Modelling

of

Alkali-Aggregate Reaction

BEHAVIOUR OF AAR-AFFECTED CONCRETE,
Modelling

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ABSTRACT

This paper explores the theory of reactive porous media to model the behaviour of an alkali-aggregate reaction affected concrete. The aim of the model is to predict the evolution of a "diseased" structure: must major repairs be foreseen, and if so, when? Given the difficulty of the task, we will be satisfied with the order of magnitude of the response.

The proposed model is based on the mechanics of porous media and uses simplifying assumptions to deal with the case of chemical reactions active in the material. These assumptions are stated, and have led to an experimental study that will serve to match the model with reality.

Keywords: Alkali-Aggregate Reaction, modelling, thermodynamics in porous reactive media

INTRODUCTION

The alkali-aggregate reaction causes swelling and cracking of concrete, the evolution of which is most often slow (the first damage is detected after about ten years). This may lead to unacceptable damage of the structure affecting its functional behaviour under normal conditions of safety. This has prompted a surge of research activities over the last decade in this domain, aiming at modelling the effect of the AAR on the concrete behaviour (Sellier *et al.* 1995, Diab & Prin. 1992, Hoobs. 1993, May *et al.* 1992).

This paper aims at modelling the effect of the alkali-aggregate reaction at the level of civil engineering structures, to predict the rate of evolution of the structure and its long term behaviour when affected by AAR. To this end, the theory of reactive porous media proposed by Coussy (1995) is employed, which allows to account, at the macro-level of material description, for a chemical reaction occurring at a micro-level. In the case of the alkali-aggregate reaction, the physico-chemical phenomena that cause damage and swelling involve the solid and the liquid phases constituting the concrete, together with the interactions between them. We must therefore incorporate the knowledge acquired on the microscopic scale directly in a macroscopic model describing the behaviour of the material.

We first explain the theoretical approach, considering the general case of a simple reaction A ⇔ B. We show how such a model can describe swelling like that due to the alkali-aggregate reaction, given various assumptions. We then consider the identification of the chemical constituents A and B and discuss the assumptions of the model.

THEORETICAL FRAMEWORK OF THE MODEL

Definition of the system

The system (S) representing the material concrete is on a scale intermediate between that of civil engineering structures and that of the microstructure: this is typically the laboratory specimen. We consider this specimen as the superposition of several continua: the skeleton, composed of the solid matrix and the connected porous space of

the concrete, and the pore solution containing several constituents. Within the system (S), a chemical reaction may occur, such that:

$$A \Leftrightarrow B \qquad (1)$$

where A and B represent two constituents of the pore solution of (S).

The swelling measured in laboratory experiments is that of the skeleton. The reactions between the skeleton and the pore solution, and between the various constituents of the liquid phase, are the cause of the alkali-aggregate reaction, and also of other physico-chemical phenomena that can be modelled in a similar way (autogenous shrinkage or drying shrinkage, creep, etc.).

Chemical reactions within a deformable material

Consider an open porous medium of initial volume $d\Omega$. The mass variation of the open system is due to the mass variations of fluid phases A and B per unit of macroscopic volume $d\Omega$, denoted m_A and m_B. The mass conservation for the two fluid phases reads

$$\frac{dm_A}{dt} = M_A^{\circ} - m_{A \to B}^{\circ} \qquad \qquad \frac{dm_B}{dt} = M_B^{\circ} + m_{A \to B}^{\circ} \qquad (2)$$

where M_i° represents the external rate of fluid mass supply per unit volume of each fluid phase. The quantity $m_{A \to B}^{\circ}$ is the rate of mass formation of product B due to chemical reaction (1) such that the quantity $m_{A \to B}^{\circ} d\Omega\, dt$ is the mass of phase A which transforms into phase B during time interval dt.

