Chemical modelling of Delayed Ettringite Formation for assessment of affected concrete structures

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ABSTRACT

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

1. Introduction

Unexpected combinations of cement composition and curing conditions can lead to Delayed Ettringite Formation (DEF). This well-known deleterious chemical reaction takes place in the cement matrix often several years or decades after the concrete has been heated sufficiently to dissolve primary sulfoaluminate hydrates. The main causes of excessive heating can be either the exothermic reactions of cement hydration (which can occur particularly in massive structures like dams, large foundations, columns or beams), or overheating during the production of precast concrete elements. Since recommendations became available concerning the prevention of this problem (limits on the maximum temperature during hydration and of the amount of sulfates and alkali in cement), concrete structures can be built without apprehension [21]. However, the aptitude of DEF-affected structures has to be assessed to manage potential repairs or replacement. Various tools are available to help practitioners in this choice: follow-up of cracking to observe damage induced by the DEF, laboratory analysis, and residual swelling tests on core samples are the most used [28]. These experimental techniques are performed at a given moment and location. The question of the residual strength of the whole structure, and the future evolution of damage in the structure can only be addressed by combining these techniques with modelling. Unfortunately, DEF depends on many parameters (cement chemistry, interaction with aggregates, possibility of alkali leaching, concrete porosity, strength,

concrete mechanical behaviour, maximum temperature reached, duration of the hot periods, water saturation, stress and strain states, and damage), so designing a DEF model applicable at the structure scale remains a challenge. Some models based on thermodynamic considerations are already able to explain the different reactions leading to DEF [19,36]. They are highly nonlinear, as several coupled equations have to be solved simultaneously, and are thus difficult to use in the context of structural analysis in an industrial situation where several thousands of chemical and structural computation have to be performed simultaneously at each node of finite element meshes and at each step of stepwise analysis. From a mechanical point of view, efficient nonlinear models exist to analyse structural behaviour affected by swelling problems [10,23,25,37,38] but they are not yet able to consider all the chemical particularities of DEF. The purpose of this work is to propose a simplified chemical model answering the need for structural modelling. It has to be simple enough to be coupled with a nonlinear mechanical model implementable in a finite element code. The paper starts with the chemical model assumptions and equations, and this model is then fitted on a large number of experiments from the literature. Finally, the chemical model coupled with the nonlinear mechanical model based on poro-mechanics considerations is used to analyse the development of DEF expansion and cracking in a concrete cylinder. The features and the interest of a coupled chemo-mechanics approach to managing concrete structures affected by DEF is thus illustrated.

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	$C\overline{S}$	$C\overline{S}$	$(CaO)(SO_3)$
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	$(C_3A)(C\overline{S})_3H_{32}$	$(CaO)_6(Al2O3)(SO3)_3 \cdot 32H2O$
Monosulfate	M_1	$C_4A\overline{S}H_{12}$	$(CaO)_4(Al2O3)(SO3) \cdot 12H2O$
Available sulfates	$\widetilde{S}$	$\overline{S} + C\overline{S}$	$SO_4{}^{2-} + Ca\ SO_4$
Iron	F	F	Fe_2O_3
Aluminium	A	A	Al_2O_3
Available aluminates	$\widetilde{A}$	$A + C_3AH_6$	$(Al(OH)_4{}^-)_{1/2} + (CaO)_3(Al_2O_3)(H_2O)_6$
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 $\overline{S}$	SO_3
Equivalent number of moles of alkali	Na_{eq}	Na_{eq}	$Na^+ + K^{+(3)}$
Alkali concentration in saturated porosity	(Na)	$\dfrac{Na_{eq}}{\phi \cdot S_r + k^{(2)} \cdot CSH}$	$[Na^+] + [K^+]$
Ferrite fraction	ρ_F	$\rho_F = \dfrac{F}{A+F}$	–

(1) If the calculus is performed with the mass instead of the moles number.
(2) The coefficient k (0.077 l/mol) concerns alkali fixation in C-S-H. It is calculated according to [24], but this coefficient can also be taken equal to 0 if the heating takes place at early age.
(3) In moles number.

2. Principles and notations

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

The total number of moles of sulfates in a unit volume of concrete is noted S_c and the total number of moles of aluminates, A_C. According to [1], due to the solid–liquid equilibrium, the ionic concentrations of aluminates and sulfates are about 100 times smaller than the concentration of calcium or alkali. Therefore these two species are rapidly bound by the production of new phases and their mass transfer can be

Table 2

Physical data.

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

neglected at the scale of the structure. The mass balances imply that Eqs. (1) and (2) are constantly verified.

$$A_C = E_1 + E_2 + M_1 + G + \widetilde{A} \qquad (1)$$

$$S_c = 3(E_1 + E_2) + M_1 + \widetilde{S} \qquad (2)$$

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

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

The main chemical phenomena considered in this model are:

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

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

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

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