CONSTITUTIVE MODELING OF UNSATURATED DRYING DEFORMABLE MATERIALS

By O. Coussy,[1] R. Eymard,[2] and T. Lassabatère[3]

ABSTRACT: Thermodynamics of open continua, when applied directly at the macroscopic engineering scale, allows one to extend unambiguously the principal concepts of continuum thermomechanics of solids to poly-phasic porous materials, whose fluid constituents are subject to liquid-vapor phase change. This approach provides a consistent and relevant framework for the formulation of the constitutive equations of partially saturated deformable porous materials such as concrete. After recalling the general theory, the modeling is specified for porous materials that are partially saturated by a liquid water phase changing into its vapor phase, the latter forming with the dry air an ideal mixture. The nonlinear poroelasticity, as reference modeling, is then detailed. The theory is applied to the modeling of the drying shrinkage of concrete samples with isothermal sorption curves as only experimental data. The predicted shrinkage is found to be in close agreement with the observed one for a range of humidity greater than 50%. The drying shrinkage of a wall is finally examined. The analysis includes the study of the temperature variations due to latent heat effects. These variations are shown to be negligible.

INTRODUCTION

The geomaterials involved in civil engineering, whether they are natural (rocks or soils) or worked out by man (concrete), are more or less porous materials. When subject to mechanical loading, they deform. In addition, due to thermo-hygrothermal gradients, mass-energy transfer occurs. The modeling of the deformation and that of the mass-energy transfer through such materials are usually treated separately. When replaced in the global context of the continuum mechanics of solids, the constitutive equations of elastoplasticity, or, alternatively, the damage theories [see, for instance, Lemaitre and Chaboche (1990)] can render a proper account for the numerous reversible and irreversible ways of the material to be strained and damaged. On the other hand, well-consolidated theories exist [see, for instance, Bear and Bachmat (1990)] that accurately model the transport phenomena, possibly coupled, while they often involve phase changes or chemical reactions. Generally, these separate modelings of the deformation and of the mass-energy transfer are sufficient with respect to the well-distinct aims of the performed analyses.

However, subject in particular to gradients of relative humidity or temperature, the concrete shrinks or dilates. These phenomena, when hindered, lead to cracking, which can endanger the structure's durability. Therefore, for better control of the stress state of concrete and of its more or less unavoidable cracking, models are needed that properly take into account thermo-hygromechanical couplings.

The first part of this paper presents the main lines of a continuum modeling of the thermo-hygromechanical couplings that occur in deformable porous materials such as concrete or cement paste. The approach is ambitious, since it is a complete approach, but it is also a restricted approach, since

it addresses the deformation and the transport phenomena for such materials only in their simplest aspects. In view of an engineering purpose, the presented approach is, at the onset, macroscopic [i.e., without averaging procedures; see, for instance, Truesdell (1984)]. It is principally an extension of the pioneering works of M. A. Biot on the modeling of deformable porous media (see, in the references section, the sequence of his classical papers). The extension to the aforementioned phenomena is mainly based upon thermodynamics of deformable open continua. Although already developed in the past (Sih et al. 1986), this approach is rather new and has been extensively explored in Coussy (1995b). It provides a systematic link between the continuum mechanics of solids and the mechanics of deformable porous continua.

Finally, the drying shrinkage of concrete will be modeled. Heat and moisture transfer in concrete, as that of the shrinkage caused by these phenomena, have been extensively studied in the literature, from both a theoretical and an experimental point of view. Any attempt to model such coupling phenomena must be based on existing literature about the microscopic and basic physical mechanisms responsible for the shrinkage of cement paste and concrete [for a general overview of microscopic mechanisms and modeling, see Jennings et al. (1996)]. Capillary tension effects are commonly invoked to account for the drying shrinkage of cement paste and concrete. However, other mechanisms can be involved, such as surface free energy, depending on the amount of absorbed water (Wittmann 1973), or disjoining pressure developed in a narrow place where adsorption is hindered (Bazant 1972). These different explanations for the observed experimental behaviors have initially been proposed by Powers (1965, 1968). In fact, these phenomena simultaneously occur with a respective order of magnitude depending on the range of relative humidities. The observations of Feldman and Sereda (1968) have shown also the role of interlayer water movements and pointed out the various scales of description involved in the comprehension of the hygromechanical behavior of concrete [see also Bentz et al. (1995)].

However, the main concern remains here to be the macroscopic modeling of the drying shrinkage. For macroscopic observations, the reader is referred to the experimental and theoretical developments of Acker (1988), Bazant and Wittmann (1982), Bazant (1986), Baggio et al. (1993), and to the numerous other references cited in these papers. With respect to these works, the main purpose here is to show how the coupled formulation of the constitutive modeling of deformable porous materials, which are subject to drying, can be addressed directly at the engineering scale in a consistent global thermo-

[1]Res. Team Mgr., Docteur ès Sci., Sr. Lect., Ecole Polytechnique, Laboratoire Central des Ponts et Chaussées, Service Modélisation pour L'Ingénieur, 58 bd. Lefebvre, 75732 Paris Cedex 15, France.

[2]Res. Team Mgr., Laboratoire Central des Ponts et Chaussées, Service Modélisation pour l'Ingénieur, 58 bd. Lefebvre, 75732 Paris Cedex 15, France.

[3]Res. Ing., Docteur-Ingénieur, Commissariat à l'Énergie Atomique, Service d'Entreposage et de Stockage des Déchets, CEN Saclay bât. 158, 91191 Gif-sur-Yvette, France.

dynamic framework. This modeling is mainly based upon the assumption of the existence of a macroscopic thermodynamic potential. For a range of humidity higher than 50%, it is shown that there is strong experimental evidence that this assumption is relevant for concrete and cement paste.

BASIC CONCEPTS OF MACROSCOPIC MODELING

Porous Material Viewed as Superposition of $n + 1$ Interacting Continua

Any concrete structure Ω at the macroscopic level can be viewed as the superposition of $n + 1$ mechanically interacting media; n of them represent the n saturating fluids, while the remainder corresponds to the deformable skeleton. More precisely, extract from Ω an elementary system $d\Omega$. This elementary system is constituted of a connected porous space through which fluid mass exchanges occur and a solid matrix that possibly includes an occluded porosity through which no filtration occurs. In what follows, the term "porosity", when used without further explanation, will exclusively refer to the connected porosity and is noted as ϕ. The elementary system $d\Omega$ can therefore be viewed as the superposition of $n + 1$ particles. The skeleton particle is the macroscopic particle constituted by the matrix and the connected porous space. The fluid particle is the particle constituted by the material part of the connected porous space occupied by the considered fluid phase and the remaining complementary space (see Fig. 1 for $n = 1$). In many civil engineering applications and in the examples considered in what follows, the n saturating fluid phases are the water in liquid form (subscript l), its vapor (subscript v), and the dry air (subscript a), with the two latter phases forming a mixture. Therefore, the subscript i used to design an unspecified fluid phase generally stands for $i = l, v,$ or a.

When the porous structure is submitted to various external actions, a stress field σ is generated (Fig. 1). Note that σ is the total stress supported by the porous material viewed as a whole, without making a distinction between the part supported by the skeleton particle and that supported by the fluid particles. Therefore, for the porous structure of mass density r, submitted to the body forces $\mathbf{F}$ per mass unit, the quasi-static momentum balance reads

$$\text{div } \sigma + r\mathbf{F} = 0; \quad t_\sigma = \sigma \quad (1)$$

Porous Material Viewed as Open System

Owing to the relative motion of the saturating fluids with respect to the skeleton, the elementary system $d\Omega$ has not the same fluid mass content after deformation as it had before. In this sense, it is an open system exchanging fluid mass with the outside. Let $m_i \, d\Omega$ be the variation in fluid mass content relative to phase i (see Fig. 2 for $n = i = 1, m = m_1$).