Using thermodynamics of open porous continua, the Clausius-Duhem inequality, which expresses locally the second law of thermodynamics, reads independent of dissipations associated with the transport phenomena of heat and fluid mass

$$\Phi = \Phi_1 + \Phi_{A \to B} \geq 0 \qquad (3)$$

where Φ_1 is the intrinsic dissipation associated with irreversible skeleton evolution (for example, cracking)

$$\Phi_1 = \sigma : \frac{d\varepsilon}{dt} - S\frac{dT}{dt} + g_m^A \frac{dm_A}{dt} + g_m^B \frac{dm_B}{dt} - \frac{d\Psi_1}{dt} \geq 0 \qquad (4)$$

and $\Phi_{A \to B}$ the dissipation associated with chemical reaction (1) :

$$\Phi_{A \to B} = \left(g_m^A - g_m^B \right) m_{A \to B}^{\circ} \geq 0 \qquad (5)$$

which are assumed to be non-negative independent of each other.

In these equations, σ represents the stress tensor applied to (S), ε the strain tensor, S the entropy of (S), T the temperature, g_m^A and g_m^B designate the free enthalpies per unit of mass of A and B. Ψ_1 is the free energy of the open elementary system. In the absence of irreversible skeleton evolution ($\Phi_1 = 0$), free energy Ψ_1 defines the thermodynamic state of the system only in terms of external variables, i.e. strain tensor ε, temperature T and fluid mass m_j (j=A,B) :

$$\Psi_1 = \Psi_1\left(\varepsilon, T, m_A, m_B\right) \qquad (6)$$

Using Eq. (6) in (4) yields

$$\Phi_1 = \left(\sigma - \frac{\partial \Psi_1}{\partial \varepsilon}\right) : \frac{d\varepsilon}{dt} - \left(S + \frac{\partial \Psi_1}{\partial T}\right)\frac{dT}{dt} + \left(g_m^i - \frac{\partial \Psi_1}{\partial m_i}\right)\frac{dm_i}{dt} = 0 \qquad i = A, B \qquad (7)$$

and the constitutive equations are given by the state equations

$$\sigma = \frac{\partial \Psi_1}{\partial \varepsilon} \qquad S = -\frac{\partial \Psi_1}{\partial T} \qquad g_m^i = \frac{\partial \Psi_1}{\partial m_i} \qquad i = A, B. \qquad (8)$$

In that case, the only source of dissipation is associated with the chemical reaction. It is given by inequality (5), where $g_m^A - g_m^B$ is the difference in chemical potentials between reactant phase and product phase. This gradient of specific free enthalpies expresses the thermodynamic imbalance between the chemical constituents involved in reaction (1). Chemical dissipation $\Phi_{A \to B}$ can be equally written in the form

$$\Phi_{A \to B} = A_m \, \xi^\circ \geq 0 \qquad (9)$$

where A_m is the affinity of the chemical reaction, and ξ° its reaction rate, related to the gradient of free mass enthalpies and to the rate of mass formation by

$$A_m = \gamma\left(g_m^A - g_m^B\right) \qquad \text{and} \qquad \xi^\circ = \frac{m_{A \to B}^\circ}{\gamma} \qquad (10)$$

with γ a constant which relates the mass formation rate and the reaction rate. In a more refined modelling, γ accounts for the stochiometry and the molar masses of the substances constituting the reactant and the product phases.

All equations introduced here before are purely macroscopic, since they involve only macroscopic state variables. In particular, reaction rate ξ° is proportional to the rate of mass formation in the chemical reaction. Furthermore, from Eq. (9), chemical affinity A_m is identified as the thermodynamic force associated in the chemical dissipation to reaction rate ξ°. It expresses the thermodynamic imbalance between the reactant and the product phases (= difference in chemical potentials). This explicit identification holds irrespective of transport phenomena of the reactant and product phase through the structure and is essential when defining the kinetics of the chemical reaction considered at the macro-level of material description (*i.e.* scale of laboratory tests). More precisely, according to expression (9) of chemical dissipation $\Phi_{A \to B}$, the kinetics of the reaction must be specified by a relation linking affinity A_m to reaction rate ξ°. In a first approach, the following expression may be adopted:

$$A_m = k_d \exp\left(\frac{E_a}{RT}\right)\xi^\circ \qquad k_d \geq 0 \qquad (11)$$

where k_d is a viscous coefficient which accounts for the micro-diffusion of chemical constituents involved in reaction (1), E_a is an activation energy which accounts for the effect of temperature upon the kinetics of the chemical reaction (1) and R the universal constant for ideal gas.

