MODELING OF THERMOCHEMOMECHANICAL COUPLINGS OF CONCRETE AT EARLY AGES

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ABSTRACT: This paper explores the theory of reactive porous media in the modeling of thermochemomechanical couplings of concrete at early ages. The formulation is based upon thermodynamics of open porous media composed of a skeleton and several fluid phases saturating the porous space. It accounts explicitly for the hydration of cement by considering the thermodynamic imbalance between the chemical constitutents in the constitutive modeling at the macrolevel of material description. In particular, the diffusion of water through the layers of hydrates is considered as the dominant mechanism of the hydration with respect to the kinetics of two apparent phenomena: aging and autogeneous shrinkage—the first related to the formation of hardened cement gel, the latter induced by capillary effects related to the formation of menisci due to water consumption through hydration. The intrinsic relations concerning heat generation, aging, and autogeneous shrinkage are so derived. Furthermore, it allows to make precise the decoupling hypothesis in order to clarify the linkages between different aging models: solidification theory and maturity models. In particular, it is shown that hydration degree, autogeneous shrinkage, and maturity are equivalent state variables, provided that stress and temperature evolutions do not effect the thermodynamic imbalance of hydration.

INTRODUCTION

Hydration of cement is a highly exothermic and thermally activated reaction. The exothermic nature of the chemical reactions leads to heat generation, which, in the hours after pouring, may result in high temperature rises of up to 50°C in massive structures. In return, being thermally activated, the temperature evolution influences the kinetics of the hydration: the higher the temperature, the faster the reaction occurs. The concrete then sets hot. As the rate of hydration slows down the temperature decreases resulting in a thermal shrinkage, which induces stresses of thermal origin. Moreover, the hydration of cement is at the base of what is called the aging phenomenon, which—at a macrolevel of material description (i.e., scale of laboratory test specimen)—appears as a change of mechanical properties in time [see Byfors (1980)]. At a microlevel of material description, the aging cannot be regarded as an actual change of the mechanical properties of the matter constituting concrete, but rather as a change in the concentrations of the nonaging constituents [e.g., Bazant (1994)], i.e., the hardened cement gel (roughly the tubermorite gel, consisting mainly of tri- and bicalcium silicate hydrates). Furthermore, this change in concentration of the hardened cement gel is accompanied by a volume reduction: the (absolute) volume of formed hydrates is inferior to the sum of the volumes occupied by the consumed water and hydrated cement (Le Chatelier 1900). This phenomenon results in a chemical shrinkage, coupled with a capillary shrinkage related to the formation of menisci due to water consumption through hydration. The basic micromechanisms continue to be a matter of intensive research (Wittmann 1976; Buil 1979; Neville 1981; Wittmann 1982; Acker 1988; Hua 1992; Jennings and Xi 1993).

Strains of thermal and chemical origin are not the only ones. Further strains can be observed experimentally [drying shrinkage, drying creep, and basic creep in the case of load application; cf. Acker (1993)]. They are of different physical origin still to be explored (Wittmann 1982). Furthermore, these phenomena are in competition: the shrinkage (if restrained) and the temperature gradients induce a severe state of stresses, which might be of a magnitude beyond the strength developed. An accurate modelling of the behavior of concrete at early ages is therefore crucial to predict cracking, which affects the durability of the structure and requires often expensive treatments. This has prompted a surge of research activities over the last decade in this domain (Springenschmid and Breitenbücher 1986; Ballardini et al. 1993; Chui and Dilger 1993; Emborg and Bernander 1984; Acker et al. 1985; Singh 1985; van den Bogert et al. 1987; Emborg 1989; Laube 1990; Harada et al. 1990; Breugel 1991; Tanabe and Ishikawa 1993; Huckfeldt 1993; Mazars and Bournazel 1993; Torrenti et al. 1992, 1994; Springenschmid 1994).

This paper aims to model concrete at early ages as a thermomechanical chemoreactive porous media. To this end, the theory of reactive porous media proposed by Coussy (1995) is employed. For the sake of clarity, we will start by considering only the hydration in the formulation of the constitutive equations. This leads to the modeling of two phenomena related to the hydration reaction: autogeneous shrinkage and aging.

The modeling will be carried out in the framework of physical linearization (hypothesis H1) and infinitesimal transformations (hypothesis H2).

THERMODYNAMIC FRAMEWORK OF REACTIVE POROUS MEDIA

In this section, we will briefly recall the basic relations of the theory of reactive porous media to account at the macrolevel of material description for a chemical reaction. For the general theory of open reactive nonsaturated porous media, the interested reader is referred to Coussy (1995).

Consider an open porous medium composed of a matrix and a porous space. Let the porous space be saturated by n fluid phases, assumed to be, and to remain, continuous. The porous media can then be viewed as the superposition of 1 + n continua, the skeleton and the n saturating fluids. For the sake of clarity, we will consider here only a reactant phase and a product phase; a chemical reaction may occur between them such that

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

where A = reactant phase of mass increase m_A; and B = product phase of mass increase m_B with respect to a reference state.

The underlying ideas to model such a reaction in the framework of reactive porous media are mass conservation considerations and thermodynamics of open porous media. In particular, in the absence of overall mass creation, the overall continuity equation, which locally expresses the overall mass conservation, reads as follows:

$$dm_T/dt = \sum_{i=A,B} M_i^o \qquad (2)$$

where m_T = total mass increase; and $M_i^o = -\text{div}\mathbf{M}_i$ = external rate of fluid mass supply of each fluid phase. In return, the mass conservation for each fluid phase accounts for reaction (1) in terms of mass-rate formation, as follows:

$$dm_A/dt = M_A^o - m_{A \rightarrow B}^o; \quad dm_B/dt = M_B^o + m_{A \rightarrow B}^o \qquad (3a,b)$$

where $m_{A \rightarrow B}^o$ = rate of mass formation of the product phase. It is a priori not the time derivative of a function, because the mass increases of reactant and product phase may be due to external supply (i.e., the terms M_A^o and M_B^o).

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

$$\Phi_1 + \Phi_{A \rightarrow B} = \boldsymbol{\sigma}:\dot{\boldsymbol{\varepsilon}} - S\dot{T} + g_m^j \dot{m}_j - \dot{\Psi} + \Phi_{A \rightarrow B} \geq 0 \qquad (4)$$

where an overdot denotes time derivation; Φ_1 = dissipation related to intrinsic dissipative mechanisms (such as cracking), which are not considered here (i.e., $\Phi_1 = 0$); and $\Phi_{A \rightarrow B}$ = dissipation associated to chemical reaction (1). In the previous equation, $\boldsymbol{\sigma}$, S, and g_m^j = stress tensor, entropy, and free enthalpies per mass unit of fluid phase $j = A, B$. They are the thermodynamic forces associated in dissipation (4) to the rates of strain tensor $\boldsymbol{\varepsilon}$, temperature T, and fluid mass m_j ($j = A, B$). They derive from free energy Ψ

$$\Psi = \Psi(T, \boldsymbol{\varepsilon}, m_A, m_B) \qquad (5)$$

in the habitual manner

$$S = -\frac{\partial \Psi}{\partial T}; \quad \boldsymbol{\sigma} = \frac{\partial \Psi}{\partial \boldsymbol{\varepsilon}}; \quad g_m^j = \frac{\partial \Psi}{\partial m_j}; \quad \text{with } j = A, B \qquad (6a-c)$$

