RECENT MODELLING ADVANCES TO PREDICT EARLY AGE BEHAVIOUR AND PREVENT INDUCED DISORDERS IN CONCRETE STRUCTURES

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Abstract
Sustainable development, economic considerations and technologic reasons lead to adopt more and more often blended cement for massive concrete structures. Most of the time slags are used combined or not with silica fume or fly ash. Hydration processes of these mixes are more complex than for single clinker cement. In fact activation energy is different for additions and clinker: so, the hydration kinetics of each component depends on the temperature during hydration. At high temperature addition reactions are more activated than clinker, consequently the Portlandite created during clinker hydration is consumed more quickly, and the Ca/Si ratio of its C-S-H increases with temperature while portlandite amount decreases. So, in large structures, hydration products, and consequently mechanical behaviour, are different in the core than near the edge due to the difference of temperature of this zone during hydration. This paper focus on the particularity of models developed in LMDC Toulouse to take into account this aspect in order to predict early age poro-mechanics behaviour of concrete as well as long term induced consequences.

Résumé
Le développement durable, les considérations économiques et des raisons technologiques conduisent à utiliser de plus en plus de ciments composés pour les structures massives en béton. La plupart du temps des laitiers sont utilisés, combinés ou pas avec des fumées de silice ou des cendres volantes. Les processus d’hydratation de ces mélanges sont plus complexes que pour un clinker seul. En effet les énergies d’activation de ces additions minérales et du clinker sont différentes, par conséquent la cinétique d’hydratation de chacun des composants dépend de la température pendant l’hydratation. A température élevée, les additions sont plus thermoactivées que le clinker, par conséquent elles consomment plus rapidement la portlandite issue de l’hydratation du clinker. Le rapport moyen Ca/Si des C-S-H présents dans la pâte augmentera donc avec la température, en contrepartie la quantité
résiduelle de Portlandite à un instant donné diminuera. L’eau liée est également affectée par le processus. Ainsi, dans les grandes structures, les hydrates, et par conséquent le comportement mécanique, sont différents entre le cœur de l’ouvrage et le bord en raison de la différence de température entre ces zones pendant l’hydratation. Cet article se focalise sur les particularités des modèles développés au LMDC de Toulouse pour prendre en compte cet aspect dans le but de prédire le comportement poro-mécanique au jeune âge de structures en béton ainsi que les effets induits à long terme.

1. INTRODUCTION

First the paper focus on enhancement required for classical hydration models such as the LMDC one [1] to model blended cements. The need to have a variable Ca/Si ratio in secondary C-S-H is shown and taken into account in the model thanks to an original method. Next the opportunity to consider ettringite during hydration process is discussed; it leads to a complementary chemical module which modifies the hydration products amounts according to the hydration temperature. The chemical module together with the hydration model allows managing ettringite dissolution at early age and re-precipitation at long term, especially in relation with alkali release. The dependence of hydrates nature on the temperature needs to consider the consequences in terms of mechanical properties and shrinkage. On purpose, a homogenisation model coupled with the percolation theory is clarified. Once the poro-mechanics characteristics are supplied by the homogenisation model, a water retention curve model allows computing capillary pressure and then shrinkage from early age until long term. The cement paste shrinkage constrained by aggregates in concrete is also interpreted to explain the statistical size effect which is seen as a consequence of the stress field heterogeneity induced by these paste contraction around aggregates. A method to consider this link is proposed to assess tensile strength decrease in large structures.

2. HYDRATION OF BLENDED CEMENT IN TEMPERATURE

2.1 Principles

The model of composed binder hydration is based on the coupled resolution of hydration kinetic, water mass balance and heat balance equations [1]. This coupled solving allows taking into account the respective effects of temperature and watering content on reaction kinetic of each phase of the binder (additions and clinker).