Consider now the elementary system as closed for the chemical constituents: there is no possible external supply of A and B (*i.e.* $M_i^\circ = 0$ in (2) with i=A, B). The mass variations of A and B results then only from the reaction (1):

$$m^\circ_{A \to B} = \dot{m}_B = -\dot{m}_A = \gamma \, \xi^\circ \tag{12}$$

The previous assumption allows to reduce the number of state variables. In fact, because the Clausius-Duhem inequality of the closed system reads :

$$\Phi = \sigma : \dot{\varepsilon} - S\dot{T} - \dot{\Psi}_2 \geq 0 \tag{13}$$

a comparison with (3) allows to consider reaction extent ξ as an internal variable because its evolution is spontaneous and cannot be controlled by external flow. Free energy Ψ_2 of the closed system then reads :

$$\Psi_2 = \Psi_2(\varepsilon, T, \xi) = \Psi_1(\varepsilon, T, m_A = -\gamma\xi, m_B = \gamma\xi) \tag{14}$$

and state equations become

$$\sigma = \frac{\partial \Psi_2}{\partial \varepsilon} \qquad S = -\frac{\partial \Psi_2}{\partial T} \qquad A_m = -\frac{\partial \Psi_2}{\partial \xi} \tag{15}$$

where stress tensor σ, entropy S and chemical affinity A_m are the thermodynamic forces associated in dissipation Φ with the rates of state variables ε, T and ξ respectively . In contrast to the open elementary system, affinity A_m derives now explicitly from free energy Ψ of the closed system, and

$$\Phi = -\frac{\partial \Psi_2}{\partial \xi} \dot{\xi} = A_m \dot{\xi} \tag{16}$$

The evolution of ξ is still governed by the kinetics law (11) with $\xi^\circ = \dot{\xi}$.

Swelling due to a chemical reaction

In the above, a simple reaction (1) was considered, and it was shown how it can be integrated in a constitutive modelling at the macro-level of material description. In turn, this framework of closed reactive porous media will be employed to model swelling due to this chemical reaction. For the sake of clarity, only isothermal evolutions will be considered, and shear effects will be set aside.

Consider a reactive porous continuum, closed with respect to the chemical constituents. Hence, the state equations are given by relations (15), and the constitutive modelling can be worked out from specifying expression of free energy $\Psi = \Psi_3(\varepsilon, \xi)$ of the closed system. The following expression can be adopted for an isotropic material

$$\Psi = \Psi_3(\varepsilon, \xi) = \frac{1}{2} K \varepsilon^2 - \alpha K \varepsilon \xi - A_{m0} \, \xi + \frac{1}{2} L \xi^2 \tag{17}$$

The above expression corresponds to a stress relieved reference state (initial stress $\sigma_0 = 0$), to an initial thermodynamic imbalance between the chemical constituents A_{m0}, and to a linearization with respect to both volume strain $\varepsilon = \mathrm{tr}\varepsilon$ and reaction extent ξ. K, L and α are intrinsic characteristics of the materials .

Using expression (17) in Eq. (15) the state equations read explicitly

$$\sigma = K(\varepsilon - \alpha \, \xi) \qquad \text{and} \qquad A_m = A_{m0} + \alpha K \varepsilon - L \xi \tag{18}$$

where $\sigma = \frac{tr\sigma}{3}$ is the mean stress. In addition, substituting Eq. (17) in kinetics law (11) yields

$$A_m = A_{m0} + \alpha\, K\, \varepsilon - L\, \xi = k_d \exp\!\left(\frac{E_a}{RT}\right) \dot{\xi} \tag{19}$$

Furthermore, the first of state equations (18) can be inverted:

$$\varepsilon = \frac{\sigma}{K} + \alpha\, \xi \tag{20}$$

which allows to identify

$$\varepsilon_{ch} = \alpha\, \xi \tag{21}$$

as the strain of chemical origin, related with reaction extent ξ by coefficient α which can be considered as a chemical dilatation coefficient. Eqs. (20) and (21) allow to rewrite the constitutive equations in the equivalent form

$$\sigma = K\big(\varepsilon - \varepsilon_{ch}\big) \qquad \frac{A_m}{\alpha} = \left(\sigma + \frac{A_{m0}}{\alpha}\right) - \kappa\, \varepsilon_{ch} = \eta\, \dot{\varepsilon}_{ch} \tag{22}$$

$$\text{with} \quad \kappa = \frac{L}{\alpha^2} - K \quad \text{et} \quad \eta = \frac{k_d}{\alpha^2}\exp\!\left(\frac{E_a}{RT}\right) \tag{23}$$

