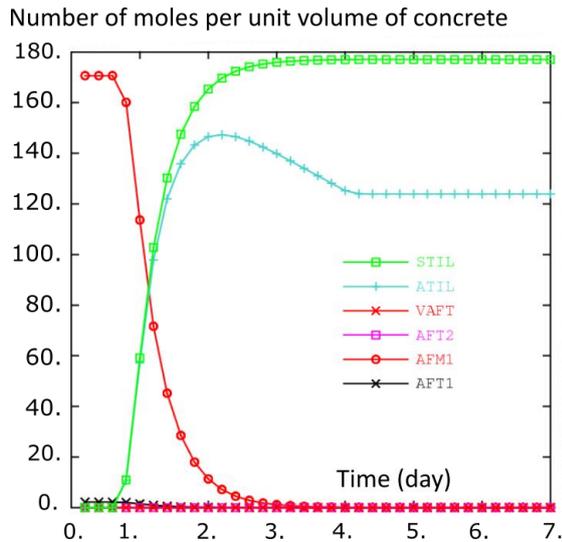
652



653

654 **Figure 14: Chemical species evolution versus time at the centre of the specimen (a), Effective Volume of DEF at 100 days**  
 655 **on deformed mesh (displacement x100) (b)**

656 Figure 15 is a zoom of Figure 14(a) for the first 7 days. During the temperature plateau at 80°C, the  
 657 number of moles of primary AFm (AFM1 in Figure 15) decreases in favour of available sulfates (STIL)  
 658 and aluminates (ATIL). From day two, the available aluminate starts to decrease due to the formation  
 659 of hydrogarnet, which occurs while the temperature exceeds  $T_{th,f} = 70^\circ\text{C}$ . Afterwards, the evolutions  
 660 stop because the temperature passes below the threshold value ( $T_{th,d}$ ), and the alkali content in the  
 661 specimen is still too high for DEF. DEF occurs later as illustrated in Figure 14, with alkali leaching.