In the system of constitutive equations, the variables managed at each time step and each point of the 3D finite element mesh are:

- The degree of hydration of each anhydrous phase (clinker and additions)
- The temperature
- The water content
- The porosity
- The volume of the different hydrated phases produced by each anhydrous
- The volume of portlandite (produced by clinker and consumed by additions).

Recent advances in LMDC focuses on prediction of the different volume of hydrate phases using time-varying stoichiometry of the products of hydration in composed binder and more particularly in slag blended binder. Next sections will present two original aspects of these
improvements: the use of variable Ca/Si and W/Si ratios in C-S-H produced by slag when it is combined with clinker and the prediction of ettringite formation in the case of structures that can be sensitive to DEF.

2.2 Ca/Si et W/Si management during hydration of slag blended binders

Calcium consumable for slag hydration comes either from Portlandite produced during clinker hydration, either from slag itself. If calcium comes from Portlandite it is able to increase the instantaneous Ca/Si (applicable for secondary C-S-H in formation at this stage) which tends to the one of clinker alone \((\text{Ca/Si})^C\). On the contrary if Portlandite is missing, calcium can be provided only by anhydrous slag, consequently Ca/Si ratio tends to the stoichiometry value deduced from the composition of Slag alone \((\text{Ca/Si})^S\). For intermediate situation, it is proposed to use distribution coefficients which consider the probabilities to supply calcium from Portlandite \((P^C)\) of from Slag \((P^S=1-P^C)\). The instantaneous Ca/Si ratio of C-S-H produced by slag hydration at a given time is then given by (1)

\[
\text{Ca/Si} = (\text{Ca/Si})^C P^C + (\text{Ca/Si})^S (1 - P^C)
\]

With \(P^C\) the probability for calcium used in the hydration reaction to come from Portlandite:

\[
P^C \approx \frac{N^P}{N^P + N^S}
\]

\(N^P\) and \(N^S\) are respectively, the mole number of calcium in Portlandite and in non hydrated slag at a given time for a unit volume of paste.

In equation (1) \((\text{Ca/Si})^C\) is taken equal to 1.75 while \((\text{Ca/Si})^S\) depend on the slag composition which leads generally to a value close to 1.1

The amount of combined water in the C-S-H produced by clinker and slag is assessed according to the empiric relation ship (3).

\[
\text{W/Si} = \text{Ca/Si} + 1.45(Ca/Si - 1.2)^+
\]

In equation (3), the term \((.)^+\) means “positive part” and 1.2 is the W/Si ratio obtained in C-S-H produced by pure slag.

These 3 equations are used in a global step by step finite element hydration model [1] in which C-S-H from Clinker, C-S-H from slag, Portlandite, mono and tri-sulfaloaminates, \(C_3A_{16}\), \(M_2A_{13}\), \(C_4A_{13}\) are also computed for each time step. Then, by combining them with classical hydration kinetic equations which consider the activation energy of clinker and slag [2], the amount of each hydrate and of free and combined water can be predicted accurately. This assessment is made for each time step and for each location in a classical 3D finite element analysis. Details of the model are available in [2]. Figure 1 and Figure 2 show the ability of the model to simulate consumption of Portlandite and to obtain automatically realistic CA/Si ratio.
2.3 Link between early age hydration phenomena and DEF risk at long term

If no precautions are taken into account in the hydration model, an assumption could be false sometimes. In fact in the previous model, it is assumed that ettringite (trisulfoalminate) can be formed at early age. Practically this assumption is not always verified, particularly for high hydration temperatures. So the hydration equation system has to be modified according to the temperature during hydration. To consider this aspect LMDC develops a complementary chemical module which manages ions in solution. The chemical module is applicable since early age until long term and modifies the amount of hydrate according to thermodynamics conditions written in terms of ions concentrations. In this complementary module, the concentrations are computed for the following ions (4), this for each time step:

\[ \{Ca^{2+}, SO_4^{2-}, Al(OH)_4^{-}, OH^{-}, Na^{+}, H_3O^+\} \]  

(4)