Referring all the movements to that of the skeleton, let $\mathbf{w}_l$
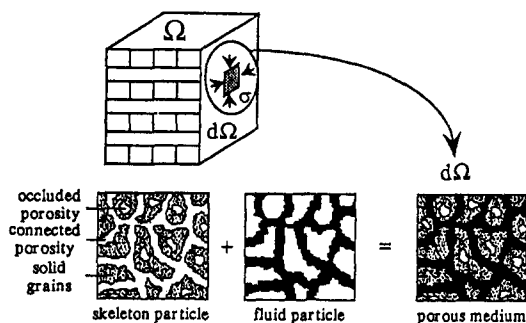

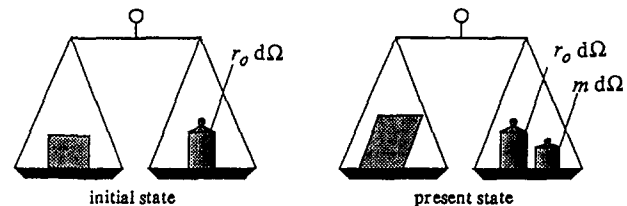FIG. 1. Porous Structure Viewed as Superposition of Two Continuous Media

FIG. 2. Variation in Fluid Mass Content

be the relative flow vector of fluid mass associated with phase i, so that $-\text{div } \mathbf{w}_i \, dt \, d\Omega$ represents the external supply in fluid mass of phase i to the open system $d\Omega$ during the time interval dt. The very definition of m_i implies that the continuity equation, which expresses the mass conservation of fluid phase i, reads

$$\frac{dm_i}{dt} = -\text{div } \mathbf{w}_i \quad (2)$$

In (2), infinitesimal transformations are assumed so that the initial configuration and the deformed one can be considered as coinciding as far as spatial derivations are concerned. This assumption, as also that of infinitesimal displacements, is adopted in what follows.

Furthermore, (2) assumes that no fluid mass creation occurs. For instance, the continuity equation for the fluid phase that represents the dry air in concrete consists in letting $i = a$ in (2). When a liquid-vapor phase change occurs, as is the case for water, the continuity equations for the liquid and vapor phases read

$$\frac{dm_l}{dt} = -\text{div } \mathbf{w}_l - \overset{0}{m}_{l \rightarrow v}; \quad \frac{dm_v}{dt} = -\text{div } \mathbf{w}_v + \overset{0}{m}_{l \rightarrow v} \quad (3)$$

where $\overset{0}{m}_{l \rightarrow v} \, dt \, d\Omega$ represents liquid mass changing into vapor in the elementary system $d\Omega$ during the time interval dt.

ELEMENTS OF THERMODYNAMICS OF POROUS MATERIALS CONSIDERED AS DEFORMABLE OPEN SYSTEMS

Applying First and Second Laws

Let E be the internal energy per unit of initial volume $d\Omega$ of the whole matter enclosed at time t in the elementary system when it is followed in the movement of the solid skeleton. Note that, owing to the open character of the system considered, $E \, d\Omega$ does not represent the internal energy of the same matter as time flows. In the absence of external heat sources and for quasi static evolutions, the first law applied to the open elementary system followed in the skeleton movement yields

$$\frac{dE}{dt} = -\text{div}(e_i \mathbf{w}_i) - \text{div } \mathbf{q} + \sigma : \frac{d\varepsilon}{dt} - \text{div}\left[\left(\frac{p}{\rho_{fi}}\right)_i \mathbf{w}_i\right] + \mathbf{w} \cdot \mathbf{F} \quad (4)$$

where, as in what follows, repeated subscript i stands for summing. In (4), e_i, p_i, and ρ_{fi}^i are, respectively, the internal energy per mass unit, the fluid pressure, and the mass density of phase i. Furthermore, $\mathbf{q}$ is the heat efflux vector and ε is the strain tensor associated with the skeleton deformation. In (4), the right-hand member takes into account all forms of energy supplied to the open system, those due to heat and mass transfer as well as those due to the straining of the skeleton.

Let S be the entropy per unit of initial volume $d\Omega$ of the whole matter enclosed at time t in the elementary system followed in the movement of the solid skeleton. The second law applied to the open elementary system followed in the skeleton movement yields

$$\frac{dS}{dt} \geq -\text{div}(s_i \mathbf{w}_i) - \text{div } \frac{\mathbf{q}}{T} \quad (5)$$

where s_i = internal entropy per mass unit of fluid phase i; and T = absolute temperature. In (5), the right-hand side takes into account all the entropy rates that are externally supplied to the open system, those due to the heat transport as well as those due to the mass transfer. The second law stipulates that there is still a possible spontaneous (internal) production of entropy.

Identification of Dissipations: Thermal Equation

Let Ψ be the free energy of the elementary open system $d\Omega$

$$\Psi = E - TS \qquad (6)$$

A combination of (2)–(6) yields

$$\frac{dS}{dt} = -\operatorname{div}(s_i \mathbf{w}_i) - \operatorname{div}\frac{\mathbf{q}}{T} + \frac{\Phi}{T} \qquad (7)$$

$$\Phi = \Phi_1 + \Phi_\rightarrow + \Phi_2 + \Phi_3 \geq 0 \qquad (8)$$

Eq. (7) is the thermal equation where Φ corresponds to a spontaneous heat source due to energy dissipation. Eq. (8) indicates that the total dissipation is the sum of four terms.

In the prior equation, Φ_1 is the intrinsic dissipation that is associated with the irreversible behavior of the skeleton. It reads

$$\Phi_1 = \sigma : \frac{d\varepsilon}{dt} + g_i \frac{dm_i}{dt} - S\frac{dT}{dt} - \frac{d\Psi}{dt} \qquad (9)$$

where g_i = Gibbs potential per mass unit of fluid of phase i. When there is no interaction at the microscopic level between the fluid phases (i.e., when the mixture composed of all the fluid phases is an ideal mixture at the microscopic level), g_i satisfies the standard relations

$$g_i = e_i + (p/\rho_{fi})_i - Ts_i = g_i(p_i,T); \quad \frac{\partial g_i}{\partial p_i} = \frac{1}{\rho_{fi}}; \quad \frac{\partial g_i}{\partial T} = -s_i \quad (10)$$

The term $\Phi_\rightarrow$ is the dissipation possibly associated with phase change, reading

$$\Phi_\rightarrow = (g_l - g_v)\overset{o}{m}_{l\rightarrow v} \qquad (11)$$

The terms Φ_2 and Φ_3 are the dissipations associated, respectively, with the heat and the fluid mass transport. Using (10) and neglecting the effects of body forces $\mathbf{F}$, their explicit expressions are

$$\Phi_2 = -\frac{\mathbf{q}}{T}\cdot\operatorname{grad} T; \quad \Phi_3 = -\left(\frac{\mathbf{w}}{\rho_{fi}}\right)_i \cdot \operatorname{grad} p_i \qquad (12)$$

Eq. (8) corresponds to the most general formulation of the second law, which may involve couplings between the dissipations, as, for instance, the possible well-known coupling between the heat transport and the fluid mass transport (the so-called Soret-Dufour effect). However, for the sake of clarity, only the more restricted formulation

$$\Phi_1 \geq 0; \quad \Phi_\rightarrow \geq 0; \quad \Phi_2 \geq 0; \quad \Phi_3 \geq 0 \qquad (13)$$

is adopted in what follows.

Heat and Fluid Conduction Laws

The simplest formulation of conduction laws consists in adopting linear laws. For the heat conduction law, this corresponds to the adoption of Fourier's law

$$\mathbf{q} = -\kappa\cdot\operatorname{grad} T \qquad (14)$$

where κ = heat conductivity tensor. For the transport of a fluid phase, as, for instance, the liquid water phase l or the mixture composed of the dry air and the water vapor phase (subscript

mix), it corresponds to the adoption of Darcy's law. When assumed to be decoupled from the other conduction laws, it reads

$$\left(\frac{\mathbf{w}}{\rho_{fi}}\right)_l = -\mathbf{k}_l\cdot\operatorname{grad} p_l; \quad \varphi\mathbf{V}_{mix} = -\mathbf{k}_{mix}\cdot\operatorname{grad} p_{mix} \qquad (15)$$

where $\mathbf{k}_l$ and $\mathbf{k}_{mix}$ = relative permeabilities associated, respectively, with the liquid phase and with the vapor-dry air phase. Furthermore, $\mathbf{V}_{mix}$ is the averaged molar velocity of the vapor-dry air mixture, while

$$p_{mix} = p_v + p_a \qquad (16)$$

is the pressure of the mixture. The latter is assumed to be an ideal mixture and occupies the porous volume $\varphi\, d\Omega$. Finally, the transport of the vapor through the dry air can be described by Fick's law according to

$$\varphi(\mathbf{V}_v - \mathbf{V}_a) = -\mathbf{f}\cdot\operatorname{grad}(p_v/p_{mix}) \qquad (17)$$

The quadratic forms associated with tensors κ, $\mathbf{k}_l$, $\mathbf{k}_{mix}$, and $\mathbf{f}$ have to be positive since inequalities [(13)] have to be satisfied.

