

Creep and plasticity due to chemo-mechanical couplings

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Summary The paper explores the theory of reactive porous media for the modelling of creep and plasticity due to chemo-mechanical couplings at the macro-level of material description. The formulation is based upon thermodynamics of open porous media composed of a skeleton and several fluid phases saturating the porous space. This theoretical framework allows to introduce the kinetics of a chemical reaction directly at the macro-level of material description. In turn, it is used to model creep due to chemo-mechanical couplings within a closed reactive porous continuum, as well as ageing creep due to two chemical reactions, one associated with the apparent creep phenomenon, the other with the apparent ageing phenomenon. Furthermore, it is shown how the modelling can be extended to account for plastic (i.e. permanent) phenomena, including hardening/softening and damage phenomena, coupled with a chemical reaction (chemical hardening).

Key words creep, ageing, plasticity, damage, coupling

List of symbols

A	reactant phase;
A_m, A_x	chemical affinities of reactions of extent ξ and x ;
A_{x_0}	initial affinity;
A_χ	plastic affinity;
B	product phase;
\mathbf{B}	tensor of chemical dilatation coefficients;
E_a, E_x	activation energies relative to reactions of extent and x ;
f	loading function;
g	plastic potential;
g_m^j	free mass enthalpy of fluid phase j ;
H	hardening modulus;
h	hardening potential;
\mathbf{I}	2nd-order unit tensor;
K	bulk modulus;
k_d	viscous coefficient associated to a micro-diffusion process;
ℓ	coefficient;
M_i°	external mass supply rate of fluid i ;
m_j	increase in fluid mass of phase j ;
$m_{i \rightarrow j}^\circ$	rate of mass change from phase i to phase j ;
\mathcal{R}	universal constant for ideal gas;
S	entropy;
T	temperature;
t	time;
$U(\chi)$	frozen energy due to hardening/softening;

Received 17 August 1995; accepted for publication 15 February 1996

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x	extent of the ageing reaction;
β	isotropic chemical dilatation coefficient;
$\chi, \boldsymbol{\chi}$	hardening/softening/damage variable (scalar, tensor);
$\boldsymbol{\varepsilon}$	strain tensor;
ε	volume strain ($\text{tr} \boldsymbol{\varepsilon}$);
$\boldsymbol{\varepsilon}^v, \varepsilon^v$	viscous strain tensor; viscous volume strain ($\text{tr} \boldsymbol{\varepsilon}^v$);
$\boldsymbol{\varepsilon}^p, \varepsilon^p$	plastic strain tensor; plastic volume strain ($\text{tr} \boldsymbol{\varepsilon}^p$);
Φ_1	intrinsic dissipation of the open elementary system;
$\Phi_{A \rightarrow B}$	chemical dissipation of the open elementary system;
φ_1	intrinsic dissipation of the closed porous medium;
η_i	viscosity relative to physico-chemical phenomenon i ;
κ	material parameter;
$d\lambda$	plastic multiplier;
$\mu(t)$	maturity function or equivalent age;
$\boldsymbol{\sigma}$	stress tensor; initial stress tensor
σ, σ_0	mean stress, initial mean stress;
ξ, ξ^0	extent of the creep reaction, creep reaction rate;
Ψ	free energy of the open elementary system;
ψ	free energy of the closed elementary system;
ζ, ζ	hardening force;
$\dot{x} = dx/dt$	time derivative of function x ;
x^0	rate of quantity x ;
$():()$	double tensor contraction;
$()\cdot()$	scalar product;
$\text{tr}()$	first invariant of tensor $()$.

1

Introduction

Geomaterials involved in civil engineering, whether natural (rocks, soils) or man-made (concrete), are more or less porous materials, which deform when subjected to mechanical loading. In addition, chemical reactions may occur within them, influencing the mechanical behaviour, and leading to strains of chemical origin. Furthermore, the stress applied may be of a magnitude beyond the current material strength: the material then deforms in an irreversible manner, and may deteriorate. Finally, mechanical response (elastic properties, material strength etc.) may also depend upon the extent of a chemical reaction. An accurate modelling of chemo-mechanical couplings is thus required to predict, and possibly prevent, a deterioration of engineering structures composed of reactive porous materials.