Constitutive equations (22) are linear with respect to strain ε and stress σ. The second one shows that an interaction between σ and the affinity of the reaction is taken into account. If it is negligeable, the two equations can be solved separately. η is the viscosity governing the kinetics. η depends from k_d, α, Ea and T. k_d corresponds to the fact that as the reaction advances *i.e.* as ξ increases, the reactants have to bypass the layers of products already formed to meet and form new products. k_d may not be constant, but may increase as the reaction advances, *i.e.* $k_d = k_d(\xi)$ or $k_d = k_d(\varepsilon_{ch})$. This renders complementary evolution law (22) non-linear with respect to chemical strain ε_{ch}.

In the case of a constant viscosity and for σ constant, equations (21) and (19) lead to

$$\varepsilon = \frac{\sigma}{K} + \varepsilon_\infty\left(1 - \exp\!\left(-\frac{t}{\tau}\right)\right) \quad \text{where} \quad \varepsilon_\infty = \frac{\sigma}{\kappa} + \frac{A_{m0}}{\alpha\kappa} \quad \text{and} \quad \tau = \frac{\kappa}{\eta} \tag{24}.$$

The curve representing the free swelling versus time, obtained from this theoretical framework, is represented in figure 1. With all the restrictive assumptions made in this example, its shape is in satisfactory agreement with the experimental curves for length versus time obtained on mortar bars and on concrete prisms (Bollote. 1992, Pleau *et al.*, 1989, Rigden *et al.* 1995, Shayan & Ivanusec. 1989, Wang & Gillot. 1992 and many others).
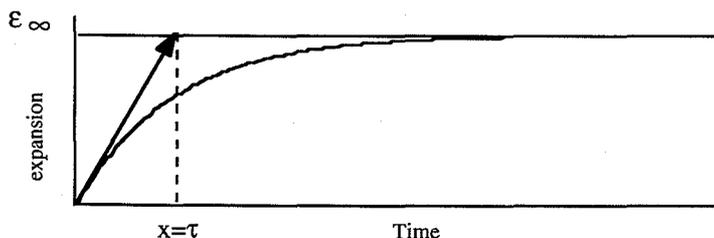

Fig. 1: *Shape of the swelling curves yielded by the model*

ADAPTING THE MODEL TO THE ALKALI-AGGREGATE REACTION

The theoretical framework described here can be used to model the behaviour of porous materials in which a great variety of physico-chemical phenomena occur (chemical reaction in solution, creep, liquid-vapour phase change, osmosis, etc.). It can be extended to any type of skeleton behaviour (inelastic, non linear, anisotropic, etc.). However, the practical interest of the model reduces with the number of phenomena taken into account.

The application of this framework to a problem like the alkali-aggregate reaction involves examining the validity of the various assumptions and checking that the simplest possible model suitably accounts for the behaviour of the material.

We previously described the behaviour of a system (open, then closed) in which a chemical reaction occurs within the pore solution. A major step of the alkali-aggregate reaction is the dissolution of a part of the aggregates. This case would be treated in a similar way with $\dot{\xi}$ representing the mass of the skeleton going into the solution per unit of time and $-\dfrac{\partial \Psi}{\partial \xi}$ identified with the affinity of the dissolution reaction. Identifying A and B is thus the first assumption to discuss.

Identification of the controlling step

The alkali-aggregate reaction is a set of physical and chemical processes leading to the formation of reaction products in concrete that cause swelling and cracking. We can distinguish:
* stages of diffusion: transport of ions through the cement paste and its porous network to the reactive silica of the aggregates,
* stages of dissolution: dissolution of the silica and of the portlandite of the cement paste as the calcium is consumed,
* stages in solution: reactions of coagulation and/or precipitation of gels and precipitates, as well as the formation of various crystals (Dron & Brivot, 1993).