Constitutive Equations

The free energy state of the elementary open system is completely defined by the set of external variables ε, m_i, T and a set of internal variables associated with the intrinsic dissipation, and is represented by the vector χ.

$$\Psi = \Psi(\varepsilon, m_i, T, \chi) \qquad (18)$$

A substitution of (18) into (9) and (13) yields

$$\Phi_1 = \left(\sigma - \frac{\partial\Psi}{\partial\varepsilon}\right) : \frac{d\varepsilon}{dt} + \left(g_i - \frac{\partial\Psi}{\partial m_i}\right)\frac{dm_i}{dt} - \left(S + \frac{\partial\Psi}{\partial T}\right)\frac{dT}{dt} \geq 0 \qquad (19)$$

In the case of thermo-poroelastic behavior, the intrinsic dissipation Φ_1 is zero. The constitutive equations are then reduced to the sole state equations

$$\sigma = \frac{\partial\Psi}{\partial\varepsilon}; \quad g_i = \frac{\partial\Psi}{\partial m_i}; \quad S = -\frac{\partial\Psi}{\partial T} \qquad (20)$$

where the equation involving the potential g_i applies for each fluid phase.

In the case of nonreversible behavior of the skeleton, the state equations [(20)] still hold. A substitution of (20) into (19) yields the intrinsic dissipation in the form

$$\Phi_1 = \zeta\cdot\frac{d\chi}{dt} \geq 0; \quad \zeta = -\frac{\partial\Psi}{\partial\chi} \qquad (21)$$

The constitutive equations are then formed of the state equations (20) and of the complementary evolutions laws. The latter are the relations describing the irreversibility of the skeleton behavior. More precisely, they are constituted of relations that link the rate of the internal variables χ and the thermodynamic forces ζ, which are the forces causing the dissipation [see (21)]. For instance, the internal variables χ can be the couple of variables constituted by the irreversible plastic strain and the plastic porosity, with the latter corresponding to the irreversible evolution of the connected porous space (Coussy 1989a,b, 1995b). This irreversible evolution can model the formation of cracks (Fauchet et al. 1991).

Law of Phase Change

The water liquid↔vapor phase change is generally considered as occurring without dissipation ($\Phi_\rightarrow = 0$). Moreover, the liquid and the vapor phases cannot coexist in a stable manner

when their potentials have different values. Therefore, the water liquid↔vapor phase change will be considered as occurring in an instantaneous manner within the porous material so that the potentials g_v and g_l remain always equal

$$g_v(p_v,T) = g_l(p_l,T); \quad dg_v(p_v,T) = dg_l(p_l,T) \quad (22)$$

A substitution of (10) for $i = l$ or v in the second part of (22) yields

$$\frac{dp_v}{\rho_v} - \frac{dp_l}{\rho_l} = (s_v - s_l)\, dT \quad (23)$$

The quantity $T(s_v - s_l)$ is the heat required for the liquid water mass unit to change into vapor

$$s_v - s_l = \frac{L_{l \to v}}{T} \quad (24)$$

where $L_{l \to v}$ = latent heat per mass unit of liquid↔vapor phase change. A substitution of (24) into (23) leads to the generalized Clapeyron's law

$$\frac{dp_v}{\rho_v} - \frac{dp_l}{\rho_l} = L_{l \to v} \frac{dT}{T} \quad (25)$$

Assuming that the vapor is an ideal gas, it is

$$\frac{1}{\rho_v} = \frac{RT}{M_v p_v} \quad (26)$$

where R and M_v =, respectively, constant of ideal gases and the vapor molar mass. Considering isothermal evolutions ($dT = 0$) and that the liquid is incompressible (i.e., ρ_l remains constant), a substitution of state equation (26) into (25) and an integration yield

$$\ln \frac{p_v}{p_v^0} = -\frac{M_v}{RT\rho_l}\, (p_l^0 - p_l) \quad (27)$$

where p_v^0 and p_l^0 = reference pressures of the vapor and the liquid in thermodynamic equilibrium. A convenient liquid reference pressure p_l^0 is the atmospheric pressure p_{at}, i.e., the pressure of the vapor-dry air mixture prevailing outside the porous material. With the choice $p_l^0 = p_{at}$ the vapor reference pressure p_v^0 is the corresponding vapor saturating pressure. If the vapor within the porous material is in equilibrium with the vapor of the atmosphere, the ratio p_v/p_v^0 is then identified to the atmospheric relative humidity h_r.

The capillary pressure p_c is defined by

$$p_c = p_{\text{mix}} - p_l \quad (28)$$

where p_{mix} = vapor-dry air mixture pressure [see (16)]. If the vapor-dry air mixture within the porous medium is in thermodynamic equilibrium with the external atmosphere, its pressure p_{mix} is equal to the atmospheric pressure p_{at}. Assuming this equilibrium to hold and adopting the choice $p_l^0 = p_{at}$, the difference $p_l^0 - p_l$ in (27) is identified to the capillary pressure. Provided that all of the preceding equilibriums actually hold and that the evolutions can be considered as isothermal, the well-known Kelvin's law is recovered

$$\ln h_r = -\frac{M_v}{RT\rho_l}\, p_c \quad (29)$$

ELEMENTS OF NONLINEAR POROELASTICITY FOR PARTIALLY SATURATED POROUS MATERIALS

Incremental Formulation

The poroelasticity is defined by the intrinsic dissipation Φ_1 being zero and, consequently, by the absence of internal var-

iables χ. The constitutive equations are then reduced to state equations (20). Restricting to isothermal evolutions (10) yields

$$g_i = g_i(p_i); \quad dg_i = \left(\frac{dp}{\rho}\right)_i; \quad (i = l,\, v,\, \text{or } a) \quad (30)$$

A differentiation of state equations (20) and use of (30) yield

$$d\sigma = \frac{\partial^2 \Psi}{\partial^2 \varepsilon} : d\varepsilon + \frac{\partial^2 \Psi}{\partial \varepsilon \partial m_i}\, dm_i \quad (31)$$

$$\left(\frac{dp}{\rho}\right)_i = \frac{\partial^2 \Psi}{\partial \varepsilon \partial m_i} : d\varepsilon + \frac{\partial^2 \Psi}{\partial m_i \partial m_j}\, dm_j \quad (32)$$

Note that

$$\frac{\partial^2 \Psi}{\partial^2 \varepsilon} = \mathbf{C}; \quad \rho_i \rho_j \frac{\partial^2 \Psi}{\partial m_i \partial m_j} = M_{ij}; \quad \rho_i \frac{\partial^2 \Psi}{\partial \varepsilon \partial m_i} = -M_{ij}\mathbf{B}_j \quad (33)$$

without summation on repeated subscripts when considering the left-hand members. With the prior notation, (31) and (32) are rewritten in the form

$$d\sigma = \mathbf{C} : d\varepsilon - \left(\frac{dm}{\rho}\right)_i M_{ij}\mathbf{B}_j \quad (34)$$

$$dp_i = M_{ij}\left[-\mathbf{B}_j : d\varepsilon + \left(\frac{dm}{\rho}\right)_j\right] \quad (35)$$

Alternatively, use of (35) in (34) gives

$$d\sigma = \mathbf{C}_0 : d\varepsilon - \mathbf{B}_j dp_j \quad \text{with } \mathbf{C}_0 = \mathbf{C} - M_{ij}\mathbf{B}_i \otimes \mathbf{B}_j \quad (36)$$

Eqs. (34)–(36) are the most general incremental formulations of isothermal poroelastic constitutive equations.