This paper explores the theory of reactive porous continua as developed in [5] for the modelling of chemo-mechanical couplings, which allows to account for chemical reactions directly at the macro-level of material description, i.e. at the scale of laboratory test specimens. The formulation is based upon thermodynamics of open porous media composed of a deformable skeleton and several fluid phases saturating the porous space. This theoretical framework allows to introduce the kinetics of a chemical reaction directly at the macro-level of material description. In turn, it will be used to model standard apparent phenomena, like creep, ageing etc. due to chemo-mechanical couplings within a closed reactive porous continuum. The detailed study of the phenomena, of which the actual understanding involves the molecular level, lies beyond the purpose of the presentation. Attention will merely be drawn to establish a theory capable of predicting the macroscopic behaviour of materials subjected to such phenomena. Furthermore, it will be shown, how the modelling can be extended to account for plastic (i.e. permanent) creep effects, including hardening/softening phenomena, coupled with a chemical reaction (chemical hardening). The modelling will be carried out in the framework of physical linearization and infinitesimal transformations.

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Thermodynamic framework of reactive porous media

In this part, we will briefly recall the basic relations of the theory of reactive porous media to account for a chemical reaction at the macro-level of material description. For the general theory of open reactive non-saturated porous media, the interested reader is referred to [5].

Consider an *open* porous medium of initial volume $d\Omega$ composed of a matrix and a porous space which is saturated by two fluid phases, a reactant phase A and a product phase B . A chemical reaction may occur between them such that

$$A \rightarrow B.$$

The observable strain is that of the skeleton and is denoted ε . The mass variation of the open system is due to the mass variations of fluid phases A and B per unit of macroscopic volume $d\Omega$, denoted m_A and m_B . The mass conservation for the two fluid phases reads

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

where M_i° represents the external rate of fluid mass supply of each fluid phase. The quantity $m_{A \rightarrow B}^\circ$ is the rate of mass formation of product phase B due to chemical reaction (1) such that quantity $m_{A \rightarrow B}^\circ dt d\Omega$ is the mass of phase A which transforms into phase B during time interval dt . It is noteworthy that mass-formation rate $m_{A \rightarrow B}^\circ$ is *a priori* not the time derivative of a function (i.e. $f^\circ \neq df/dt$), since the mass increases of the reactant and the product phase may be due to external supply, i.e. the terms M_A° and M_B° .

Using thermodynamics of open porous continua, the generalized Clausius-Duhem inequality which expresses locally the second law of thermodynamics, reads

$$\Phi_1 + \Phi_{A \rightarrow B} \geq 0, \quad (3)$$

where Φ_1 is the intrinsic dissipation associated with the irreversible behaviour of the skeleton

$$\Phi_1 = \sigma : \frac{d\varepsilon}{dt} - S \frac{dT}{dt} + g_m^j \frac{dm_j}{dt} - \frac{d\Psi}{dt} \geq 0 \quad j = A, B, \quad (4)$$

and $\Phi_{A \rightarrow B}$ the dissipations associated with chemical reaction (1)

$$\Phi_{A \rightarrow B} = (g_m^A - g_m^B) m_{A \rightarrow B}^\circ \geq 0, \quad (5)$$

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

In the expression for the intrinsic dissipation (4) σ , S and g_m^j are the stress tensor, the entropy and the chemical potentials or free enthalpies per mass unit of fluid phase $j = A, B$, associated to the rates of strain tensor ε , temperature T and fluid mass m_j ($j = A, B$), respectively. Furthermore, Ψ is the free energy of the open elementary system which defines the thermodynamic states of the system in terms of external variables, i.e. strain tensor ε , temperature T and fluid mass m_j ($j = A, B$), and a set of internal variables χ associated with the dissipation due to the irreversible skeleton behaviour

$$\Psi = \Psi(T, \varepsilon, m_A, m_B, \chi). \quad (6)$$

Using Eq. (6) in (4) yields

$$\Phi_1 = \left(\sigma - \frac{\partial \Psi}{\partial \varepsilon} \right) : \frac{d\varepsilon}{dt} - \left(S + \frac{\partial \Psi}{\partial T} \right) \frac{dT}{dt} + \left(g_m^j - \frac{\partial \Psi}{\partial m_j} \right) \frac{dm_j}{dt} - \frac{\partial \Psi}{\partial \chi} \frac{d\chi}{dt} \geq 0. \quad (7)$$