Furthermore, chemical dissipation $\Phi_{A \rightarrow B}$ depends on the rate of mass formation $m_{A \rightarrow B}^o$, such that

$$\Phi_{A \rightarrow B} = (g_m^A - g_m^B)m_{A \rightarrow B}^o \geq 0 \qquad (7)$$

where $g_m^A - g_m^B$ = difference in free mass enthalpy between product phase and reactant phase, which expresses the thermodynamic imbalance between the chemical constituents involved in reaction (1). Chemical dissipation (7) can be equally written in the following form:

$$\Phi_{A \rightarrow B} = A_x x^o \geq 0 \qquad (8)$$

where A_x = affinity of the chemical reaction; and x^o = its reaction rate, related to the gradient of free mass enthalpies and to the rate of mass formation by the following:

$$A_x = k(g_m^A - g_m^B); \text{ and } x^o = m_{A \rightarrow B}^o/k \qquad (9a,b)$$

with k = a constant that relates the mass formation rate and the reaction rate. In a more refined modeling, k accounts for the stoichiometry and the molar masses of the substances constituting the reactant and the product phases.

Note that all equations introduced here are purely macroscopic, because they involve only macroscopic state variables. In particular, reaction rate x^o is proportional to the rate of mass formation in the chemical reaction, and affinity A_x expresses the thermodynamic imbalance (free enthalpy gradient) between products and reactants—directly at the macrolevel of material description. Furthermore, from (8), chemical affinity A_x is identified as the thermodynamic force associated in the (chemical) dissipation to reaction rate x^o. It expresses the thermodynamic imbalance between the reactant and the product phase (difference in chemical potentials). This explicit identification holds irrespective of transport phenomena of the reactant and product phase through the structure, and will be essential when precising the kinetics of the chemical reaction considered at the macrolevel of material description (i.e., scale of laboratory tests).

Consider now the elementary system as closed for the chemical constituents (i.e., no external supply)

$$M_i^o = 0 \qquad (10)$$

Then, according to (3) and (9), the rate of mass formation $m_{A \rightarrow B}^o$ is actually a time derivative, as well as reaction rate $x^o = dx/dt = \dot{x}$

$$m_{A \rightarrow B}^o = \dot{m}_{A \rightarrow B} = -\dot{m}_A = \dot{m}_B = k\dot{x} \qquad (11)$$

Closure condition (11) allows to reduce the number of state variables that characterize the thermodynamic states of the porous media. In fact, because intrinsic dissipation φ_1 of the closed elementary system reads as follows:

$$\varphi_1 = \boldsymbol{\sigma}:\dot{\boldsymbol{\varepsilon}} - S\dot{T} - \dot{\psi} \geq 0 \qquad (12)$$

a comparison with (4) allows us to consider reaction extent x as an internal state variable because its evolution is spontaneous and cannot be controlled by external flow. In other words, in a closed system a chemical reaction is an internal process, and reaction extent x is a measure of the progress of the reaction considered [cf. Atkins (1994)]. Free energy ψ of the closed system then reads as follows:

$$\psi = \psi(T, \boldsymbol{\varepsilon}, x) = \psi(T, \boldsymbol{\varepsilon}, m_b = -m_a - kx) \qquad (13)$$

and state equations (6a–c) become

$$S = -\frac{\partial \psi}{\partial T}; \quad \boldsymbol{\sigma} = \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}}; \quad A_x = -\frac{\partial \psi}{\partial x} \qquad (14a-c)$$

where entropy S, stress tensor σ, and chemical affinity A_x = thermodynamic forces associated in intrinsic dissipation φ_1 with the rates of state variables T, $\boldsymbol{\varepsilon}$, and x. In contrast to the open elementary system, affinity A_x derives now explicitly from free energy ψ of the closed system. Because other (intrinsic) dissipative mechanisms (such as cracking) are not considered (i.e. $\Phi_1 = 0$, thus assuming an elastic behavior of the bulk material), intrinsic dissipation φ_1 is here equal to the chemical dissipation, $\varphi_1 = \Phi_{A \rightarrow B} \geq 0$, given by (8) with $x^o = \dot{x}$.

In the foregoing, only one simple reaction [(1)] was considered, and it was shown how it can be integrated in a constitutive modeling at the macrolevel of material description. In what follows, this theory of closed porous media will be applied to the hydration reaction.

APPLICATION TO HYDRATION REACTION

Hydration of cement is a fairly complex set of competing chemical reactions of different kinetics and amplitudes [cf. Copeland et al. (1960) and Granju and Grandet (1988)], related to complex physicochemical phenomena at the microlevel of material description [cf. Regourd (1982)]. At the level of the porous media, the hydration may be roughly viewed as follows (Fig. 1): at instant t, the solid part of the porous
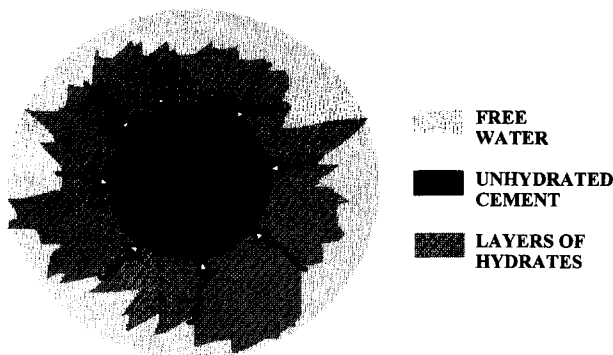
FIG. 1. Diffusion of Water through Layers of Hydrates

Legend:
- FREE WATER
- UNHYDRATED CEMENT
- LAYERS OF HYDRATES

media is formed of unhydrated cement and hydrates. For the reaction to occur, water diffuses through the layers of hydrates already formed to the unhydrated cement. Once they meet, new hydrates are formed in an instantaneous manner relative to the timescale of the diffusion process; then the water is chemically and/or physically combined. Therefore the diffusion of water through the layers of hydrates may be considered as the dominant mechanism of the hydration with respect to the kinetics. In terms of reaction (1), reactant phase A corresponds to the free water, and product phase B to the water combined in the hydrates

$$\text{Free water} \rightarrow \text{Combined water} \qquad (15)$$

Therefore mass formation rate $m^o_{A \rightarrow B}$ represents the mass rate of (nonevaporable) water combined in the solid phase. It is approximately proportional to the rate of mass formation of hardened cement gel (Powers and Brownyard 1948). In this light, reaction rate x^o can be considered the hydration rate of the diffusion controlled reaction (15). It is controlled by the thermodynamic imbalance (affinity A_x) between free water and water combined in the solid phase, and amplified by thermal activation when the free water combines with unhydrated cement to form the hydrates. This will be used when precising the kinetics of the reaction.

Finally, assuming the elementary system as closed (hypothesis H3) hydration extent x can be considered as an internal state variables, related by (11) to the mass of nonevaporable water combined in the hydrates. Then the state equations are given by relations (14a–c), and the constitutive modeling can be worked out from specifying expression (13) of free energy ψ of the closed system.