Consider now the isotropic case. Let ε and σ be the volume strain and the mean pressure. Also let $\mathbf{e}$ and $\mathbf{s}$ be, respectively, the strain deviator and the stress deviator

$$\varepsilon = \text{tr } \boldsymbol{\varepsilon}; \quad \sigma = \frac{1}{3}\,\text{tr } \boldsymbol{\sigma}; \quad \mathbf{e} = \boldsymbol{\varepsilon} - \frac{\varepsilon}{3}\mathbf{1}; \quad \mathbf{s} = \boldsymbol{\sigma} - \sigma\mathbf{1}$$

Then, in the isotropic case, (35) and (36) become

$$d\mathbf{s} = 2\mu\, d\mathbf{e}; \quad d\sigma = K_0\, d\varepsilon - b_j\, dp_j \quad (37)$$

$$dp_i = M_{ij}\left[-b_j\, d\varepsilon + \left(\frac{dm}{\rho}\right)_j\right]; \quad (M_{ij} = M_{ji}) \quad (38)$$

In the foregoing equations, μ and K_0 = respectively, the shear modulus and the drained bulk modulus; M_{ij} = the matrix of Biot's moduli; and b_j = Biot's coefficients. Owing to state equations (20) and (30), σ is a function of ε and p_j, i.e., $\sigma = \sigma(\varepsilon, p_j)$. Therefore, the second part of (37) corresponds to the differentiation of such a function, so that

$$K_0 = K_0(\varepsilon, p_j); \quad b_i = b_i(\varepsilon, p_j); \quad M_{ij} = M_{ij}(\varepsilon, p_j) \quad (39)$$

$$\frac{\partial K_0}{\partial p_i} = -\frac{\partial b_i}{\partial \varepsilon}; \quad \frac{\partial b_i}{\partial p_j} = \frac{\partial b_j}{\partial p_i} \quad (40)$$

Case of Both Incompressible Matrix and Liquid

Now, the saturating fluids will exclusively be the liquid (subscript l), its vapor (subscript v), and the dry air (subscript a), with the two latter forming an ideal mixture (subscript mix). The liquid incompressibility reads

$$d\rho_l = 0 \quad (41)$$

If the matrix (see the first section) is incompressible, the relative volume variation ε of the skeleton is only due to that of the connected porous space, reading

$$d\varepsilon = \frac{d\phi}{1 - \phi} \qquad (42)$$

Moreover, since ε represents the relative volume variation, the very definition of the variation in fluid mass content m_j implies the relations

$$\frac{dm_l}{\rho_l} = \phi_l \, d\varepsilon + d\phi_l; \quad \left(\frac{dm}{\rho}\right)_i = \phi \left(\frac{d\rho}{\rho}\right)_i + \phi \, d\varepsilon + d\phi; \quad i = v \text{ or } a \qquad (43)$$

where relation (41) was used. Furthermore, let

$$\phi = \phi_l + \phi \qquad (44)$$

where ϕ_l = porosity associated with the liquid water phase; and ϕ = porosity associated with the vapor-dry air mixture. The fluid bulk modulus K_i fluid phase i is defined by

$$dp_i = K_i \left(\frac{d\rho}{\rho}\right)_i; \quad (i = v \text{ or } a) \qquad (45)$$

From (42)–(45), it follows that

$$dp_v = \frac{K_v}{\phi} \left(-d\varepsilon + \frac{dm_l}{\rho_l} + \frac{dm_v}{\rho_v}\right) \qquad (46)$$

$$dp_a = \frac{K_a}{\phi} \left(-d\varepsilon + \frac{dm_l}{\rho_l} + \frac{dm_a}{\rho_a}\right) \qquad (47)$$

The factors of terms $(dm/\rho)_i$ in (38) (with $i = v$ or a) have to be the same as those in (46) and (47). This leads to the identifications

$$M_{vv} = M_{vl}(=M_{lv}) = \frac{K_v}{\phi}; \quad M_{aa} = M_{al}(=M_{la}) = \frac{K_a}{\phi}; \quad M_{va}(=M_{av}) = 0 \qquad (48)$$

Since the mixture is assumed to be ideal, there is no microscopic interaction between the vapor and the dry air phases. Since the liquid and the matrix are assumed to be incompressible, no macroscopic coupling can occur via the other phases. Consequently, as stipulated by (48), $M_{va}(=M_{av}) = 0$. Moreover, using the previous identities, a comparison of the factors of dE in (38) (with $i = v$ or g) with those of (46) and (47) yields

$$b_v = b_a = b_{\text{mix}} = 1 - b_l \qquad (49)$$

Use of (49) in the second part of (37) yields

$$d\sigma = K_0 \, d\varepsilon + b_l \, dp_c - dp_{\text{mix}} \qquad (50)$$

Combination of Maxwell's relations (40) and of identity (49) yields

$$\frac{\partial K_0}{\partial p_l} = -\frac{\partial K_0}{\partial p_v} = -\frac{\partial K_0}{\partial p_a}; \quad \frac{\partial b_l}{\partial p_l} = -\frac{\partial b_v}{\partial p_v} = -\frac{\partial b_a}{\partial p_a} \qquad (51)$$

Eqs. (39) and (51) imply

$$K_0 = K_0(\varepsilon, p_c); \quad b_l = b_l(\varepsilon, p_c) \qquad (52)$$

From (38) for $i = l$ and from relations (46) and (47), it follows that

$$dp_c = -M \left(-b_l \, d\varepsilon + \frac{dm_l}{\rho_l}\right); \quad \left(M = M_{ll} - \frac{K_v}{\phi} - \frac{K_a}{\phi}\right) \qquad (53)$$

The foregoing relation implies that m_l is a function of only ε and p_c, with $-\rho_l/M$ being the derivative of this function with respect to p_c. Since ρ_l is constant on account of the assumed incompressibility of the fluid, it follows that

$$M = M(\varepsilon, p_c) \qquad (54)$$

In the case of an isotropic poroelastic material with an in-

compressible matrix, which is partially saturated by an incompressible liquid and an ideal mixture formed of the vapor of the former and of dry air, the constitutive equations are completely specified through the first of (37), (46) and (47), (50), and (53). Assuming, in addition, that the vapor and the dry air are ideal gases [see (26)], it follows that $K_v = p_v$ and $K_a = p_a$. The functions and macroscopic characteristics that remain to be experimentally identified are μ, K_0, M, and b_l.

In view of still simplifying the constitutive equations, a very common hypothesis consists in letting

$$b_l = S_l = S_l(p_c) \qquad (55)$$

where S_l = liquid water saturation defined by

$$S_l = \frac{\phi_l}{\phi} \qquad (56)$$

The hypothesis (55) is discussed in Lassabatère (1994) and Coussy (1995b). According to Maxwell's relation (40) and (51), the relation (55) entails

$$K_0 = K_0(\varepsilon) \qquad (57)$$

Substitution of (55) into (50) yields

$$d\sigma = K_0 \, d\varepsilon + S_l \, dp_c - dp_{\text{mix}} \qquad (58)$$

The preceding equation, together with the first part of (37), yields

$$ds = 2\mu \, de; \quad d\sigma' = K_0 \, d\varepsilon \text{ with } \sigma' = \sigma + P;$$

$$P = P_0 - \int_{p_c^0}^{p_c} S_l(p_c) \, dp_c + p_{\text{mix}} \qquad (59)$$

The mean stress $\sigma' = \sigma + P$ is often called the (average) effective stress tensor [see de Boer and Ehlers (1988)] since, according to (59), it is the stress producing the skeleton volume strain. A substitution of (55) into (53) yields

$$dp_c = -M \left(-S_l \, d\varepsilon + \frac{dm_l}{\rho_l}\right) \qquad (60)$$

From (42), the first part of (43), and (56), it follows that

$$-S_l \, d\varepsilon + \frac{dm_l}{\rho_l} = \phi \, dS_l \qquad (61)$$

Substitution of (61) into (60) gives

$$dp_c = -M\phi \, dS_l \qquad (62)$$

which can replace (60).

Under assumption (55), which is adopted in all of what follows, the constitutive equations are formed of the set of (46), (47), (59), and (60). The unknown properties to be experimentally determined are now reduced to μ, K_0 (assumed to be constant in what follows), and the unknown function $p_c(S_l)$. According to (62), the function $-M\phi$ is now determined as the derivative of the function $p_c(S_l)$ with respect to S_l.