In the case of a thermo-poro-elastic behaviour, the intrinsic dissipation is zero, and the constitutive equations are reduced to the sole state equations

$$\sigma = \frac{\partial \Psi}{\partial \varepsilon} \quad S = -\frac{\partial \Psi}{\partial T} \quad g_m^j = \frac{\partial \Psi}{\partial m_j} \quad \text{with } j = A, B. \quad (8)$$

State equations (8) still hold in the case of a non-reversible behaviour of the skeleton. A substitution of Eqs. (8) in Eq. (7) yields the intrinsic dissipation in the form

$$\Phi_1 = \zeta \dot{\chi} \geq 0 \quad \zeta = -\frac{\partial \Psi}{\partial \chi}. \quad (9)$$

The constitutive equations are then formed of the state equations (8) and of complementary evolution laws, which describe the irreversibility of the skeleton behaviour. More precisely, these complementary evolution laws are the relations linking the rate of the internal variables χ to the thermodynamic forces ζ which cause the intrinsic dissipation, see Eq. (9), i.e. the dissipation of effective mechanical work into heat form associated to the irreversible skeleton behaviour.

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

$$\Phi_{A \rightarrow B} = A_m \xi^\circ \geq 0, \quad (10)$$

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

$$A_m = \ell (g_m^A - g_m^B) \quad \text{and} \quad \xi^\circ = m_{A \rightarrow B}^\circ / \ell, \quad (11)$$

with ℓ a constant which relates the mass formation rate and the reaction rate. In a more refined modelling, ℓ accounts for the stoichiometry and the molar masses of the substances constituting the reactant and the product phases, cf. [4, 3, 5 and 6].

Note that all equations introduced here until now are purely macroscopic, since they involve only macroscopic state variables. In particular, reaction rate ξ° is proportional to the rate of mass formation in the chemical reaction. Furthermore, from Eq. (10), chemical affinity A_m is identified as the thermodynamic force associated in the chemical dissipation to reaction rate ξ° . It expresses the thermodynamic imbalance between the reactant and the product phase, i.e. the difference in chemical potentials. This explicit identification holds irrespective of transport phenomena of the reactant and product phase through the structure, and is essential when making precise the kinetics of the chemical reaction considered at the macro-level of material description, i.e. at the scale of laboratory tests. More precisely, according to expression (10) of chemical dissipation $\Phi_{A \rightarrow B}$, the kinetics of the reaction must be specified by a relation linking affinity A_m to reaction rate ξ° . In the limits of a diffusion-controlled reaction, a linear evolution law can be adopted, see for instance [1]. It reads

$$A_m = k_d \xi^\circ \quad k_d > 0, \quad (12)$$

where k_d is a viscous coefficient, which accounts for the micro-diffusion of chemical constituents involved in reaction (1). More precisely, in the case of a diffusion-controlled reaction, reaction rate ξ° corresponds to a diffusion rate. At the microscopic level, this diffusion rate depends upon the free enthalpy gradient between the reactant and the product phase, which is expressed at the macro-level of material description by affinity A_m . Thus, k_d is a diffusion coefficient. Furthermore, the combination of reactants to form products may be activation-controlled. In this case, an evolution law of the Arrhenius type may be adopted, reading

$$A_m = k_d \xi^\circ \exp\left(\frac{E_a}{\mathcal{R}T}\right) \quad k_d > 0, \quad (13)$$

where E_a is a certain activation energy, and \mathcal{R} the universal constant for ideal gas. In this case, the micro-diffusion process is at the basis of the chemical dissipation (10), amplified by the latter thermal activation.