FREE ENERGY OF AGING MATERIALS

Due to physical linearization (hypothesis H1), the expression of free energy ψ is limited to a second-order expansion with respect to external state variables t and ε, as follows:

$$\psi = \psi_o + \psi_1 + \psi_2 \qquad (16a)$$

In the case of an isotropic material, these terms read as follows:

$$\psi_o = \sigma_o \text{tr}\varepsilon/3 + s_o{:}e - S_o(T - T_o) - A_{xo}x \qquad (16b)$$

$$\psi_1 = -3K(x)\text{tr}\varepsilon(\alpha(T - T_o) + \beta x) + 1/T_o F(x)(T - T_o) \qquad (16c)$$

$$\psi_2 = (1/2)K(x)\text{tr}^2\varepsilon + G(x)e{:}e$$
$$\quad - (1/2)(C_\varepsilon/T_o)(T - T_o)^2 + (1/2)\kappa x^2 \qquad (16d)$$

ψ_o represents the contribution of the initial conditions in stress $\sigma_o = s_o + \sigma_o 1$ (initial mean stress $\sigma_o = \text{tr}\sigma_o/3$, initial stress deviator s_o), in entropy S_o and affinity A_{xo} of the hydration reaction; ψ_2 considers the terms of second-order expansion with respect to arguments $\varepsilon = e + \text{tr}\varepsilon/3 1$, T, and x; and ψ_1

accounts for the possible coupling between volume strain $\text{tr}\varepsilon$, temperature variation $T - T_o$, and hydration extent x. As shown below, function $F(x)$ represents the heat generated by hydration. The meaning of coefficients α and β will appear later.

The previous equations of free energy account for aging by considering the (instantaneous) material properties at the macrolevel of material description, bulk modulus K and shear modulus G, as a function of hydration extent x; i.e.

$$K(x) = \frac{E(x)}{3(1 - 2\nu)} \quad \text{and} \quad G = G(x) = \frac{E(x)}{2(1 + \nu)} \qquad (17a,b)$$

where $E = $ Young's modulus; and $\nu = $ Poisson's ratio. In aging formulation (17), we refer to experimental results, which have shown that Young's modulus E depends on the hydration degree, but Poisson's ratio ν does not change in time significantly (Laplante 1993).

It is worthwhile to note that aging formulation (17) derives its essential characteristics from the thermodynamic framework of reactive porous media, as briefly presented earlier. In fact, without referring to this thermodynamic framework, (17a) and (17b) relate only the change of macromaterial properties to any macroscopic variable, noted x, chosen to represent the state of "aging" of the material. For instance, an equivalent age, also called maturity μ, is often employed here (e.g., Eymard et al. (1991) and Bournazel (1992)]. On the contrary, using the thermodynamic framework of reactive porous media, aging formulation (17) together with (11) relates explicitly the actual change of macromechanical properties to the change in the concentration of the nonaging constituents, i.e., the hardened cement gel. This relation was also pursued by Bazant (1977), Bazant and Prasannan (1989a, b) and Carol and Bazant (1993) with a solidified fraction law $v(t) = V(t)/V(\infty)$, where $V(t) = $ effective volume of solidified constituent at time t; and $V(\infty) = $ final value when all the chemical reactions have been completed. However, their solidification theory is not based on mass conservation considerations [(2), (3), (10), and (11)], but on relations linking macroscopic stresses to stresses in the solidified material; this is below the macroscopic level adopted here for the continuous description of the evolutions of the reactive porous media. Therefore, with respect to this approach, aging formulation (17) together with (11) may be considered as a modified solidification theory that is on the onset macroscopic. Then, certain relations can be derived, reconciling maturity-type aging models with solidification-type aging models, as successively derived in what follows.

STATE EQUATIONS

The state equations of the thermochemoelastic isotropic material are obtained using expressions (16b), (16c), and (16d) of free energy ψ in (14). They read as follows:

$$\sigma = s + \sigma 1; \quad \sigma = \sigma_o + K(x)[\text{tr}\varepsilon - 3\alpha(T - T_o) - 3\beta x];$$
$$s = s_o + 2G(x)e \qquad (18a–c)$$

$$S = S_o + (1/T_o)[C_\varepsilon(T - T_o) + 3K(x)\alpha T_o \text{tr}\varepsilon - F(x)] \qquad (19)$$

$$A_x = A_{xo} - \kappa x + 3[\partial K(x)/\partial x][\alpha(T - T_o) + \beta x]\text{tr}\varepsilon$$
$$\quad + 3\beta K(x)\text{tr}\varepsilon - f(x)(T - T_o)/T_o - (1/2)[\partial K(x)/\partial x]\text{tr}^2\varepsilon$$
$$\quad - [\partial G(x)/\partial x]e{:}e \qquad (20)$$

where $f(x) = dF(x)/dx$.

State equations (18)–(20) show clearly the thermochemomomechanical coupling: the thermodynamic forces σ, S, and A_x do not depend only on their proper state variable ε, T,

and x, with which each one is associated in the dissipation (i.e., $\sigma \to \varepsilon$, $S \to T$, $A_x \to x$), but equally on the other variables.

STATE-EQUATION INVERSION

State equation (18) is inverted, reading as follows:

$$\mathrm{tr}\varepsilon = [1/K(x)](\sigma - \sigma_o) + 3\alpha(T - T_o) + 3\beta x;$$

$$\mathbf{e} = (\mathbf{s} - \mathbf{s}_o)/[2G(x)] \qquad (21a,b)$$

which can be written in the equivalent following form:

$$\mathrm{tr}\varepsilon = \mathrm{tr}\varepsilon^e + \mathrm{tr}\varepsilon^t + \mathrm{tr}\varepsilon^c \qquad (22)$$

with superscripts e = elastic; t = thermal; and c = chemical.

In (21), coefficient α = thermal dilatation coefficient that relates the volume dilatation of thermal origin to temperature variation $T - T_o$. It may eventually depend upon hydration extent x due to the difference in thermal dilatation between the free water and the solid phase (Laplante 1993; Boulay and Paties 1993), i.e., on the mass increase of nonevaporable water combined in the hydrates (which is proportional to the mass increase of hardened cement gel).

In (22), $\mathrm{tr}\varepsilon^c$ = volume strain induced by shrinkage effects related to chemical volume changes (hydration shrinkage) and related capillary effects (capillary shrinkage) in the closed reactive porous medium (no exchange with the exterior, no drying). According to relations (21) and (22), it is related to hydration extent x by the following:

$$\mathrm{tr}\varepsilon^c = 3\beta x \qquad (23)$$

where coefficient β—in analogy with thermal dilatation coefficient α—may be considered as a chemical-dilatation coefficient. The previous equation accounts for hydration shrinkage and related capillary shrinkage. The hydration shrinkage is caused by the volume change due to the hydration of cement (Le Chatelier contraction). The consumption of water by the hydration reaction leads to the formation of menisci with an increasing pressure difference (capillary pressure) between the liquid and the gaseous phase saturating the porous space. Consequently, the skeleton suffers an increasing internal compression, inducing an overall (capillary) shrinkage that depends upon the quantity of water combined by hydration in the solid phase, and thus on hydration extent x. With respect to this origin of autogeneous shrinkage, coefficient β accounts for involved capillary phenomena, by relating hydration extent x to volume strain $\mathrm{tr}\varepsilon^c$ induced by capillary effects. This relation may eventually be nonlinear, and coefficient β thus not constant, but a function of hydration extent x [i.e., $\beta = \beta(x)$, to be determined from capillary pressure curves; cf. Wittmann (1976)]. Furthermore, these capillary effects may (partially) be at the basis of the apparent overall stiffening (i.e., ageing) of the material. In fact, with water mass decreasing (consumed by hydration), the capillary pressure increases, which stiffens the porous medium. These effects of capillary pressure on the apparent ageing phenomenon need still to be explored.