EXPERIMENTAL IDENTIFICATION OF CONSTITUTIVE EQUATIONS OF POROELASTICITY FOR CONCRETE

Isothermal Sorption Curves

The shear modulus μ and the (drained) bulk modulus K_0 are properties to be determined by standard measurements. As outlined at the end of the last section, the most important function to be experimentally determined is $p_c(S_l)$. For porous materials such as rocks, this function is generally directly determined through capillary desorption experiments [see, for

instance, Bourbié et al. (1987)]. This experiment consists of applying an increasing capillary pressure p_c directly on the gas within the sample in order to progressively expel the liquid.

For porous materials such as concrete, this kind of experiment is not well suited. The determination of the sought function $p_c(S_l)$ is therefore indirectly carried out through isothermal sorption experiments (Baroghel-Bouny 1994). In contrast with the capillary desorption experiment, the isothermal sorption experiment consists of maintaining the mixture at atmospheric pressure (i.e., $p_{mix} = p_{at}$) and imposing a vapor pressure p_v, or, equivalently, the relative humidity h_r, as defined in the law of phase change section. This assumes that the vapor and the mixture within the sample remain at any time in thermodynamic equilibrium with, respectively, the vapor and the air outside the porous medium, whose partial and total pressure can be controlled. Therefore, Kelvin's law (29) applies. Differentiating the latter yields

$$\frac{dh_r}{h_r} = -\frac{M_v}{RT\rho_l} dp_c \quad (63)$$

In the isothermal sorption experiment, the (atmospheric) mixture pressure p_{mix} is applied on the external surface of the whole sample. This leads to the relation $d\sigma = -dp_{mix}$. When substituting the latter into (59) it follows that

$$d\varepsilon = -\frac{S_l}{K_0} dp_c \quad (64)$$

Eqs. (63) and (64) imply

$$d\varepsilon = \frac{RT\rho_l}{M_v K_0} \frac{S_l}{h_r} dh_r \quad (65)$$

From (61) and (64) it follows that

$$\frac{S_l^2}{K_0} dp_c + \frac{dm_l}{\rho_l} = \phi\, dS_l \quad (66)$$

In the sorption experiment, it is the variation of the liquid water mass content m_l that is actually measured, and not the saturation S_l. However, the first term in the left-hand member of (66) is generally neglected, which results in one disregarding the effect of the volume strain ε on the capillary pressure p_c. This assumption yields $dm_l/\rho_l = \phi_0\, dS_l$, where ϕ_0 is the initial porosity. In the isothermal sorption experiment, the relative humidity h_r is externally controlled. According to (63), the capillary pressure p_c is also indirectly controlled, while the liquid saturation variation dS_l is evaluated through the measurement of the variation dm_l of the liquid water mass content.
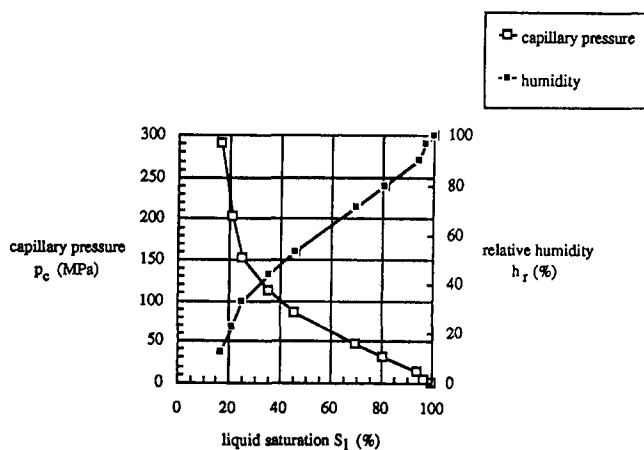

FIG. 3. Results from Isothermal Sorption Experiment for Ordinary Concrete Sample [Capillary Pressure p_c is Derived from Relative Humidity h_r by Using Kelvin's Law (2.26) with $T = 296°K$]
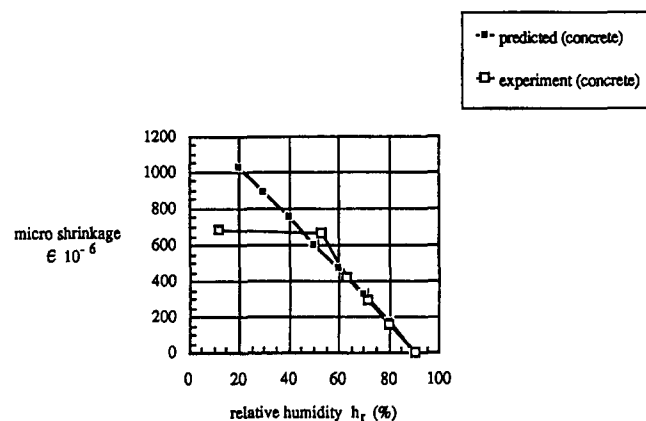

FIG. 4. Experimental Validation of Modeling through Comparison between Observed and Predicted Shrinkage

Fig. 3 illustrates typical results obtained by such an experiment for an ordinary sample of concrete (Baroghel-Bouny 1994).

Experimental Validation of Model

As the relative humidity decreases, capillary forces arise within the sample, which shrinks, as explained more precisely in the next section. The isothermal sorption experiment provides curves such as those represented in Fig. 3, which give the relative humidity versus the liquid water saturation. These curves can be used to predict the shrinkage of the sample when using (64) and (65) (with an experimental value of the bulk modulus K_0 here equal to 25.4 GPa). These theoretical predictions can then be compared with the shrinkage actually observed when the thermodynamic equilibrium is reached between the vapor outside the sample and that within the sample [Baroghel-Bouny (1994) for the experimental data, Lassabatère (1994) for the comparison]. This is represented in Fig. 4, with a discrepancy between the theoretical predictions and the experimental data for values of relative humidity lower than 50%. In fact, for this low range of humidity, the sorption process involves principally the liquid water contained in the nanoporosity, which cannot be modeled as a continuous liquid phase as required by the theory presented here. In contrast, the close agreement between the theoretical predictions and the experimental values for values of humidity higher than 50% shows the relevancy of the modeling in this range of humidity, especially the relevancy of postulating the existence of a macropotential Ψ upon which the proposed approach is mainly based. Note in particular the linearity of the shrinkage versus the relative humidity. According to (65), this linearity is due to the linearity of the relative humidity as a function of the liquid saturation (see Fig. 3). Indeed, if the relative humidity was not a linear function of the degree of saturation, the drying shrinkage as a function of the relative humidity would reproduce this nonlinear effect. This has been recently observed by Camerliet (1996) using the same approach.

DRYING SHRINKAGE

Drying Shrinkage Process

Consider a porous sample saturated by liquid water and a mixture. The latter formed of water vapor and dry air is assumed to remain at atmospheric pressure. Let the sample be suddenly put in contact with the exterior containing the same mixture at atmospheric pressure, but at a lower relative humidity than that initially prevailing in the sample. Hence, an initial thermodynamic imbalance occurs between the external vapor concentration and that within the sample. To restore thermodynamic equilibrium, the sample exchanges water va-

por with the exterior. Consequently, the vapor pressure within the sample decreases. For the liquid and the vapor to remain in (isothermal) equilibrium within the sample, the liquid pressure also decreases. This requires the water to evaporate (if it cannot leave the sample as a liquid). Since the pressure decreases and since the pressure of the mixture (atmosphere) remains unchanged, the capillary pressure increases and the matrix suffers an increasing internal compression. Therefore, the sample shrinks. If this shrinkage cannot freely occur, this generates tensile stresses in the sample, which can lead to cracking.

Linear Modeling of Homogeneous Drying Shrinkage of Sample

As a first approach, consider the linear formulation of constitutive equations of poroelasticity (46), (50), and (53)

$$\delta\sigma = K\varepsilon - Mb_l \frac{m_l}{\rho_l}; \quad K = K_0 + b_l^2 M \tag{67}$$

$$\delta p_c = Mb_l\varepsilon - M\frac{m_l}{\rho_l} \tag{68}$$

$$\delta p_v = -V\varepsilon + V\frac{m_l}{\rho_l} + V\frac{m_v}{\rho_v}; \quad V = \frac{K_v}{\varphi} \tag{69}$$

where $\delta(.)$ = difference between the current value of quantity (.) and its initial value $(.)_0$. For instance, since p_{mix} is equal to the atmospheric pressure p_{at} throughout the experiment, $\delta p_{\mathrm{mix}} = 0$, which was used to write (67). The bulk modulus K in (67) may be interpreted as the undrained modulus with respect to the liquid water (i.e., when $m_l = 0$). In conformity with the physical evidence, its expression shows that capillary effects stiffen the porous material (term $b_l^2 M$).