Consider now the elementary system as *closed* for the chemical constituents, i.e. there is no external supply

$$M_i^\circ = 0. \quad (14)$$

Then, according to Eqs. (2) and (11), the rate of mass formation $m_{A \rightarrow B}^\circ$ is actually a time derivative, as it is reaction rate $\xi^\circ = d\xi/dt = \dot{\xi}$

$$m_{A \rightarrow B}^\circ = \dot{m}_{A \rightarrow B} = -\dot{m}_A = \dot{m}_B = \ell \dot{\xi}. \quad (15)$$

Closure condition (14) allows to reduce the number of state variables which characterise the thermodynamic states of the porous media. In fact, since intrinsic dissipation φ_1 of the closed elementary system reads

$$\varphi_1 = \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - S \dot{T} - \dot{\psi} \geq 0, \quad (16)$$

a comparison with Eq. (3) allows to consider reaction extent ξ as an internal state variable, since 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 ξ is a measure of the progress of the reaction considered, see [1]. Free energy ψ of the closed system then reads

$$\psi = \psi(T, \varepsilon, \xi, \chi) = \Psi(T, \varepsilon, m_a = -k\xi, m_b = k\xi, \chi), \quad (17)$$

and state equations (8) yield

$$S = -\frac{\partial\psi}{\partial T} \quad \sigma = \frac{\partial\psi}{\partial\varepsilon} \quad A_m = -\frac{\partial\psi}{\partial\xi}, \quad (18)$$

where entropy S , stress tensor σ and chemical affinity A_m are the thermodynamic forces associated in intrinsic dissipation φ_1 with the rates of state variables T , ε and ξ . In contrast to the open elementary system, affinity A_m derives now explicitly from the free energy ψ of the closed system, and

$$\varphi_1 = \Phi_1 + \Phi_{A \rightarrow B} = \zeta \cdot \dot{\chi} + A_m \dot{\xi} \geq 0 \quad \zeta = -\frac{\partial\psi}{\partial\chi}, \quad (19)$$

where χ are still the internal state variables modelling intrinsic dissipative phenomena of the skeleton, while ξ is now an internal state variable. In return, the evolution of ξ is still governed by kinetic laws (12) and (13), with $\xi^\circ = \dot{\xi}$, and the evolution of variables χ by complementary evolution laws linking its rate to the thermodynamic force ζ .

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Creep due to a chemical reaction

In the above, only one simple reaction (1) was considered, and it was shown how it can be integrated in the constitutive modelling at the macro-level of material description. In turn, this framework of closed reactive porous media will be employed to model creep due to a chemical reaction. In a first step, other dissipative mechanisms than the one related to the chemical reaction will be not considered, i.e. $\Phi_1 = 0$, and $\varphi_1 = \Phi_{A \rightarrow B} \geq 0$, thus assuming an elastic behaviour of the bulk material. Furthermore, only isothermal evolutions will be considered, see [15] for an extensive discussion of the modelling of thermo-chemo-mechanical couplings of closed reactive porous media. Finally, for the sake of clarity, shear effects will be set aside.

Consider a porous continuum, *closed* with respect to the chemical constituents. Hence, the state equations are given by relations (18), and the constitutive modelling can be worked out from specifying expression (17) of free energy $\psi = \psi(\varepsilon, \xi)$ of the closed system. The following expression can be adopted for an isotropic material:

$$\psi = \frac{1}{2}K\varepsilon^2 - \beta K\varepsilon\xi + \frac{1}{2}\mathcal{L}\xi^2. \quad (20)$$

The above expression corresponds to a stress-relieved reference state (initial stress $\sigma^\circ = 0$) being at thermodynamic equilibrium (no initial thermodynamic imbalance between the chemical constituents, i.e. $A_{m^\circ} = 0$), and to a linearization with respect to both volume strain $\varepsilon = \text{tr}\varepsilon$ and reaction extent ξ . Using expression (20) in Eqs. (18), the state equations read explicitly

$$\sigma = K\varepsilon - \beta K\xi, \quad A_m = \beta K\varepsilon - \mathcal{L}\xi, \quad (21)$$

where $\sigma = \text{tr}\sigma/3$ is the mean stress. In addition, substituting Eqs. (21) in kinetic law (12) or (13) yields

$$A_m = k_d \dot{\xi} \quad \text{or} \quad A_m = k_d \dot{\xi} \exp\left(\frac{E_a}{\mathcal{R}T}\right). \quad (22)$$