Each ion of (4) is managed according to a mass balance equation in which source terms are derived from kinetic equations of dissolution precipitation of solids. In fact, in this model, anhydrous are affected by a dissolution equation, and for each main hydrate related in 2.1 a precipitation-dissolution equation is used. For example for ettringite, the equation has the following expression (5):

\[
\frac{\partial A_{Ft}}{\partial t} = k_{AFt} \left( \log \left( Ca^{2+} \right)^6 \left( SO_4^{2-} \right)^3 \left( Al(OH)_4^{-} \right)^2 \left( OH^{-} \right)^4 - \log \left( K_{AFt} \right) \right) \]

(5)

In (5) the thermodynamic constant \( K_{AFt} \) depends on the temperature according to the Vant’Hoff law (6).

\[
\ln(K_{AFt}) = \ln(K_{AFt}^0) + \frac{\Delta H_F^0}{R} \left( \frac{1}{T^0} - \frac{1}{T} \right) 
\]

(6)

Thanks to the Vant’Hoff law (6) used in the kinetic equation (5), the solubility of ettringite is controlled properly. At high temperature ettringite dissolves and ions’ are fixed in C-S-H,
when temperature comes back to a current level, ions are released in water. But as releasing kinetics are thermal dependent, ettringite formation is delayed.

Figure 3: Delayed ettringite formation conditioned by alkali leaching in a cylindrical concrete specimen (11 cm x 22 cm) submitted to high temperature cycle at early age

Another reason of ettringite delay is the alkali concentration evolution in porous water. In fact in this model, thermodynamic equilibriums allow to consider effects of alkali on pH and effect of pH on formation constants (especially via $OH^-$ concentration in eq 5). So, ettringite formation kinetic depends indirectly on the alkali content, details of this model are available in [4]. Figure 3 illustrates briefly this aspect: the mole number of delayed ettringite is computed at long term in a concrete specimen (cylinder diameter 11 cm x 22 cm high) submitted to a temperature cycle at early age, and to an alkali leaching in water at long term. The profiles of ettringite given on the left side of Figure 3 show the evolution since early age (none ettringite) until long term (maximum values). The effect of leaching increases the ettringite concentration near the edge of the specimen in contact with water.

3. HOMOGENISATION ASSUMPTIONS TO ASSESS PORO-ELASTIC PROPERTIES AT EARLY AGE

The two chemical models briefly presented previously supply the moles number of various phases (hydrates, combined water, free water, and residual anhydrous...). Combining these results and the concrete mix parameters (W/C, aggregate content...) allows computing, for each time step, the composition of concrete in terms of phase’s volumes. More, as each phase has mechanical properties issue from micro indentation tests [5], it is possible to assess mechanical properties versus time from very early age until long time. On purpose a homogenisation model is proposed by LMDC. It allows assessing poro-mechanics properties (bulk and shear modules, Biot coefficient), as suggested in [6].
3.1 Elastic properties assessment

The main differences between this model and previous ones concern the assumptions adopted for the volumes phases to consider, more than the homogenisation scheme itself. In fact the homogenisation scheme consists in a classical three stages one (paste, mortar, concrete). The first stage is a self consistent scheme at the paste scale. Once the paste properties are determined, they are used in a Mori-Tanaka scheme to take into account the sand fraction; to finish the homogenised mortar obtained is used as matrix in a second Mori Tanaka stage to consider larges aggregates. If these three stages of homogenisation are used in their classical form, what consists to consider all the phases in presence for each homogenisation stage, an over estimation of Young modulus is obtained at early age as shown in Figure 4, where results are compared to experimental ones supplied by Boumiz [7].

This overestimation of Young module at early age is due to the assumption of stress continuity between the different phases. But during hydration, anhydrous particles aggregates are not glued one-another before a certain amount of hydrate is created, this amount is called “mechanical percolation threshold”. So it is necessary to consider this effect in modelling as suggested in [8] and [9]. On purpose, a percolation function can be used. It gives the fraction of material glued by hydrates, and then allows computing the volume fraction of particles to consider in the homogenisation scheme. The originalities of the model proposed by LMDC consists to use a simple percolation function able to take into account the positive effect of aggregate to accelerate paste percolation on one hand, and to distinguish behaviour in compression and shear on the other hand.