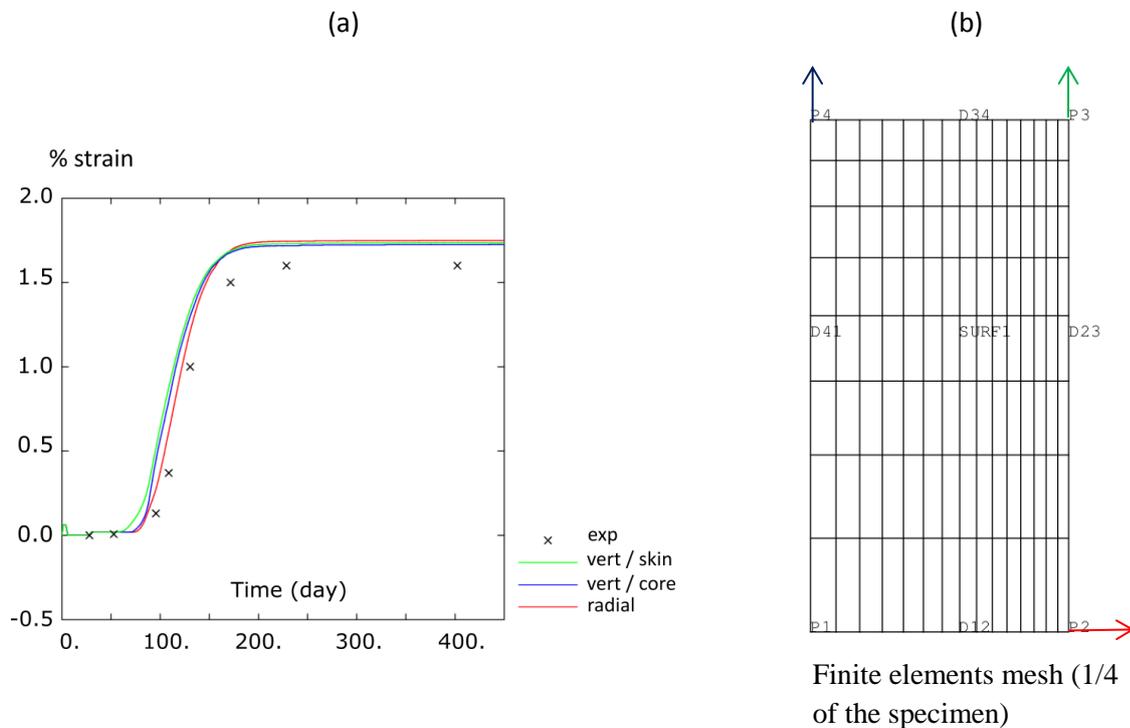


662

663 **Figure 15: Chemical concentration versus time (zoom on first 7 days including heating period)**

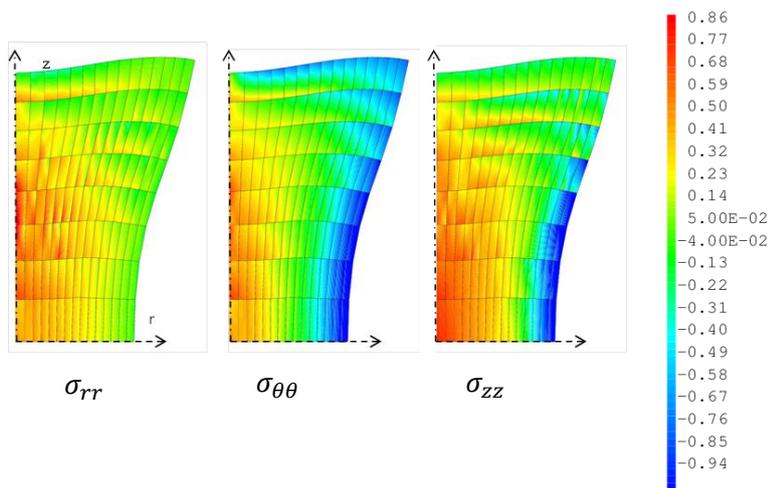
664 Figure 16 (a) shows the swelling versus time computed by the model (lines), compared with  
 665 experimental swelling (crosses). Each coloured line represents the swelling direction (radial direction  
 666 in red and vertical in green and blue) and location (in core in blue and along external surface in  
 667 green) given on the mesh (b). The swelling starts at the upper right corner (green line in (a) starts  
 668 first; it corresponds to the green arrow swelling in (b)).