Here, for the sake of simplicity, both dilatation coefficients (thermal and chemical) are assumed to be constant, which has already been assumed when deriving state equation (20). Using (21), state equation (19) is rewritten in the following form:

$$S = S_o + (1/T_o)[C_r + 9T_o\alpha^2 K(x)](T - T_o)$$

$$+ 3\alpha(\sigma - \sigma_o) + 9\alpha\beta K(x)x - [F(x)/T_o] \qquad (24)$$

Furthermore, in the hypothesis of infinitesimal deformations (hypothesis H2), which includes that of infinitesimal strains

(i.e., $\varepsilon \ll 1$), the second-order terms of $\mathrm{tr}\varepsilon$ and $\mathbf{e}$ in (20) can be neglected. Using decomposition (22), this hypothesis applies equally to volume strains of thermal and chemical origin (i.e., $\mathrm{tr}\varepsilon^t \ll 1$, $\mathrm{tr}\varepsilon^c \ll 1$). Therefore, retaining in expression (20) only the terms of the same order of magnitude, affinity A_x reads

$$A_x \cong A_{xo} - \kappa x + 3\beta K(x)\mathrm{tr}\varepsilon - (1/T_o)f(x)(T - T_o) \qquad (25)$$

or, using (21)

$$A_x = A_{xo} - [\kappa - 9\beta^2 K(x)]x - (1/T_o)[f(x)$$

$$- 9\alpha\beta K(x)T_o](T - T_o) + 3\beta(\sigma - \sigma_o) \qquad (26)$$

Therefore, in this model, without further hypothesis, hydration extent x, temperature variation $T - T_o$, and mean stress variation $\sigma - \sigma_o$ may induce a thermodynamic imbalance (affinity A_x) between the free (nonevaporable) water and the water combined in the hydrates.

HEAT-CONDUCTION LAW

For the temperature evolution, a linear heat-conduction law (Fourier law) may be adopted, relating the heat flux vector $\mathbf{q}$ to $-\mathrm{grad}\,T$ as follows:

$$\mathbf{q} = -\mathbf{K} \cdot \mathrm{grad}\,T \qquad (27)$$

where $\mathbf{K} = k\mathbf{1}$ = thermic conductivity tensor in the isotropic case. It might depend on reaction extent x, i.e., $k = k(x)$, but little has been reported on the subject.

KINETICS OF HYDRATION

As mentioned previously, the diffusion of water through the layers of hydrates controls the kinetics of the hydration. Hence, hydration rate $\dot{x}$ can be viewed as a measure of the rate of diffusion. It is controlled by the thermodynamic imbalance (affinity A_x) between free water and water combined in the solid phase, and amplified by thermal activation when the free water combines with unhydrated cement to form the hydrates (see Fig. 1). An evolution law of the Arrhenius type may be adopted, as follows:

$$A_x = \eta_x \dot{x} \exp\left(\frac{E_x}{\bar{R}T}\right) \text{ or } \dot{x} = \frac{A_x}{\eta_x} \exp\left(-\frac{E_x}{\bar{R}T}\right) \qquad (28a,b)$$

where E_x = hydration activation energy; and $\bar{R}$ = universal constant for ideal gas.

From a pure empirical standpoint, evolution laws for maturing concrete based upon the Arrhenius concept are widely used since they have shown good agreement with experimental data [cf. Byfors (1980) and Regourd and Gautier (1980)]. From a thermodynamic point of view, evolution laws (28) refer to expression (8) of dissipation $\Phi_{A \to B}$, according to which the kinetics must be specified by a relation linking affinity A_x to hydration rate $\dot{x}$. From a physicochemical point of view, the complementary evolution laws (28) account for two distinct phenomena. First, that hydration rate $\dot{x}$ is controlled by the rate at which the free water diffuses through the layers of hydrates already formed. This diffusion rate depends on the gradient between the free water and the water combined in the hydrates. At the macrolevel of material description, this gradient is expressed by affinity A_x, from which we get the relation $A_x = \eta_x \dot{x}$. Second, that the combination of free water with unhydrated cement to form the hydrates is activation controlled, which the Arrhenius term $\exp(E_x/\bar{R}T)$ takes into account. The first is at the basis of the chemical dissipation amplified by the latter thermal activation. Viscosity η_x accounts for this microdiffusion, so it may not be constant, because the remaining free water has to bypass the

layer of hydrates already formed [i.e., $\eta_x = \eta_x(x)$] in order to meet the unhydrated cement and to form new hydrates.

Moreover, because we considered only one overall hydration reaction, activation energy E_x is an apparent activation energy at the macrolevel of material description in an average sense of the activation energies E_{xi} ($i = 1, N$) proper to the N chemical reactions involved with different water consumption and thus with different kinetics in the hydration of cement. The apparent activation energy may therefore not be constant [cf. Freiesleben-Hansen et al. (1982)]. A refined modeling would consider these reactions separately by using N chemical extent variables x_i ($i = 1, N$), for which the kinetics need to be described (with constant activation energies E_{xi} ($i = 1, N$) proper to the N reactions). In a more rough manner, considering only one hydration reaction the apparent activation energy may be determined as a function of hydration extent x [i.e., $E_x = E_x(x)$].

Using hydration kinetics (28), the nonnegativeness of intrinsic dissipation (15) on account of (8) and closure condition (11) reads as follows:

$$\varphi_1 = \Phi_{A \to B} = (A_x^2/\eta_x)\exp(-E_x/\bar{R}T) \geq 0 \qquad (29)$$

which is satisfied for $\eta_x > 0$.

FIELD EQUATIONS

The field equations of the considered thermomechanical problem of the elementary system (closed with respect to the chemical constituents) are the momentum balance equation

$$\text{div}\boldsymbol{\sigma} + \rho\mathbf{F} = 0 \qquad (30)$$

with $\rho\mathbf{F}$ = volume forces; and the following thermal equation [e.g., Mandel (1966, 1974)]:

$$T_o\dot{S} = Q^o + \varphi_1 \qquad (31)$$

where $Q^o = R - \text{div}\mathbf{q}$ represents the external rate of heat supply to the elementary system provided both by conduction (term $-\text{div}\mathbf{q}$) and by eventual external volume heat sources (term R). The latter will be assumed zero in what follows (i.e., $R = 0$, thus $Q^o = -\text{div}\mathbf{q}$). It is worthwhile noting that inequalities (12) and (29) stipulate the nonnegativeness of intrinsic dissipation φ_1, which appears as an internal spontaneous heat source in (31). In fact, the second law of thermodynamics postulates that the variation of entropy (term $T_o dS$) may not be inferior to the external entropy ($Q^o dt$) supplied to the system during time interval dt, thus $T_o\dot{S} \geq Q^o$.