Since $\delta p_{\mathrm{mix}} = 0$ and according to Fick's law (17), the rate $\overset{0}{m}_{v\to\mathrm{ext}}$ of vapor mass exchange with the exterior in the case of homogeneous state of vapor pressure within the sample depends on the difference between the external vapor pressure $p_{v\infty}$ and the internal one p_v. In a first linear approach it is

$$\overset{0}{m}_{v\to\mathrm{ext}} = -\rho_v f[p_{v\infty} - (\delta p_v - p_{v0})]/p_{\mathrm{mix}} \tag{70}$$

When imposing that the water cannot leave the sample as a liquid, the conservation of the liquid and the vapor mass reads here as

$$\frac{dm_l}{dt} = -\overset{0}{m}_{l\to v}; \quad \frac{dm_v}{dt} = -\overset{0}{m}_{v\to\mathrm{ext}} + \overset{0}{m}_{l\to v} \tag{71}$$

Assuming that the liquid water and its vapor are constantly in equilibrium, Clapeyron's law (25) must be satisfied at any time. In the isothermal linearized case, it reads

$$\frac{\delta p_v}{\rho_v} = -\frac{\delta p_c}{\rho_l} \tag{72}$$

where the condition $\delta p_{\mathrm{mix}} = 0$ was used, which entails $\delta p_l = -\delta p_c$. The preceding equation shows very clearly that, when the vapor pressure decreases (i.e., $\delta p_v < 0$), the capillary pressure increases (i.e., $\delta p_c > 0$). Furthermore, the sample is being surrounded by the atmosphere at constant pressure

$$\delta\sigma = 0 \tag{73}$$

Substituting (70) into (71) yields

$$\frac{1}{\rho_v}\left(\frac{dm_l}{dt} + \frac{dm_v}{dt}\right) = f[p_{v\infty} - (\delta p_v - p_{v0})]/p_{\mathrm{mix}} \tag{74}$$

Also substituting (73) into (67)–(69) yields

$$\frac{m_l}{\rho_l} = \frac{K}{Mb_l}\varepsilon; \quad \delta p_c = -\frac{K_0}{b_l}\varepsilon; \quad \frac{m_v}{\rho_v} = -\frac{m_l}{\rho_l} + \varepsilon + \frac{dp_v}{v} \tag{75}$$

From (72) and (76), it follows that

$$\delta p_v = \frac{\rho_v}{\rho_l}\frac{K_0}{b_l}\varepsilon \tag{76}$$

Eqs. (76) and (76) may be used in order to express any quantity as a function of ε, so that (74) yields

$$\tau_d \frac{d\varepsilon}{dt} + \varepsilon = \varepsilon_\infty; \quad \tau_d \frac{dm_l}{dt} + m_l = m_{l\infty} \tag{77}$$

where reference time τ_d, strain ε_∞, and variation in liquid mass content $m_{l\infty}$ are defined by

$$\tau_d = \frac{1}{f}\left[\frac{K}{K_0 M}\frac{\rho_l}{\rho_v}\left(\frac{\rho_l}{\rho_v} - 1\right) + \frac{1}{v} + \frac{\rho_l}{\rho_v}\frac{b_l}{K_0}\right]p_{\mathrm{mix}} \tag{78a}$$

$$\varepsilon_\infty = -\frac{\rho_l}{\rho_v}\frac{b_l}{K_0}(p_{v0} - p_{v\infty}); \quad m_{l\infty} = \frac{\rho_s K}{Mb_l}\varepsilon_\infty \tag{78b}$$

From solving (77), it follows that

$$\varepsilon = \varepsilon_\infty\left[1 - \exp\left(-\frac{t}{\tau_d}\right)\right]; \quad m_l = m_{l\infty}\left[1 - \exp\left(-\frac{t}{\tau_d}\right)\right] \tag{79}$$

Therefore, τ_d appears as the characteristic time of drying, while ε_∞ and $m_{l\infty}$ =, respectively, asymptotic shrinkage and asymptotic variation in liquid mass content.

The drying was assumed to be isothermal. That causes one to consider that the (latent) heat required for the liquid to evaporate is instantaneously supplied from the exterior on account of the rapidity of the heat conduction, when comparing the latter to the slowness of the vapor conduction. The isothermal assumption can be roughly checked as follows. Neglecting the heat sources associated with dissipation effects, the entropy balance for the sample, which is assumed to be in a homogeneous state, yields

$$T\frac{dS}{dt} = -Ts_i\overset{0}{m}_{i\to\mathrm{ext}} + \overset{0}{Q} \tag{80}$$

where $\overset{0}{Q}$ and $\overset{0}{m}_{i\to\mathrm{ext}}$ = rates of the heat supply and of the fluid mass exchange with the exterior of liquid phase i. According to Fourier's law, in a first linear approach

$$\overset{0}{Q} = -\kappa\theta \tag{81}$$

where $\theta = T - T_0$ = difference between the temperature T of the sample and the temperature T_0 of the atmosphere, which is also the initial sample temperature. The scalar κ is the conductivity of the sample with the exterior. Neglecting the latent heat effects associated with the strain and the thermic dilatations relative to variations of fluid mass content, the last of the state equations (20), when differentiated, yields

$$dS = s_i dm_i + rC\frac{d\theta}{T} \tag{82}$$

where C = specific heat of the sample. Since the sample exchanges no water in liquid form with the exterior, $\overset{0}{m}_{l\to\mathrm{ext}} = 0$, while $\overset{0}{m}_{l\to v} = dm_v/dt$. With the help of these remarks and recalling (24), a substitution of (71), (73), and (82) into (80) leads to

$$\tau_\theta\frac{d\theta}{dt} + \theta = \frac{L_{l\to v}}{\kappa}\frac{dm_l}{dt}; \quad \tau_\theta = \frac{rC}{\kappa} \tag{83}$$

where τ_θ = characteristic time of thermal diffusion. A rough overestimation of the temperature decrease, which is associated with the cooling process of the sample due to latent heat effects of the liquid-vapor phase change, is to disregard the limiting effect of the cooling upon the phase change. This consists in substituting the isothermal solution (79) for m_l into (83). Integrating the latter, this procedure yields

$$\theta = -\theta_0 \left[\exp\left(-\frac{t}{\tau_d}\right) - \exp\left(-\frac{t}{\tau_\theta}\right) \right];$$

$$\theta_0 = \frac{\tau_\theta}{\tau_d} \frac{L_{l \rightarrow v} m_{l\infty}}{rC} (1 - \tau_\theta/\tau_d)^{-1} \tag{84}$$

The reference variation temperature θ_0 provides a rough evaluation of the temperature decrease in the cooling process due to the evaporation. For porous materials such as concrete, the time ratio τ_θ/τ_d is so low that θ_0 is actually negligible in spite of the high value of the latent heat term when compared to the heat capacity.

Drying Shrinkage of Wall

The preceding modeling of the drying shrinkage can only be considered as a first approach. It is a linear modeling, and transport phenomena through the sample were not considered. A more realistic model of isothermal drying shrinkage consists of solving the closed set of equations formed by

- Field equations (1)–(3)
- Darcy's and Fick's laws [(15) and (17)]
- Kelvin's law (assuming, therefore, that the conditions given in the law of phase change section are fulfilled)
- State equations (46), (47), (59), and (60) or (62)

A finite-volume scheme has been used in order to discretize (2) and (3), as described in Eymard and Gallouët (1993). For Darcy's and Fourier's laws, partially implicit one-dimensional finite difference approximations have been implemented. A numerical approximation has been kept in order to compute the integral in (59). From all these numerical procedures, nonlinear equations are obtained. They are solved at each time step, using a Newton-Raphson method. Time step size is computed, according to predictor-corrector criteria; this leads to a numerical control of the time discretization error. The following results have been obtained, using a 50-grid block mesh.