Furthermore, the first of state equations (21) can be inverted, reading

$$\varepsilon = \frac{\sigma}{K} + \beta\xi, \quad (23)$$

which allows to identify

$$\varepsilon^v = \beta \xi, \quad (24)$$

as the strain of chemical origin, related with reaction extent ξ by coefficient β , which can be considered as a chemical dilation coefficient. Equations (23) and (24) allow to rewrite the constitutive equations in the equivalent form

$$\sigma = K(\varepsilon - \varepsilon^v), \quad \frac{A_m}{\beta} = \sigma - \mathcal{K} \varepsilon^v = \eta_d \dot{\varepsilon}^v \quad \text{or} \quad \frac{A_m}{\beta} = \eta_d \dot{\varepsilon}^v \exp\left(\frac{E_a}{\mathcal{R}T}\right), \quad (25)$$

with

$$\mathcal{K} = \frac{\mathcal{L}}{\beta^2} - K, \quad \eta_d = \frac{k_d}{\beta^2}. \quad (26)$$

Constitutive equations (25) are linear with respect to strain ε and stress σ . They show, that a sudden stress application induces a thermodynamic imbalance between reactant and product phase, and starts the chemical reaction: the material creeps. In fact, constitutive equations (25) correspond to those of a viscoelastic material, or more precisely to those of a Kelvin-Voigt material, with a viscosity η_d governing the kinetics: the higher η_d , the slower the reaction. In the case of linear kinetics, i.e. $\eta_d = \text{const.}$, the material behaves like a linear viscoelastic material. However, the kinetics of the physical phenomenon at the origin of the apparent creep phenomenon may not be linear. More precisely, in the case of a diffusion-controlled reaction, the reactants have to bypass the layers of products already formed, to meet and form new products. As the reaction advances, i.e. as ξ increases, the layer extends, and the diffusion process becomes slower. Hence, viscosity η_d may not be constant, but increases as the reaction advances, i.e. $\eta_d = \eta_d(\xi)$ or $\eta_d = \eta_d(\varepsilon^v)$. This renders the complementary evolution law (25), nonlinear with respect to creep strain ε^v , and corresponds to a nonlinear visco-elastic material which creeps due to a chemical reaction.

Finally, note that a Maxwell material is recovered by setting $\mathcal{K} = 0$ in constitutive equations (25). Furthermore, a Kelvin-Chain model, as frequently used for the modelling of concrete creep [2], is obtained when considering N uncoupled reactions, and associating with each reaction its own reaction extent ξ_i ($i = 1, N$). The evolution of each chemical reaction is still given by kinetic law (22), while the total viscous strain ε^v reads as a sum of the viscous strains $\gamma_i = \beta_i \xi_i$ (without summation) of the individual units of the Kelvin chain. From a more physical standpoint, such a modelling implies that N different physical processes with different kinetics and amplitudes are, *in fine*, active in the material, which cannot be considered as instantaneous with respect to the time of observation.

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Ageing creep due to two chemical reactions

So far, only one reaction was considered, leading to a modelling of creep due to chemo-mechanical coupling. This part is devoted to the modelling of ageing creep due to two distinct physical phenomena, one related to the basic creep phenomenon, the second to the ageing phenomenon, which appears as a variation of mechanical characteristics in time at the macro-level of material description. With respect to these distinct physical origins, consider a second reaction, and let x be its reaction extent. Considering an isotropic elastic behaviour of the bulk material, and disregarding shear effects, a modified expression for free energy $\psi = \psi(\varepsilon, \xi, x)$ of the closed system can be adopted

$$\psi = \frac{1}{2}K(x)(\varepsilon - \varepsilon^v)^2 + \frac{1}{2}\mathcal{K}(x)\varepsilon^v{}^2 + \mathcal{V}(x) \quad (27)$$