The percolation function ($P$ in eq 7) takes into account, with the factor $f$ (equation 8), the possibility to consider the beneficial effect of aggregates on percolation from the paste level homogenisation. This effect is due to the fact that large aggregates are able to establish bridges on large distances between hydrates with a low quantity of hydrates, what accelerates the percolation process comparatively to a material with a low density of aggregates.

$$P = \left( \frac{f}{f_{cr}} \right)^{1/m} \leq 1$$  \hspace{1cm} (7)

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**Figure 4**: Young’s modulus versus hydration degree; Homogenisation solution without percolation theory compared to Boumiz experimental results [7]

**Figure 5**: Young’s modulus versus hydration degree: Homogenisation solution considering the percolation experiment results [7]
The factor \( f \) in (7) depends on the relative fraction of hydrate (\( \phi_h \)) in concrete related to the paste volume \((1 - \phi_c)\), with \( \phi_c \) the aggregates volume fraction in concrete.

\[
f = \frac{\phi_h}{(1 - \phi_c)}
\]  

(8)

Parameters \( f_{cr} \) and \( m \) in (7) are independent of the paste composition and of the concrete composition. They allow, especially, explaining the weak Young modulus at early age observed by Boumiz for low W/C ratios (Figure 5).

### 3.2 Biot coefficient assessment

The second originality of the homogenisation procedure developed in LMDC Toulouse consists to apply the percolation function only to the shear stress transmission. In fact, even if solid particles are not glued by hydrates, they are able to transmit a compressive stress. So, for the non percolated part of the cement paste, each non percolated fraction of a given phase keeps its bulk modulus but loses its shear modulus. This allows having a realistic response of the low hydrated cement paste which looks like a fluid at the very early age: It is then able to transmit isotropic stress but not deviatoric ones.

![Figure 6](image-url)

**Figure 6:** Drained and skeleton bulk modules and Biot coefficients versus hydration degree, predicted by the homogenisation model combined with the hydration model.

The realism of the bulk modulus assessment is of first importance to assess realistically a Biot coefficient as illustrated in **Figure 6**. To obtain the Biot coefficient (defined by eq 9), homogenisation is first done once with the real fraction of solid and the void but without the free water, in order to obtain the drained bulk modulus \( K_d \); and secondly without the void to assess the skeleton bulk modulus \( K_s \). The Biot coefficient \( b \) (eq 9) is deduced classically from these two homogenisation calculi.

\[
b = 1 - \frac{K_d}{K_s}
\]  

(9)

As both the volume of free water and the poro-elastic properties are supplied by the previous models. It is now possible using these results to predict shrinkage induced by drying from very early age to long term (drying induced by hydration reactions as well as external drying).
4. FROM PORO-MECHANICS TO SHRINKAGE

4.1 Shrinkage

From a poro-elastic point of view, shrinkage is the consequence of the capillary pressure applied on the compressible solid skeleton. The relation between an increment of shrinkage strain $d\varepsilon_{sh}$ and water pressure $P_w$ can then be expressed as follows:

$$d\varepsilon_{sh} = \frac{b \times d(Sr \times P_w)}{k_d}$$  \hspace{1cm} (10)

In (10), $Sr$ is the void saturation degree in water, $P_w$ the water pressure deduced from the capillary pressure assuming a null gas pressure ($Pg$ in the Kelvin’s law evoked in 11).

$$P_c = P_g - P_w = -\frac{RT}{M} \rho \ln(RH)$$ \hspace{1cm} (11)

In (11) $R$ the gas constant, $T$ the absolute temperature, $M$ the molar mass of water, $\rho$ its volumetric mass, $RH$ the relative humidity. Therefore, to assess the capillary pressure at early age, it is necessary to know the relative humidity in the pores. On purpose a water retention curve must be modelled. To be used at early age this model must consider properly the hydration degree and the temperature effects.