669



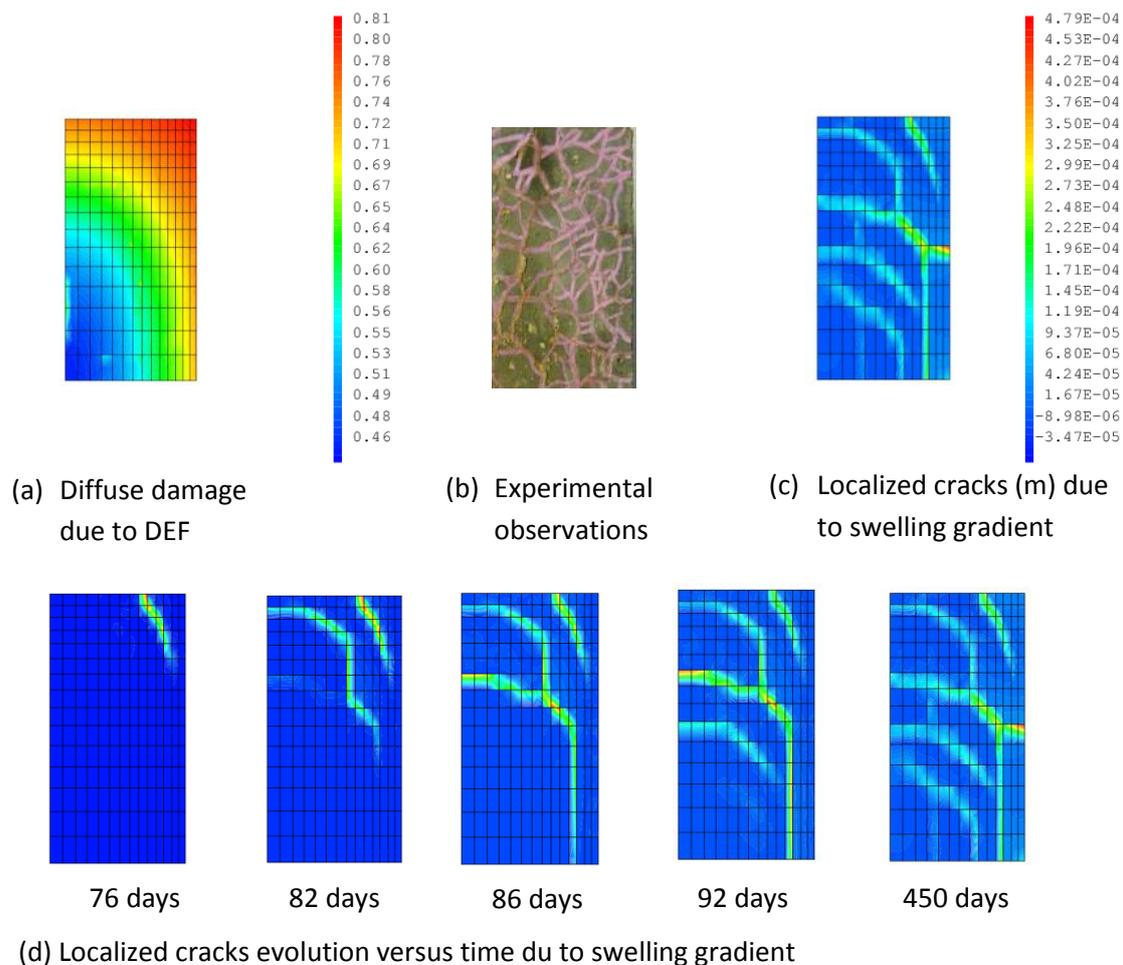
670 **Figure 16 : Simulated Swelling strain at different points versus time compared to experimental results of Martin's tests**  
 671 [29]

672 Figure 17 illustrates the stress state computed by the poro-mechanical model at 100 days. As the  
673 model used is based on linear interpolation functions in the finite elements for the displacements  
674 fields, the stresses appear quite discontinuous, this is a numerical artefact induced by the great  
675 gradient of swelling in this zone at this stage. However, their magnitudes remain correct, because  
676 they correspond to the better approximation allowed by the weak form of the variational principle  
677 applied to the equilibrium equation, with an admissible relative accuracy of 5.e-4. At this stage, the  
678 swelling is more developed close to the surface of the specimen than at its centre. Consequently,  
679 compressive stresses appear near the surface (blue zones), while the core of the specimen is in  
680 tension. This stress state evolves during the DEF and, at the end of the test, the stress state reverses  
681 and the edges in contact with water crack. Figure 18 gives the damage and localized cracks opening  
682 predicted by the model. The crack pattern at 100 days (c) is compared to a picture from Kchakech  
683 PhD thesis [26] (b) in which the same concrete than in Martin's work is used. Experimentally  
684 localized and diffuse cracking coexist. The model is able to distinguish cracks due to local swelling to  
685 cracks due to the swelling gradients. The diffuse damage is mainly due to the internal pressure of  
686 DEF, while localized cracks are induced by the gradient of swelling, they are the "structural" cracks  
687 and appear progressively between the swelling zone and the core of the specimen as illustrated in  
688 Figure 18 (d). After 100 days most of the localized cracks are developed and do not evolve anymore  
689 until the end of the test because the  $\sigma_{swelling}$  becomes quasi-homogenous over the specimen after  
690 this date.