Using state equation (19) in field equation (31), and retaining in the derivation of entropy S with respect to time only first-order terms, the thermal equation becomes

$$T_o\dot{S} = C_v\dot{T} - f(x)\dot{x} + 3\alpha T_o K(x)\text{tr}\dot{\varepsilon} = Q^o + A_x\dot{x} \qquad (32)$$

Eqs. (32) and (19) allow to identify the following:

- $C_v = \rho c$ as the volume heat capacity per unit of volume in an isodeformation ($\varepsilon = 0$) experiment carried out at constant hydration extent x (no microdiffusion of free water to the unhydrated cement), with ρ = volume mass density; and c = specific heat.
- Heat $F(x)$ as the latent heat of the hydration reaction released to the outside per unit of volume in an isothermal ($T = T_o$) and isodeformation ($\varepsilon = 0$) experiment, and $f(x) = dF/dx$ as the latent heat per unit of hydration extent dx [the latter is positive if the reaction is exothermic and negative for endothermic reactions].
- Heat $3\alpha T_o K(x)\text{tr}\varepsilon$ as the latent heat due to deformation released to the outside per unit of volume in an isothermal ($T = T_o$) experiment carried out at constant hydration

extent x (no microdiffusion of free water to the unhydrated cement). It can be considered as negligible with respect to the latent heat of the hydration {i.e., $|3\alpha T_o K(x)\text{tr}\varepsilon| \ll \dot{F}(x)$ in the exothermic reaction considered}.

- The term $A_x\dot{x}$ as given by (29) as the dissipation into heat due to the hydration reaction. Therefore the rate of heat given out by the hydration reaction is due to latent heat effects [term $\dot{F}(x) = f(x)\dot{x}$] as well as to the chemical dissipation [term $\Phi_{A \to B} = A_x\dot{x}$] even though the latter may be considered as negligible with respect to the former [i.e., $\Phi_{A \to B} \ll \dot{F}(x)$ in the exothermic reaction considered].

Therefore, assuming latent heat due to deformation and the heat due to (chemical) dissipation negligible with respect to the latent hydration heat, (32) becomes the following:

$$C_v\dot{T} = Q^o + \dot{F}(x) \qquad (33)$$

which is the field equation generally used.

DECOUPLING HYPOTHESIS, EQUIVALENT STATE VARIABLES

State equations (18)–(20) [or their transformed expressions (21)–(26)] show clearly the thermochemomechanical coupling between the different variables of the model. Some couplings may be considered as weak, as for instance the thermomechanical coupling induced by the latent heat due to deformation [i.e., (33) instead of (32)]. Other couplings may be carefully broken down to bridge over to established aging models and solidification theories. This is the purpose of what follows, where the basic decoupling hypothesis will be precised.

H4: Stress and temperature variations do not effect the thermodynamic imbalance (affinity A_x) between the chemical constituents of the hydration reaction, i.e., between the free water and the water combined in the solid phase.

It is shown, that—if hypothesis H4 holds—an "equivalent age" (or "maturity") may be defined as an equivalent thermodynamic state variable describing the "aging" of the material.

Stress Effects on Affinity: Isothermal Experiment

Consider first an isothermal experiment, for which $\dot{T} = 0$. The thermal equation (33) reads as follows:

$$-Q^o = \dot{F}(x) = f(x)\dot{x}_{T=0} \qquad (34)$$

where $-Q^o$ = (measurable) rate of external heat supply that has to be taken from the system in order to conserve isothermal conditions ($T = T_o$). Furthermore, $\dot{x}_{T=0}$ is the hydration rate that occurs in the isothermal experiment. Using hydration kinetics (28) in (34), we have the following:

$$-Q^o = \dot{F}(x) = (1/\eta_x)f(x)A_{x,T=0}\exp[-E_x/(\bar{R}T_o)] \qquad (35)$$

where $A_{x,T=0}$ = affinity in the isothermal experiment

$$A_{x,T=0} = A_{xo} - \kappa x + 3\beta K(x)\text{tr}\varepsilon \qquad (36a)$$

$$A_{x,T=0} = A_{xo} - [\kappa - 9\beta^2 K(x)]x + 3\beta(\sigma - \sigma_o) \qquad (36b)$$

Hypothesis H4 implies that $|3\beta K(x)\text{tr}\varepsilon| \ll |A_{xo} - \kappa x|$, and the previous equation becomes

$$\forall(\sigma - \sigma_o), \frac{A_{x,T=0}}{\kappa} = \left[\frac{A_{xo}}{\kappa} - x(t)\right] = \frac{\eta_x}{\kappa}\exp\left(\frac{E_x}{\bar{R}T_o}\right)\dot{x} \qquad (37)$$

In fact, hypothesis H4 eliminates a stress-induced thermodynamic imbalance, and therefore macroscopic creep effects

in the modeling (Coussy 1995). Furthermore, assuming that hydration affinity A_x does not depend on the mechanical loading, means that the aging is independent of the stress applied. Finally, this hypothesis implicitly eliminates any stress influence in heat equation (32), as already assumed when neglecting the latent heat due to deformation [term $\alpha T_o K(x) \mathrm{tr}\varepsilon$] in thermal equation (33).

Hypothesis H4 allows one to determine the asymptotic hydration extent. In fact, if the thermodynamic imbalance does not depend on the stress state, affinity A_x tends to zero for $t \to \infty$, which corresponds to thermodynamic equilibrium [i.e., $A_x(\infty) = 0$]. The asymptotic extent of the hydration reaction then reads as follows:

$$\forall(\sigma - \sigma_o), \quad x_{\dot{T}=0}(\infty) = A_{xo}/\kappa \tag{38}$$

The final value of the hydration extent under isothermal conditions depends only upon initial affinity A_{xo}, which expresses the initial thermodynamic imbalance between the chemical constituents (roughly between the free water and unhydrated cement with no water combined). Independent of any particular experiment, this initial affinity may depend on initial temperature T_o and characteristics relative to the concrete mix design, as for instance the water/cement ratio w/c, as follows:

$$A_{xo} = A_{xo}(T_o, w/c, \ldots) \tag{39}$$

Moreover, rewriting differential equation (37) in the form

$$\frac{dx}{x(\infty) - x(t)} = \frac{\kappa}{\eta_x} \exp\left(-\frac{E_x}{RT_o}\right) dt = d\mu \tag{40}$$

and integrating, the commonly used maturity function $\mu(t)$, or equivalent age, is obtained

$$\mu(t) = \ln\left[\frac{x(\infty)}{x(\infty) - x(t)}\right] = \int_{s=0}^{s=t} \frac{\kappa}{\eta_x} \exp\left(-\frac{E_x}{RT_o}\right) ds \tag{41}$$

When assuming the ratio κ/η_x and activation energy E_x constant, the maturity is linearly related to physical time t as follows:

$$\mu(t) = kt, \quad \text{with } k = \frac{\kappa}{\eta_x} \exp\left(-\frac{E_x}{RT_o}\right) \tag{42}$$

It is related with hydration extent x by the following:

$$r(t) = \frac{x(t)}{x(\infty)} = \frac{V(t)}{V(\infty)} = 1 - \exp[-\mu(t)] \tag{43}$$

The ratio of current to final hydration extent, $x(t)/x(\infty)$, is often called hydration degree $r(t)$, which varies between 0 and 1 (Powers and Brownyard 1948). Because the hydration extent is proportional to the mass formation of hardened cement gel, ratio $r(t)$ is equal to the solidified fraction $v(t) = V(t)/V(\infty)$ used in the solidification theory (Bazant 1977), provided that the mass densities of the hydrates are constant in time. These relations are general and independent of any particular experiment. On the contrary, the relation that links hydration extent $x(t)$, hydration degree $r(t)$, or solidified fraction $v(t)$ to maturity $\mu(t)$ is, strictly speaking, only relevant under isothermal conditions. In fact, maturity $\mu(t)$ was derived from a state equation of affinity A_x that depends neither on stress variations (hypothesis H4), nor on temperature variations (isothermal conditions). In other words, using maturity $\mu(t)$ as a state variable in nonisothermal conditions to characterize the aging state of concrete implies that temperature effects are not significant for the affinity of the reaction. To illustrate this, consider the adiabatic experiment.