4.2 Water retention curve dependence on hydration degree

Water pressure used in eq. 10 must be deduced from the isotherm which links the water content and the relative humidity in the non saturated part of the pores. On purpose, an isotherm model depending on the volume fraction of C-S-H supplied by the hydration model is used as proposed in [10]. But in the present model, the volume fraction of voids contained in C-S-H is a constant, and these C-S-H’s voids are assumed to be saturated at 20°C for a relative humidity greater or equal to 75%. The branch of the isotherm between 0 and 75% is a Van Genuchten form as suggested in [10]. To achieve the sorption branch of the isotherm, it is assumed that 80% of the voids are full of water at 99% of relative humidity. This assumption is justified in [11]. Concerning the desorption branch it is approached using a polynomial function assuming an hysteretic cycle with an amplitude also proportional to the C-S-H amount. Finally the isotherm depends on the total void and on the C-S-H amount, the both computed by the hydration model. Figure 7 gives an example of isotherm computed with these assumptions. Both the adsorption and desorption curves are given for two hydration degrees close from the one estimated for the experimental results. As the C-S-H amount and the void volume fraction are assessed by the hydration model, it becomes possible to predict water retention curves from very early age to long term. Figure 8 is an illustration of desorption simulation for various hydration degrees (at 20°C). In Figure 8 when the amount of C-S-H is low, the saturation occurs only for high relative humidity values.
Concerning the temperature effect, it has been shown experimentally [12] that it leads to a decrease of the hysteresis and to a shift of the retention curve. These two phenomena have been studied by P. Souyris in his PhD works and leads to the proposition of an empirical relationship able to transform the isotherm according to the temperature. A first parameter moves the RH characteristic of C-S-H saturation from 75% to higher RH at high temperature; another one decreases the hysteresis amplitude of the isotherm.

The model is currently confronted to experimental results of shrinkage at very early age. It is able to explain shrinkage from the very beginning of hydration until long term (note for long term application a coupling with creep is used as described in [14]). It is also able to explain the modification of shrinkage amplitude with the amount of aggregates and comparison with experimental results from [13] validates this aspect.

CONCLUSIONS

This paper summarizes recent advances in models clarified in LMDC Toulouse in the framework of French research projects CEOS.fr and MEFISTO. Objectives of these modelling methods are to consider new blended cements, to prevent DEF risks at long term, to improve early age poro-mechanics modelling in order to assess realistically damage.

Among the main originalities clarified recently note:
- An hydration model able to change the hydrate nature function of slag contain and temperature.
- A possible coupling of hydration model with a chemical model able to explain dissolution of ettringite in temperature and to capture the effect of alkali on the DEF.
- An homogenisation approach which separates shear behaviour and bulk behaviour thanks to a percolation function.
- A model of water retention curve, function of hydration degree and temperature, able to supply capillary pressure to compute (in the poro-mechanics framework issue from homogenisation) paste and concrete shrinkage.

![Figure 7: Isotherm prediction for hydration degrees of 0.7 and 0.8 (exp results from [11])](image1)

![Figure 8: Prediction of the desorption branch of the isotherm for various hydration degrees from 0.1 to 0.8](image2)
LMDC works currently on a theory to link statistical scale effect with shrinkage at early age, and then chose objectively a reduced tensile strength in large structures in relation with phenomena described in the paper.

ACKNOWLEDGEMENTS

The authors acknowledge French research minister for the funding of projects CEOS.fr and Mefisto, Vinci Construction Grands Projets for its support concerning early age modelling and CEOS.fr large scale tests, EDF-CIH for its support to the chemical model clarification, Andra for its contribution to the research project dealing with shrinkage, creep and scale effects phenomena.

REFERENCES