The model described above applies directly to the case of dissolution of the reactive silica.

According to a recent study (Lombardi *et al.* 1996), it seems that the coagulation and precipitation reactions are clearly faster than the silica dissolution. These reactions are therefore ruled out as controlling steps.

Two categories of phenomena are still likely to impose their kinetics on the set of damage processes: diffusion and dissolution.

Many tests (Bollote. 1992, Sibick & Page. 1992) show that the total swelling and the swelling rate can vary considerably for a given cement paste, depending on the type of aggregate. The dissolution of the silica therefore at least partially imposes its velocity on the process.

What is actually missing is a better understanding of the exact role of water in the material swelling. Does the absence of external water prevent the formation of the reaction products, or only their swelling? Does water act only as a vector allowing the diffusion of the hydroxyl ions to the reactive silica, or is it consumed in the reaction? We shall attempt a partial experimental reply (Larive *et al.* 1996).

Quantification of the progress of the reaction within the concrete

Being able to determine the progress of the dissolution reaction would of course be of great help in quantifying the variable ξ of the model. Very few methods yield a quantitative idea of the stage reached by the alkali-aggregate reaction within the concrete. We have already tested on mortars the new version of the "MINÉRAUX" program

developed at the Laboratoire Central des Ponts et Chaussées (Deloye & Divet. 1992). The first results were very satisfactory, so we have used the method on concrete to calculate the percentage of the silica in the aggregates (insoluble in nitric acid at 1/50 by volume) that is transformed into reaction products (soluble under the same conditions).

This would make it possible to evaluate the variable ξ introduced above.

We encountered two difficulties: the representativeness of the sample analysed and the sensitivity of the method. The former makes it impossible for us to state definitive results, because many analyses led to results for cement content that are incompatible with the proportion of concrete; however, the method can detect the existence of the alkali-aggregate reaction, but this quantification is extremely tricky because, compared to that of a mortar, the specific surface area of the aggregates is proportionally much smaller in a concrete, and aggregates may contain clays and pyrites, causing the formation of ettringite and further complicating the calculation of dissolved silica.

Another method reveals the evolution of the alkali-aggregate reaction in concrete: fluorescence of AAR-products impregnated with uranyl acetate and illuminated by suitable ultraviolet radiation (Guédon *et al.* 1996). But this method is not really quantitative.

In the current state of our knowledge, it is difficult to reliably compare the quantity of reaction products in two specimens. This makes any experimental quantification of the coupling between the physico-chemical phenomena and the mechanical behaviour risky.

Influence of mechanical stresses

As just mentioned, the quantification of the influence of mechanical stresses on the rate of the reaction is difficult. However, it is important to see how the application of a stress modifies the concrete swelling. We performed tests under a uniaxial stress and measured simultaneously the longitudinal and transverse expansion. It allows us to see if the strains blocked in one direction are fully transferred to the other or if, in volume, the swelling is decreased (Larive *et al.* 1996).

Isotropy

It is difficult to find experimental data on that topic in the literature: many standardized tests require measurement of the longitudinal elongation of the specimens, but none considers their transverse expansion. However this is required in order to confirm the isotropy of the swelling. Our experimental plan will be concerned with this point.

Linear elasticity

One of the first consequences of the alkali-aggregate reaction is cracking of the concrete, in particular of the skin. However, since a detailed description of the cracking is not the objective of our model, we have assumed *a priori* that the behaviour of the material is linear elastic. If this turns out to be inadequate, inelastic variables are to be added, as for any ordinary solid, as state variables (*i.e.* in the equations of state and the complementary laws) or as arguments of a function such as k_d in (11). We therefore considered the evolution of the mechanical properties of the material to determine whether the assumption of linear elasticity is pertinent.

CONCLUSION

The approach used in the model consists in applying the mechanics of porous media to the particular case of a chemical reaction occurring inside the material.

Simplified assumptions were made to obtain a model that is easy to use. At present, we are attempting to check these assumptions, using the many experimental results from the literature and developing an experimental plan to clarify questionable points.

This research involves frequent interactions between theory and experiment, to bring our assumptions closer to reality.

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