691

692 Figure 17: Simulation of Stress state (MPa) during swelling of Martin's tests [29] ( at 100 days, deformed mesh X 100)



693

694 **Figure 18 : Damage pattern predicted by the model compared to the cracking pattern of Kchakech's specimen at 100 days**  
 695 **(same concrete and process than Martin [29]). (a) Diffuse damage due to the DEF pressure : scale 0 undamaged to 1**  
 696 **damaged (b) picture from Kchakech PhD thesis [26](c) localized cracks predicted by the model**

## 697 4 Conclusion

698 A chemical model has been proposed for the study of structures affected by DEF. It considers the  
 699 dissolution of primary sulfoaluminate hydrates and the possible fixation of aluminates during hot  
 700 periods, which explains the pessimum effect of heating duration observed in several experiments.  
 701 The model gives importance to the role of alkali, which affects the threshold temperature of  
 702 dissolution, the kinetics of dissolution, the **thermal conditions** and kinetics of aluminates fixation at  
 703 high temperature. At low temperature, alkalis can delay or prevent DEF according to their  
 704 concentration. At low temperature, the chemical model considers that DEF can be due either to the  
 705 conversion of monosulfate into trisulfoaluminates or due directly to the formation of Aft from  
 706 available sulfates and aluminates reversibly stored in C-S-H. The model was fitted with different  
 707 materials, heating cycles and storage conditions. It is able to explain the swelling potential of various  
 708 laboratory tests with a determination coefficient  $R^2$  of 90%, using a single set of parameters. The

709 main result of the chemical model is the number of moles of ettringite, which can be used in a poro-  
710 mechanical model through the pressure induced by DEF in the pores of the concrete. The structural  
711 effects of DEF can thus be assessed: in particular the swelling, **the damage induced by DEF, and the**  
712 **localized cracks induced by swelling gradients**. If the pressure, combined with the external loading, is  
713 great enough to provoke cracking, **diffuse** damage appears, reducing the strength of the concrete,  
714 occurring differently in tension and in compression. The model has been implemented in a finite  
715 element code and tested for the simulation of different basic experiments taken from a literature  
716 review. Now the model should be applied to larger and more sophisticated structures in order to  
717 validate or to improve the mechanical formulation. Forthcoming work will concern, in particular, the  
718 modelling of beams studied at IFSTTAR, Paris, by R.P. Martin, as these beams present different  
719 reinforcement rates and should thus allow the fitting of the mechanical part of the model to be  
720 refined.

## 721 5 Acknowledgements

722 **The authors thank the C.E.A (French Atomic and Alternative Energy Center) for the supply of finite**  
723 **element software Castem in its research and development version [8].**

## 724 Appendix: Evolution of state variables during a temperature plateau

### 725 $T > T_{th}$

726 For a cement with an amount  $A_c$  of aluminate and with the initial conditions given at  $t = t_0$ :

$$727 \begin{cases} \tilde{A}(t_0) = \tilde{A}_0 \\ \tilde{S}(t_0) = \tilde{S}_0 \\ M_1(t_0) = M_{1,0} \\ E_1(t_0) = E_{1,0} \\ E_2(t_0) = E_{2,0} \end{cases}$$

728 if the ratio  $\tau_d/\tau_f > 1$  and  $T > T_{th,f}$ , the evolution of  $\tilde{A}$  is given by:

$$729 \tilde{A} = \tilde{A}_0 \exp\left(-\frac{t-t_0}{\tau_f}\right) + (M_{1,0} + E_{1,0} + E_{2,0}) \left(\frac{\tau_f/\tau_d}{\tau_f/\tau_d - 1}\right) \left(\exp\left(-\frac{t-t_0}{\tau_f}\right) - \exp\left(-\frac{t-t_0}{\tau_d}\right)\right)$$

730 and the evolution of  $\tilde{S}$  by:

$$731 \tilde{S} = \tilde{S}_0 + (M_{1,0} + 3(E_{1,0} + E_{2,0})) \left(1 - \exp\left(-\frac{t-t_0}{\tau_d}\right)\right)$$

732 The hydrate amounts during the hot period then evolve as follows:

$$733 \quad \begin{cases} M_1 = M_{1,0} \exp\left(-\frac{t-t_0}{\tau_d}\right) \\ E_1 = E_{1,0} \exp\left(-\frac{t-t_0}{\tau_d}\right) \\ E_2 = E_{2,0} \exp\left(-\frac{t-t_0}{\tau_d}\right) \end{cases}$$

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