Temperature Effects on Affinity: Adiabatic Experiment

In an adiabatic experiment, there is no external heat supply to the elementary system (i.e., $Q^o = 0$), and thermal equation (33) reads as follows:

$$C_r \dot{T}_{Q^o=0} = \dot{F}_{Q^o=0}(x) = (1/\eta_x)f(x)A_{x,Q^o=0} \exp[-E_x/\dot{R}T_{Q^o=0}] \tag{44}$$

where use was again made of hydration kinetics (28). In the previous equation, affinity $A_{x,Q^o=0}$ is defined by state equation (25), and depends a priori on state variables T, ε, and x. Assuming the stress induced thermodynamic imbalance negligible, it reads as follows:

$$\forall(\sigma - \sigma_o), \quad A_{x,Q^o=0} = A_{xo} - \kappa x - [f(x)/T_o](T_{Q^o=0} - T_o) \tag{45}$$

and the asymptotic hydration extent for $t \to \infty$, where $\dot{T} = 0$ and $\dot{F}(x) = 0$

$$\forall(\sigma - \sigma_o), \quad x(\infty) = (A_{xo}/\kappa) - k[\Delta T(\infty)/T_o],$$

$$\text{with } k = f[x(\infty)]/\kappa \tag{46}$$

In contrast to the isothermal experiment, the final value of reaction extent can depend on the total temperature variation $\Delta T(\infty) = T(\infty) - T_o$. Consequently, temperature effects would not only intervene in the kinetics of the hydration heat generation (i.e., $\dot{F}/F$), but also in its amplitude.

Assume now that also temperature effects are negligible for affinity A_x. Therefore

$$\forall(T - T_o) \quad \text{and} \quad \forall(\sigma - \sigma_o), \quad A_x \cong A_x(x) \tag{47}$$

and for the linear model developed here

$$\forall(T - T_o) \quad \text{and} \quad \forall(\sigma - \sigma_o), \quad A_x \cong A_{ox} - \kappa x \tag{48}$$

Then differential equation (40) is recovered also for nonisothermal conditions, which leads to maturity $\mu(t)$

$$\forall(T - T_o) \quad \text{and} \quad \forall(\sigma - \sigma_o), \quad \mu(t)$$

$$= \ln\{x(\infty)/[x(\infty) - x(t)]\} = \int_{s=0}^{s=t} [\kappa/\eta_x(s)]\exp[E_x/\dot{R}T(s)] ds \tag{49}$$

In other words, using maturity $\mu(t)$ as a state variable to characterize the aging state of concrete necessarily implies that neither stress variations nor temperature variations induce a thermodynamic imbalance between the chemical constituents. They are implicitly assumed in any modeling of aging with a maturity function $\mu(t)$, and some attempts of experimental justification may be found in literature [e.g., Byfors (1980), Regourd and Gauthier (1980) and Torrenti (1992)]. Based on these assumptions, hydration extent $x(t)$, hydration degree $r(t)$, solidified fraction $v(t)$, autogeneous shrinkage $\mathrm{tr}\varepsilon^c$, and maturity $\mu(t)$ can be considered as equivalent thermodynamic state variables, related at the macrolevel of material description to the water consumption through hydration, and thus to the mass formation of hardened cement gel.

However, note clearly that decoupling hypothesis H4 considers only stress and temperature effects negligible as far as affinity A_x is concerned. In other words, it does not inquestion neither the exothermic character of the reaction [latent hydration heat $F(x)$], nor the induced strains of thermal and chemical origin.

Based on this hypothesis, the following variable changes $x \to r$, $x \to v$, $x \to \mathrm{tr}\varepsilon^c$ or $x \to \mu$ can be considered as follows:

$\forall (T - T_o)$ and $\forall (\sigma - \sigma_o)$, $\quad r(t) = x(t)/x(\infty)$

$$= V(t)/V(\infty) = \mathrm{tr}\varepsilon^c(t)/\mathrm{tr}\varepsilon^c(\infty) = 1 - \exp[-\mu(t)] \qquad (50)$$

where $\mathrm{tr}\varepsilon^c(\infty) = $ asymptotic value of autogeneous shrinkage strains.

It is worthwhile to note that the variable changes $x \to r$, $x \to v$, and $x \to \mathrm{tr}\varepsilon^c$ are affin [because $dx/dr = dx/dv = $ constant and $dx/d(\mathrm{tr}\varepsilon^c) = $ constant, provided that $\beta = $ constant]. Therefore affinity A_x is, except of a multiplied constant, the thermodynamic force associated to x, r, v, and $\mathrm{tr}\varepsilon^c$ (for $\beta = $ constant). This is not the case for variable change $x \to \mu$ (because $dx/d\mu \neq $ constant), and the force associated to the rate of maturity is not affinity A_x, but the force A_μ, which is obtained from the following chemical dissipation:

$$\Phi_{A \to B} = A_\mu \dot{\mu} = A_x \dot{x} \qquad (51)$$

which gives

$$A_\mu = \frac{A_x^2}{\kappa} = A_{o\mu} \exp^2(-\mu), \quad \text{with } A_{o\mu} = \kappa x(\infty)^2 \qquad (52)$$

The nonnegativity of intrinsic dissipation then reads as follows:

$$A_\mu \dot{\mu} = A_{o\mu} \exp^2(-\mu) \frac{\kappa}{\eta_x} \exp(-E_x/\tilde{R}T) \geq 0 \qquad (53)$$

which is satisfied for $\kappa \geq 0$.

Verification and Quantification of Thermochemomechanical Couplings

In the two previous paragraphs, the decoupling hypothesis H4 was introduced to show the linkages between maturity-type and solidification-type aging models, and its physical relevance was only evoked. Some further comments will be given now on the verification and quantification of the thermochemomechanical couplings. This may show how the mechanics of reactive porous media applied to concrete can be explored from an experimental point of view, which are both on the onset macroscopic.

The proposed model is based upon the chemomechanical coupling between hydration extent x, autogeneous shrinkage (volume variation), and aging (variation of instantaneous mechanical characteristics), as follows:

$$\mathrm{tr}\varepsilon^c = 3\beta x; \quad E = E(x) \qquad (54a,b)$$

In other words, the hydration reaction is at the basis of two distinct observable phenomena. This means that the characteristic times (time period during which the phenomena occur) are of the same order of magnitude

$$\tau_c^{\mathrm{tr}\varepsilon^c} \approx \tau_c^{E(x)} \qquad (55a)$$

or equivalently

$$\frac{\mathrm{tr}\varepsilon^c(\infty) - \mathrm{tr}\varepsilon^c(t)}{\mathrm{tr}\dot{\varepsilon}^c(t)} \approx \frac{E[x(\infty)] - E[x(t)]}{\dot{E}[x(t)]} \qquad (55b)$$