The material properties are those given in the section on the experimental identification of constitutive equations of poroelasticity for concrete. These properties are macroscopic properties, directly obtained by macroscopic experiments. Such macroscopic characteristics as Young's modulus or sorption-desorption curves are intimately dependent on the constitutive properties of concrete, as the water-cement ratio and the aggregate volume fraction. These material microscopic characteristics are grossly integrated into our modeling and calculations via their influence on the macroscopic properties.

Aiming toward nonlinear numerical processing, the curve of Fig. 3 is approximated by the function of the form [see Parker et al. (1987)]

$$S_l = [1 + (a \ln h_r)^b]^c \tag{85}$$

The values adopted for a, b, and c are, respectively, $a = -1.85$, $b = 1.57$, and $c = -1$. These values give a good curve fitting for a range of relative humidity higher than 50%. In addition, a Poisson coefficient with a value of 0.18 is adopted, while the initial porosity is equal to 0.12 and the isotropic Fick's conductivity f such that $\mathbf{f} = f\mathbf{1}$ in (17) is given by $f = 10^{-7}$ m^2 s^{-1}. In fact, the actual value depends upon the liquid saturation, and therefore upon the relative humidity when Kelvin's law applies. The value adopted for the calculations corresponds to an average experimental value over the range of relative humidity 50%–100% and to a diffusity of 10^{-12} m^2 s^{-1} (Baroghel-Bouny 1994).

The examined problem is the drying of a wall of 0.8 m thickness in the Ox-horizontal direction and of infinite extent in the two orthogonal directions, i.e., the Oy- and Oz-directions. This wall is suddenly subjected at time $t = 0$ to a relative

humidity $h_r = 50\%$. The initial saturation is slightly higher than 0.9 (see Fig. 5 for an exact value and Fig. 3 for the corresponding initial relative humidity). Throughout the drying process, the vapor-dry air mixture is assumed to remain at the constant atmospheric pressure p_{at}.

Figs. 5 and 6 represent, respectively, the liquid water saturation S_l and the capillary pressure p_c versus the depth (i.e., the x-coordinate), for different values of time. At time $t = 0^+$, the relative humidity h_r drops down to the imposed external value of 50% within the extreme thin layer of the wall. Therefore, there is an instantaneous evaporation occurring within this layer, so that the liquid water saturation decreases and the capillary pressure increases according to the state equations, as represented by the curves of Fig. 3. As the time flows, owing to diffusion effects, the process slowly and progressively extends to the internal layers forming the wall. The interesting feature is the very high level of the capillary pressure so that the liquid water phase undergoes tensile stresses.

Figs. 7 and 8 represent, respectively, the longitudinal shrinkage in the Ox-direction and the stress (σ_{zz} or σ_{yy}) in the directions normal to the direction along which the shrinkage occurs. Since the shrinkage is not allowed in the Oz- and Oy-directions, the concrete forming the wall suffers a severe tensile
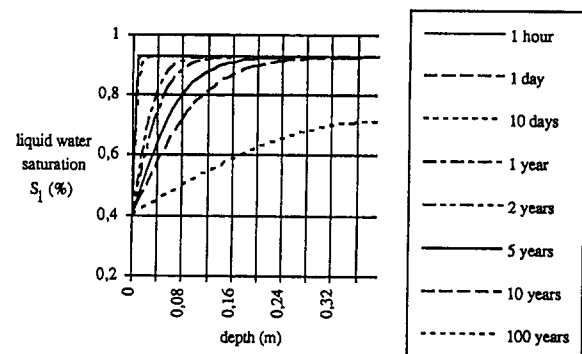

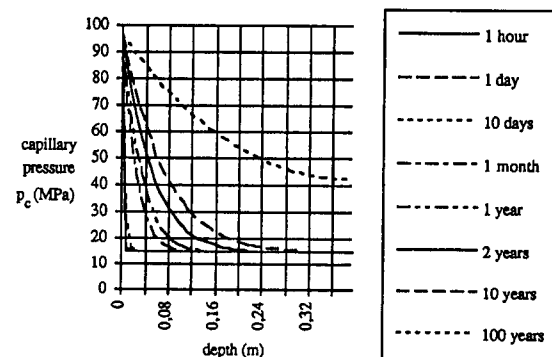**FIG. 5. Liquid Water Saturation S_l versus Depth during Drying of Wall (Half of Wall Is Represented)**

FIG. 6. Capillary Pressure p_c versus Depth during Drying of Wall (Half of Wall Is Represented)
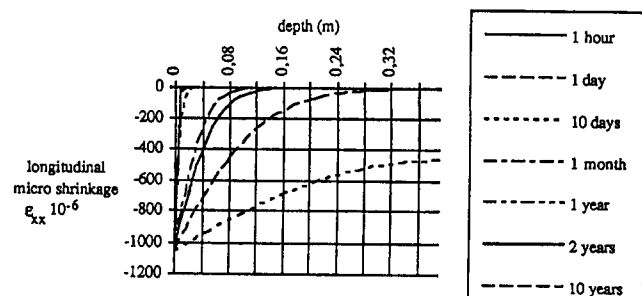

FIG. 7. Longitudinal Microshrinkage $\varepsilon_{xx} 10^{-6}$ versus Depth during Drying of Wall (Half of Wall Is Represented)
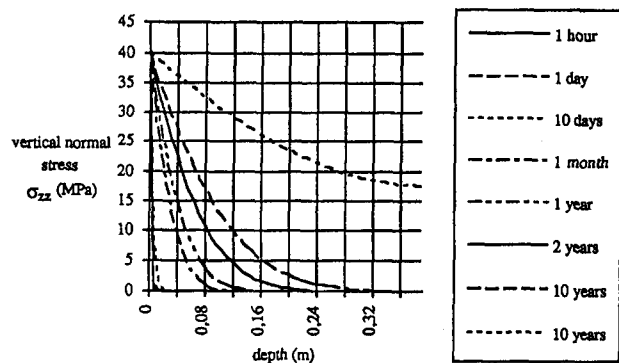
FIG. 8. Vertical Normal Stress σ_{zz} versus Depth during Drying of Wall (Half of Wall Is Represented)

stress state in these directions. In fact, cracks will necessarily develop normal to this direction. The presented poroelastic reversible modeling cannot render an account of the extent of such a cracking process. To this aim, a poroplastic modeling, as, for instance, the one developed in Coussy (1989a,b) and Coussy (1995b), is needed. However, in actual situations, the cracking process remains generally limited to the external layer of the wall. With respect to the drying process, the effects of these external cracks can be taken into account by modifying only the boundary conditions modeling the exchange of vapor of the external layer of the wall with the outside.

CONCLUSIONS

The transport phenomena have been represented here very roughly, neglecting in particular the transport of water in liquid form in the application. Even for very low values of the permeability, the high values of the capillary depressure occurring at the edge of the wall will, in most cases, generate at the early stages of the drying process movements of water in liquid form from the core of the wall toward the external layers.

The aforementioned phenomena can be modeled using the theory presented in the paper. In fact, with respect to predicting the mechanical effects, i.e., the stress and strain induced by these phenomena, the aim of the paper was mainly to show that they have to be considered in a global thermodynamic context; only then are they able to render a proper account of many couplings, especially the thermo-hygromechanical ones.

When the main purpose is a macroscopic engineering one, the proposed theory is well suited to predict the stress and the strain caused by the drying. In fact, the modeling can be extended to predict the stress and the strain caused by various physical processes, such as the hydration and the creep of concrete [see F. Ulm and O. Coussy (unpublished paper, 1995); Coussy and Ulm (1995)].

In view of analyzing the deterioration of concrete structures, a point of main concern is the prediction of the (micro) cracking of structures, which has not been addressed here. If well-established theories exist, which successfully model the cracking of concrete structures when they can be considered as saturated [see Fauchet et al. (1991)], a great amount of research remains to be conducted in order to better understand and accurately represent the irreversible mechanical behavior of partially saturated porous materials when they are submitted to internal capillary effects.

APPENDIX I.   REFERENCES

Acker, P. (1988). "Comportement mécanique du béton: apports de l'approche physico-chimique." *Rapport de Recherche LPC No. 152* (in French).

Baggio, P., Majorana, C. E., and Schrefler, B. (1993). "Thermohygrometric and mechanical analysis of concrete by a finite element method." *Numerical methods in thermal problems*, R. W. Lewis, ed., Vol. III, Pineridge Press, Swansea, Wales, U.K., 847–858.