where ε^v is still defined with respect to the chemical reaction of extent ξ , i.e. Eq.(24). Constitutive Eqs. (25) now read

$$\sigma = K(x)(\varepsilon - \varepsilon^v), \quad \sigma - \mathcal{K}(x)\varepsilon^v = \eta_d \dot{\varepsilon}^v \quad \text{or} \quad \sigma - \mathcal{K}(x) = \eta_d \dot{\varepsilon}^v \exp\left(\frac{E_a}{\mathcal{R}T}\right) \quad (28)$$

while the affinity associated with the chemical reaction of extent x is obtained from

$$A_x = -\frac{\partial \psi}{\partial x} = -\frac{1}{2}\frac{\partial K(x)}{\partial x}(\varepsilon - \varepsilon^v)^2 - \frac{1}{2}\frac{\partial \mathcal{K}(x)}{\partial x}\varepsilon^v{}^2 - \frac{\partial \mathcal{V}(x)}{\partial x}. \quad (29)$$

Assuming infinitesimal strains $\varepsilon \ll 1$, which applies equally to the strains of chemical origin $\varepsilon^v \ll 1$, the second-order strain terms in state equation (29) can be neglected, leading to

$$A_x \cong -\frac{\partial v(x)}{\partial x}. \quad (30)$$

The law governing the kinetics of the “ageing” reaction can be formally written as

$$A_x \cong -\frac{\partial v(x)}{\partial x} = f(\dot{x}), \quad (31)$$

Let $x(t)$ be the solution of the above differential equation, i.e.

$$x = x(t) \quad (32)$$

The count of time is beginning with the instant at which the ageing reaction starts, i.e., in general, with the instant of material creation. According to Eq. (31), the evolution of reaction extent x is independent of the other state variables, and, consequently, of the mechanical loading. In other words, and in contrast to the “creep” reaction of reaction extent ζ , application of stress does not induce a thermodynamic imbalance between reactants and products involved in the ageing reaction of reaction extent x . Hence, an initial thermodynamic imbalance, i.e. an initial affinity between the chemical constituents $A_{x_0} = A_x(x=0)$ exists in the reference state, in order for the reaction to start. Applying a linear expression for affinity A_x yields

$$A_x = A_{x_0} - \kappa x = \eta_x \dot{x} \exp\left(\frac{E_x}{\mathcal{R}T}\right), \quad (33)$$

where η_x is the viscous coefficient relative to the micro-diffusion process involved in the ageing reaction, and E_x the activation energy of the reaction. The positive values of function η_x ensure the non-negative dissipation associated with the reaction, while the positive modulus κ guarantees its stability. Furthermore, affinity A_x tends to zero for $t \rightarrow \infty$, which corresponds to a thermodynamic equilibrium $A_x(\infty) = 0$. The asymptotic extent of the ageing reaction then reads

$$x(\infty) = \frac{A_{x_0}}{\kappa}, \quad (34)$$

and thus depends solely upon the initial thermodynamic imbalance between the chemical constituents. Rewriting differential equation (33) in the form

$$\frac{dx}{x(\infty) - x(t)} = \frac{\kappa}{\eta_x} \exp\left(-\frac{E_x}{\mathcal{R}T}\right) dt = d\mu, \quad (35)$$

and integrating, an equivalent state variable to reaction extent x is obtained, denoted as maturity μ . It reads

$$\mu(t) = \ln \left[\frac{x(\infty)}{x(\infty) - x(t)} \right] = \int_{s=0}^{s=t} \frac{\kappa}{\eta_x} \exp\left(-\frac{E_x}{\mathcal{R}T}\right) ds. \quad (36)$$