In general, comparing the characteristic times of apparent phenomena (here, aging and autogeneous shrinkage) makes it possible to relate them to their physical cause (here, hydration). More precisely, with respect to the diffusion-controlled hydration reaction (15), time τ_c can be interpreted as a characteristic diffusion time [the diffusion process advances for time $t < \tau_c$, and is (almost) achieved for $t \gg \tau_c$]. At the microlevel of material description, diffusion time τ_c depends on the diffusion length of free water to the unhydrated cement, and thus upon the hydrates already formed. Because

the water consumed in the hydration reaction is proportional to the hydrates formed, characteristic time $\tau_c^{E(x)}$ of the apparent "aging" phenomenon is of the same order of magnitude as characteristic diffusion time τ_c relative to the diffusion process involved in the hydration reaction. The same reasoning applies to the characteristic time $\tau_c^{\mathrm{tr}\varepsilon^c}$ of the autogeneous shrinkage phenomenon (no drying!) induced by chemical volume changes and related capillary effects due to water consumption in the hydration reaction. Therefore (55) means that the diffusion process related to the hydration reaction lends its kinetics to the apparent phenomena of aging and autogeneous shrinkage. In return, the skeleton behavior may show some hereditary aspects, which may explain the delayed behavior of autogeneous shrinkage ($\tau_c^{\mathrm{tr}\varepsilon^c} \approx 2-3$ months) with regard to the diffusion process by which it is caused ($\tau_c = \tau_c^{E(x)} \approx 1$ month). These hereditary effects may eventually be due to another physicochemical phenomenon, still to be explored.

Moreover, since neither stress nor temperature variations induce a thermodynamic imbalance between the chemical constituents, it follows that the asymptotic value of autogeneous shrinkage $\mathrm{tr}\varepsilon^c(\infty)$ depends only on the initial thermodynamic imbalance (affinity A_{xo}) between the chemical constituents, i.e., only on placing temperature T_o and parameters related to the concrete mix design

$\forall (T - T_o)$ and $\forall (\sigma - \sigma_o)$,

$$\mathrm{tr}\varepsilon^c(\infty) = (3\beta/\kappa)A_{xo}(T_o, w/c, \dots) = \mathrm{tr}\varepsilon^c_\infty(T_o, w/c, \dots) \qquad (56)$$

In particular, the independence of the asymptotic value $\mathrm{tr}\varepsilon^c(\infty)$ with respect to temperature variations $T - T_o$ (i.e., hypothesis H4) may be checked from calorimetric tests carried out under different thermal conditions [e.g., an isothermal test ($\dot{T} = 0$) and an adiabatic test ($Q^o = 0$)]. In return, the kinetics of the evolution of autogeneous shrinkage depends, due to the thermally activated character of the hydration reaction, on temperature evolutions. Using $\mathrm{tr}\varepsilon^c = \beta x$ in expression (48) of affinity A_x together with hydration kinetic (28), yields the following evolution law:

$\forall (T - T_o)$ and $\forall (\sigma - \sigma_o)$,

$\mathrm{tr}\dot{\varepsilon}^c = (3\beta A_x/\eta_x)\exp[-E_x/RT(t)]$

$$= (\kappa/\eta_x)[\mathrm{tr}\varepsilon^c(\infty) - \mathrm{tr}\varepsilon^c(t)]\exp[-E_x/\tilde{R}T(t)] \qquad (57)$$

and after integration

$\forall (T - T_o)$ and $\forall (\sigma - \sigma_o)$,

$$\mathrm{tr}\varepsilon^c(t) = \mathrm{tr}\varepsilon^c(\infty)\{1 - \exp[-\mu(t)]\} \qquad (58)$$

independent of any particular experiment. Thus, carrying out an autogeneous shrinkage test [$\mathrm{tr}\varepsilon^c(t)$, $\mathrm{tr}\dot{\varepsilon}^c(t)$ measured] and a calorimetric test [$T(t)$ measured] on the same material and under the same curing conditions, leads to determine the ratio κ/η_x. As mentioned before, η_x may not be a constant, because the remaining free water has to bypass the layer of hydrates already formed. With respect to the chemomechanical coupling (54), the ratio κ/η_x will be determined from (57) as a function of $\mathrm{tr}\varepsilon^c$ [i.e., $\kappa/\eta_x = \kappa/\eta_x(\mathrm{tr}\varepsilon^c)$]. This renders evolution law (57) for autogeneous shrinkage nonlinear with respect to $\mathrm{tr}\varepsilon^c$. Then the chemomechanical coupling is completely described.

Concerning the experimental determination of the thermochemical coupling, i.e., the hydration heat generation, the system must be broken down—at the macrolevel of material description—to its intrinsic components, which means here, in the case of only one chemical reaction, to latent heat $f(x) = dF/dx$ per unit of hydration extent dx. To this end, any

calorimetric test can be used, which allows one to determine the latent hydration heat $F(t)$ and temperature evolution $T(t)$. Because hydration extent x is not easily accessible to experimental determination, variable changes (50) can be used to determine the sought intrinsic relation. In particular, having identified hydration extent x and shrinkage $\text{tr}\varepsilon^c$ as equivalent thermodynamic state variables, the variable change $x \to \text{tr}\varepsilon^c$ reads here as follows:

$$\dot{F}(x) = \dot{F}(\text{tr}\varepsilon^c), \quad \text{so} \quad \frac{dF(x)}{dx}\dot{x} = -\frac{dF}{d(\text{tr}\varepsilon^c)}\text{tr}\dot{\varepsilon}^c \quad (59a,b)$$

where $f(\text{tr}\varepsilon^c) = -dF/d(\text{tr}\varepsilon^c) =$ latent heat dF (≥ 0 for exothermic reactions) per unit of shrinkage $-d(\text{tr}\varepsilon^c)$, to be determined by the following:

$$f(\text{tr}\varepsilon^c) = -\frac{\dot{F}}{\text{tr}\dot{\varepsilon}^c} \quad (\geq \text{ for exothermic reaction}) \quad (60)$$

In the limits of decoupling hypothesis H4, using shrinkage evolution law (57) in the previous equation yields the following:

$$\forall (T - T_o) \quad \text{and} \quad \forall(\sigma - \sigma_o), \quad f(\text{tr}\varepsilon^c)$$

$$= (\eta_v/\kappa)[\dot{F}(t)/\text{tr}\varepsilon^c(\infty) - \text{tr}\varepsilon^c(t)]\exp[E_x/\bar{R}T(t)] \quad (61)$$

Eq. (61) allows for the determination of the latent heat per unit of shrinkage from two test measurements: a calorimetric test and an autogeneous shrinkage test. The calorimetric test gives experimental access to latent heat rate $\dot{F}(t)$ and temperature evolution $T(t)$ [e.g., from (34) and (44) in the case of an isothermal and an adiabatic test, respectively]. In the shrinkage test, $\text{tr}\varepsilon^c(t)$ and $\text{tr}\dot{\varepsilon}^c(t)$ are measured, and ratio κ/η_v is deduced [from (57)]. Then, the thermochemical coupling is completely described.