Baroghel-Bouny, V. (1994). "Caracterisation des pâtes de ciments et des bétons: Méthodes, analyse, interprétations." Laboratoire Central des Ponts et Chaussées, Sect. des Pub., Paris (in French).

Bazant, Z., ed. (1986). "Creep and shrinkage of concrete: Mathematical modeling." *4th RILEM Int. Symp.*, Reunion Internationale des Laboratoires d'Essais et de Recherche sur les Materiaux et les Constructions.

Bazant, Z., and Wittmann, F., eds. (1982). *Mathematical modeling of creep and shrinkage of concrete.* John Wiley & Sons, Inc., New York, N.Y.

Bazant, Z. P. (1972). "Thermodynamics of hindered adsorption and its implications for hardened cement paste and concrete." *Cement and Concrete Res.*, 2(1), 1–16.

Bazant, Z. P., and Kim, J. K. (1992). "Consequences of diffusion theory for drying shrinkage of concrete." *Mat. and Struct.*, 24, 323–326.

Bear, J., and Bachmat, Y. (1990). *Introduction to modeling in transport phenomena in porous media*, Kluwer, Amsterdam, The Netherlands.

Bentz, D. P., Quenard, D., Baroghel-Bouny, V., Garboczi, E. J., and Jennings, H. M. (1995). "Modelling drying shrinkage of cement paste and mortar. Part I: Structural models from nanometers." *Mat. and Struct.*, 28, 450–458.

Biot, M. A. (1941). "General theory of three dimensional consolidation." *J. Appl. Phys.*, 12, 155–164.

Biot, M. A. (1962). "Mechanics of deformation and acoustic propagation in porous media." *J. Appl. Phys.*, 12, 155–164.

Biot, M. A. (1972). "Theory of finite deformation of porous solids." *Indiana Univ. Math. J.*, 33, 1482–1498.

Biot, M. A. (1977). "Variational Lagrangian-thermodynamics of non-isothermal finite strain: Mechanics of porous solid and thermomolecular diffusion." *Int. J. Solids and Struct.*, 12, 155–164.

Bourbié, T., Coussy, O., and Zinzner, B. (1987). *Acoustics of porous media.* Gulf Pub. Co./Ed. Technip.

Camerliet, J. (1996). "Moisture transfer and durability of open reactive porous media." *5th Symp. on Build. Phys. in Nordic Countries.*

Coussy, O. (1989a). "A general theory of thermoporoelastoplasticity for saturated porous materials." *Transport in Pourous Media*, 4, 281–293.

Coussy, O. (1989b). "Thermodynamics of saturated porous solids in finite deformation." *Eur. J. Mech.*, A/Solids, 8, 1–14.

Coussy, O. (1995a). "Constitutive modelling of civil engineering materials subject to thermo-hydro-mechanical couplings." *Int. Workshop on Mass-Energy and Deterioration of Build. Components*, CSTB, Paris.

Coussy, O. (1995b). *Mechanics of porous continua.* John Wiley & Sons, Inc., New York, N.Y.

Coussy, O., and Ulm, F. (1995). "Creep and plasticity due to chemomechanical couplings." *4th Int. Conf. on Computational Plasticity: Fundamentals and Applications.*

de Boer, R., and Ehlers, W. (1988). "The development of the concept of effective stress." *Acta Mechanica*, 74, 1–8.

Eymard, R., and Gallouët, T. (1993). "Convergence d'un schéma de type éléments finis/volumes finis pour un système formé d'une équation elliptique et d'une équation hyperbolique." *M2AN*, 27(7), 843–861 (in French).

Fauchet, B., Coussy, O., Carrère, A., and Tardieu, B. (1991). "Poroplastic analysis of concrete dams and their foundations." *Dam Engrg.*, 2, 165–192.

Feldman, R. F. (1968). "Sorption and length-change scanning isotherms of methanol and water hydrated portland cement." *Proc., 5th Int. Congr. on Chem. of Cement, Session III.1: Struct. and Phys. Properties of Cement Paste*, Vol. 3, Cement Assoc. of Japan, Tokyo, 53–56.

Feldman, R. F., and Sereda, P. J. (1968). "A model for hydrated portland cement paste as deduced from sorption-length change and mechanical properties." *Mat. and Struct.*, 1(6), 509–520.

Halphen, B., and Salençon, J. (1987). *Elasto-plasticité.* Presses de l'Ecole Nationale des Ponts et Chaussées, Paris.

Hansen, W. (1987). "Drying shrinkage mechanisms in portland cement paste." *J. Am. Ceramics Soc.*, 70(5), 323–328.

Jennings, H., Kropp, J., and Scrivener, K., eds. (1996). *Proc., NATO/RILEM Workshop on Modeling of Microstructure and Its Potential for Studying Transport Properties and Durability*, St. Rémy-les-Chevreuses.

Lassabatère, T. (1994). "Couplages hydromécaniques en milieu poreux

non saturé avec changement de phase: Application au retrait de dessication," PhD thesis, Ecole Nationale des Ponts et Chaussées, Paris.

Lemaitre, J., and Chaboche, J. L. (1990). *Mechanics of solids materials.* Cambridge Univ. Press, London.

Parker, J. C., Lenhard, R. J., and Kuppusamy, T. (1987). "A parametric model for constitutive properties governing multiphase flow in porous media." *Water Resour. Res.*, 23(4), 618–624.

Powers, T. C. (1965). "Mechanisms of shrinkage and reversible creep of hardened cement paste." *Proc., Int. Symp. Struct. of Concrete and Its Behaviour under Load*, Cement and Concrete Assoc., London, 319–344.

Powers, T. C. (1968). "The thermodynamics of volume change and creep." *Mat. and Struct.*, 1(6), 487–507.

Shrefler, B. A., Simoni, L., Li, X., and Zienkiewicz, O. C. (1990). "Mechanics of partially saturated porous media." *Numerical methods and constitutive modelling in geomechanics*, CISM Courses and Lect. Ser. Vol. 311, C. S. Desai and Gioda, eds., Springer-Verlag, New York, N.Y., 169–209.

Sih, G. C., Michopoulos, J. G., and Chou, S. C. (1986). *Hygrothermo-elasticity*, Martinus Nijhoff Publishers.

Truesdell, C. (1984). *Rational thermodynamics*, 2nd Ed., Springer-Verlag, New York, N.Y.

Wittmann, F. H. (1973). "Interaction of hardened cement paste and water." *J. Am. Ceramics Soc.*, 56(8), 409–415.

APPENDIX II. NOTATION

The following symbols are used in this paper:

$\mathbf{B}_i$ = Biot tensor of fluid (i);
b_i = Biot coefficient of fluid (i);
$\mathbf{C}$ = undrained tensor of elasticity;
$\mathbf{C}_0$ = drained tensor of elasticity;
E = internal energy per unit of initial volume;
e_i = internal energy per unit of mass of fluid (i);
g_i = free mass enthalpy of fluid (i);
h_r = relative humidity;
K_i = microscopic bulk modulus of fluid (i);
K_0 = drained bulk modulus;
k_l = relative permeability associated with liquid phase;
k_{mix} = relative permeability associated with vapor-dry air phase;
$L_{L \to v}$ = latent heat per mass unit of liquid↔vapor phase change;
$\mathbf{M} = (M_{ij})$ = matrix of Biot moduli;
M_v = vapor molar mass;
m_i = mass variation of fluid (i);
p_c = capillary pressure;
p_g = total pressure of gas mixture;
p_i = pressure of fluid (i);
$\mathbf{q}$ = heat efflux vector;
R = constant of ideal gases;
S = total entropy per unit of volume;
S_l = volumic saturation of liquid phase (l);
s_i = mass entropy of fluid (i);
T = temperature (Kelvin);
$\mathbf{w}_i$ = mass efflux vector of fluid (i);
$\boldsymbol{\varepsilon}$ = strain tensor;
ε = volumetric strain;
$\boldsymbol{\kappa}$ = heat conductivity tensor;
$\boldsymbol{\sigma}$ = stress tensor;
σ = average stress;
ϕ = total porosity;
φ = volumic fraction of gas mixture; and
Ψ = free energy per unit of volume.

Subscripts

a = subscript referring to air;
i,j = subscript referring to interstitial fluids;
l = subscript referring to liquid water; and
v = subscript referring to vapor phase.