Due to the positive values of the integrand in definition (36), the function $\mu(t)$ is a monotonically increasing function of time. It is equal to zero at the material creation, i.e. for $t = x = 0$, and tends to infinity with $t \rightarrow \infty$ for which $x \rightarrow x(\infty)$. Hence, maturity $\mu(t)$ can be used as an appropriate argument for functions $K(\mu)$ and $\mathcal{K}(\mu)$ in constitutive equations (28) instead of the reaction extent $x(t)$. In the case of linear reaction kinetics, i.e. at $\eta_x = \text{const.}$, and at isothermal evolution i.e., at $T = T_0$, maturity μ is linearly linked with physical time t . However, η_x may not be a constant, since the reactants have to bypass the layers of products already formed. It increases with the advance of the ageing i.e. yields $\eta_x = \eta_x(x)$. Furthermore, though derived for isothermal evolution, definition (36) of maturity μ still holds at non-isothermal evolution provided that not only stress variation but also temperature variation does not induce a thermodynamic imbalance between the chemical constituents involved in the ageing reaction of extent x . A detailed discussion of these thermo-chemo-mechanical couplings and their application to concrete at early age can be found in [15].

Finally, substituting Eq. (32) in Eq. (28) yields

$$\sigma = K(t)(\varepsilon - \varepsilon^v) \quad \sigma - \mathcal{K}(t)\varepsilon^v = \eta_d \dot{\varepsilon}^v \quad \text{or} \quad \sigma - \mathcal{K}(t) = \eta_d \dot{\varepsilon}^v \exp\left(\frac{E_a}{\mathcal{R}T}\right). \quad (37)$$

The above constitutive equations are linear with respect to strain ε and stress σ , with moduli K and \mathcal{K} which depend now on time. Consequently, the porous material behaves as an ageing linear viscoelastic material, provided that $\eta_d = \text{const}$. In this linear case, the ageing concerns only the moduli variation in time, and thus the amplitude of the apparent creep phenomenon. It may equally play on the kinetics of the creep phenomenon, i.e. $\eta_d = \eta_d(x)$ or $\eta_d = \eta_d(t)$.

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Plastic creep effects

So far, the modelling of chemo-mechanical coupling has not considered plastic phenomena, by assuming an elastic behaviour (possibly nonlinear, due to ageing) of the skelton. The presentation has focused on chemical dissipation $\Phi_{A \rightarrow B}$, thus neglecting other sources of intrinsic dissipation Φ_1 , for instance the dissipation of effective mechanical work into heat due to plastic effects. To account for such irreversible creep phenomena, introduce plastic variables, namely the plastic volume strain ε^p and the hardening variable χ . The free energy $\psi = \psi(\varepsilon, \varepsilon^p, \xi, \chi)$ of the closed poroplastic material now reads

$$\psi = \frac{1}{2}K(\varepsilon - \varepsilon^p)^2 - \beta K(\varepsilon - \varepsilon^p)\xi + \frac{1}{2}\mathcal{L}\xi^2 + U(\chi). \quad (38)$$

The above expression corresponds to a stress-relieved reference state with initial stress $\sigma^\circ = 0$ being at thermodynamic equilibrium there is neither initial thermodynamic imbalance between the chemical constituents, non ageing, i.e. $A_{mo} = A_{xo} = 0$. It corresponds also to a linearization with respect to volume strain ε , plastic volume strain ε^p and reaction extent ξ . Furthermore, $U(\chi)$ is the energy related to hardening effects, which is also called *frozen* energy and assumed uncoupled from the chemical reaction. This latter coupling between the chemical reaction and the hardening phenomenon will be considered in the next section.

Using expression (38) in Eqs. (18), state equations (21) are replaced by

$$\begin{aligned} \sigma = \frac{\partial \psi}{\partial \varepsilon} &= K(\varepsilon - \varepsilon^p) - \beta K \xi, & \sigma &= -\frac{\partial \psi}{\partial \varepsilon^p} \\ A_m = -\frac{\partial \psi}{\partial \xi} &= \beta K(\varepsilon - \varepsilon^p) - \mathcal{L} \xi, & \zeta &= -\frac{\partial U(\chi)}{\partial \chi}. \end{aligned} \quad (39)$$

The dissipation expression (19) now reads

$$\varphi_1 = \Phi_1 + \Phi_{A \rightarrow B} \geq 0, \quad \Phi_1 = \sigma \dot{\varepsilon}^p + \zeta \dot{\chi}, \quad \Phi_{A \rightarrow B} = A_m \dot{\xi}, \quad (40)$$

where stress σ , like in the standard plastic model, is the thermodynamic force associated in the dissipation to the rates of both total strain ε and plastic strain ε^p , while affinity A_m , according to identification (10), is still the associated force to reaction rate $\dot{\xi}$. Furthermore, according to identification (9), ζ is the hardening force associated in dissipation Φ_1 to the rate of hardening variable χ .