Finally, the intrinsic character of latent hydration heat per unit of shrinkage (or per unit of hydration extent) can be used to determine the relevance of decoupling hypothesis H4. To this end, consider two calorimetric tests on the same concrete with the same initial temperature T_o, for instance one carried out under isothermal conditions ($\dot{T} = 0$), the other under adiabatic conditions ($Q^o = 0$). The intrinsic character of $f(x)$ implies that at the same value of hydration extent x, the same latent heat per unit of hydration extent dx will occur

$$f(x)_{\dot{T}=0} = f(x)_{Q^o=0} \quad (62)$$

or using (34) and (44)

$$\frac{C_r\dot{T}_{Q^o=0}(t)}{-Q^q_{\dot{T}=0}(t)} = \frac{\dot{x}_{Q^o=0}}{\dot{x}_{\dot{T}=0}} = \frac{A_{x,Q^o=0}}{A_{x,\dot{T}=0}}\exp\left\{\frac{E_x}{\bar{R}}\left[\frac{1}{T_o} - \frac{1}{T_{Q^o=0}(t)}\right]\right\} \quad (63)$$

where isothermal external heat supply rate $-Q^q_{\dot{T}=0}$, initial temperature T_o, and adiabatic temperature evolution $T_{Q^o=0}(t)$ are all direct measurable quantities. If hypothesis H4 holds, we have $A_{x,\dot{T}=0} = A_{x,Q^o=0}$, and (63) becomes the following:

$$\forall(T_{Q^o=0} - T_o) \quad \text{and} \quad \forall(\sigma - \sigma_o),$$

$$\frac{C_r\dot{T}_{Q^o=0}(t)}{-Q^q_{\dot{T}=0}(t)} = \exp\left\{\frac{E_x}{\bar{R}}\left[\frac{1}{T_o} - \frac{1}{T_{Q^o=0}(t)}\right]\right\} \quad (64)$$

Eq. (64) concerns only the kinetics of hydration heat generation. It has to be completed by (56), which concerns the amplitude of hydration extent x. For the considered experiment it reads as follows:

$$\forall(T_{Q^o=0} - T_o) \quad \text{and} \quad \forall(\sigma - \sigma_o),$$

$$\text{tr}\varepsilon^c(\infty) = \text{tr}\varepsilon^c_{Q^o=0}(\infty) = \text{tr}\varepsilon^c_{\dot{T}=0}(\infty) \quad (65)$$

where $\text{tr}\varepsilon^c_{Q^o=0}(\infty)$ and $\text{tr}\varepsilon^c_{\dot{T}=0}(\infty) =$ asymptotic values of shrinkage in the adiabatic and isothermal experiment, respectively. Eqs. (64) and (65) can be used to determine the domain of application of decoupling hypothesis H4, and thus the domain of application of maturity $\mu(t)$ as an equivalent thermodynamic state variable, relevant to describe the aging of concrete.

CONCLUDING REMARKS

This paper explored the theory of reactive porous media proposed in Coussy (1995) for the modeling of concrete at early ages. This framework of reactive porous media allows to account at the macrolevel of material description for cases in which mechanical and physicochemical phenomena occur together.

Here we considered only the aging phenomenon and the autogeneous shrinkage phenomenon, related to the same physicochemical origin: the hydration. The diffusion of free water through the layers of hydrates was considered as the dominant mechanism of the hydration with respect to the kinetics. This leads to a modeling of thermochemomechanical couplings of concrete at early ages at the macrolevel of material description. It is useful to sum up the major hypothesis introduced: H1 = hypothesis of physical linearization; H2 = hypothesis of infinitesimal deformations; H3 = the system is closed with respect to the chemical constituents; and H4 = stress- and temperature-induced thermodynamic imbalances are negligible for the hydration reaction.

The general modeling approach chosen has the advantage that it allows one to make precise the decoupling hypotheses, which are implicitly admitted when using the maturity (or an "equivalent age") as a variable to describe the "aging" of concrete. The relevance of these hypotheses are still under research. Here we only sought to make clear how they may be quantified in order to determine their domain of application. The model is currently used in the finite-element program CESAR-LCPC, and various numerical applications have shown the great efficiency of such a physicochemical modeling in great-scale concrete-engineering applications (Torrenti et al. 1992, 1994).

The model developed here left cracking aside. The presentation focused on hydration dissipation $\Phi_{A\to B}$, related to the diffusion of free water through the layers of hydrates already formed, neglecting other sources of intrinsic dissipation Φ_1 (i.e., dissipation of effective mechanical work into heat form!) for instance due to cracking. The latter may be considered as negligible with respect to the latent heat of hydration, as far as the thermomechanical coupling is concerned. However, it significantly effects the mechanical behavior of the material, and can influence the chemomechanical coupling.

Furthermore, hydromechanical couplings were not yet considered. They can be found in Coussy (1994) and in a refined way in Lassabatère (1993) and Lassabatère and Coussy (1993), where the same framework of reactive partially saturated porous media was applied to model drying shrinkage and drying creep.

Finally, assuming that the thermodynamic imbalance of the reactive porous medium (i.e., affinity A_x) does not depend on the stress applied, creep effects were eliminated in the modeling. Note, however, that decoupling hypothesis H4 concerns only the thermodynamic imbalance related with the hydration reaction (i.e., between the free water and the water combined in the solid phase). Other physicochemical phe-

nomena may be at the origin of a stress induced thermodynamic imbalance, which gives rise to (basic) creep effects.

Here, the frontier between material mechanics and physical chemistry needs still to be explored.

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APPENDIX II.   NOTATION

The following symbols are used in this paper:

A = reactant phase;

A_x, A_{xo} = chemical affinity, initial affinity;

B = product phase;

C_v = volume heat capacity;

c = specific heat;

div = divergence operator;

E = Young's modulus;

E_x = activation energy relative to reaction of extent x;

$\mathbf{e}$ = strain deviator tensor;

$F(x)$ = latent heat of hydration (heat generated by hydration);

$f(x)$ = latent heat of hydration per unit hydration extent dx;

G = shear modulus;

g_m^j = free mass enthalpy of fluid phase j;

grad = gradient operator;

K = bulk modulus;

$\mathbf{K}$ = thermic conductivity tensor;

k = coefficient;

M_i^o = external mass supply rate of fluid i;

m_j = increase in fluid mass of phase j;

$m_{i \to j}^o$ = rate of mass change from phase i to phase j;

Q^o = external rate of heat supply;

$\mathbf{q}$ = heat-flux vector;

R = external rate of volume heat sources;

$\bar{R}$ = universal constant for ideal gas;

r = hydration degree;

S, S_o = entropy, initial entropy;

$\mathbf{s}, \mathbf{s}_o$ = stress deviator, initial stress deviator;

T, T_o = temperature, initial temperature;

t = time;

tr( ) = first invariant of tensor ( );

$v(t)$ = solidified fraction at time t;

w/c = water-cement ratio;

x, x^o = hydration extent, hydration rate;

$\dot{x} = dx/dt$ = time derivative of function x;

x^o = rate of quantity x;

α = thermal dilatation coefficient;

β = chemical dilatation coefficient;

ε = strain tensor;

η_i = viscosity relative to physicochemical phenomenon i;

κ = material parameter;

$\mu(t)$ = maturity function or equivalent age;

ν = Poisson's ratio;

$\boldsymbol{\sigma}, \boldsymbol{\sigma}_o$ = stress tensor, initial stress tensor;

σ, σ_o = mean stress, initial mean stress;

$\tau_c^{(i)}$ = characteristic time (relative to apparent phenomenon i);

Φ = dissipation of open elementary system;

φ_1 = intrinsic dissipation of closed porous medium;

Ψ = free energy of open elementary system;

ψ = free energy of closed elementary system;

( ):( ) = double-tensor contraction;

( ).( ) = scalar product;

$\forall$ = whatever; and

$\mathbf{1}$ = second-order unit tensor.