Irrespective of total dissipation φ_1 assuming non-negative chemical dissipation $\Phi_{A \rightarrow B}$, i.e. inequality (10) with $\xi^\circ = \dot{\xi}$ together with a linear law for the kinetics linking affinity A_m and reaction rate $\dot{\xi}$, i.e. Eq. (12) or (13), we have

$$A_m = \beta K(\varepsilon - \varepsilon^p) - \mathcal{L} \xi = k_d \dot{\xi} \quad \text{or} \quad A_m = k_d \dot{\xi} \exp\left(\frac{E_a}{\mathcal{R}T}\right). \quad (41)$$

The first of state equations (39) can be inverted giving

$$\varepsilon = \frac{\sigma}{K} + \varepsilon^p + \beta \xi, \quad (42)$$

which allows to identify

$$\varepsilon^v = \varepsilon^p + \beta \zeta, \quad (43)$$

as the measurable strain which is not instantaneously recovered after a complete unloading process from a present loading state of stress σ . Substituting Eq. (43) in the first of state equation (39) and in kinetic law (41) leads to

$$\sigma = K(\varepsilon - \varepsilon^v), \quad \frac{A_m}{\beta} = \sigma - \mathcal{K} \beta \zeta = \eta_d \beta \dot{\zeta} \quad \text{or} \quad \frac{A_m}{\beta} = \eta_d \beta \dot{\zeta} \exp\left(\frac{E_a}{\mathcal{R}T}\right), \quad (44)$$

where \mathcal{K} and η_d are still defined by relations (26). Constitutive equations (44) show that a sudden application of stress induces a thermodynamic imbalance between the chemical constituents, starting the reaction and inducing strains due to chemo-mechanical couplings (cf. the term $\beta \zeta$). It is now increased in an instantaneous manner by plastic strains if the stress reaches a threshold which gives rise to irreversible creep effects.

Like in the standard plasticity model, a loading point σ cannot leave the elasticity domain C_E , thus

$$\sigma \in C_E \Leftrightarrow f(\sigma, \zeta) \leq 0, \quad (45)$$

where $f(\sigma, \zeta)$ is the loading function or plasticity criterion. Plastic evolution occurs only if a loading point σ is at the boundary of elasticity domain C_E , i.e. $f(\sigma, \zeta) = 0$, where it remains for an ideal plastic material or which it carries along for a hardening plastic material. The plasticity criterion indicates when plastic phenomena occur, while the plastic flow rule indicates how. More precisely, when assuming non-negative dissipation Φ_1 associated with plastic phenomena, i.e. Eq. (9), standard formulations can be used for both the flow rule (see [5, 9, and 11]),

$$d\varepsilon^p = d\lambda \frac{\partial f(\sigma, \zeta)}{\partial \sigma} \quad \text{or} \quad d\varepsilon^p = d\lambda \frac{\partial g(\sigma, \zeta)}{\partial \sigma}, \quad (46)$$

and the hardening rule

$$d\chi = d\lambda \frac{\partial f(\sigma, \zeta)}{\partial \zeta} \quad \text{or} \quad d\chi = d\lambda \frac{\partial h(\sigma, \zeta)}{\partial \zeta}, \quad (47)$$

where $d\lambda \geq 0$ is the plastic multiplier

$$\begin{cases} d\lambda > 0 & \text{if } f=0 \quad \text{and} \quad df=0, \\ d\lambda = 0 & \text{if } f < 0 \quad \text{or} \quad df < 0. \end{cases} \quad (48)$$

In the previous equations, the functions $g(\sigma, \zeta) \neq f(\sigma, \zeta)$ and $h(\sigma, \zeta) \neq f(\sigma, \zeta)$ are the nonassociated potentials of the plastic and the hardening evolution, which quantify the thermodynamically admissible directions $\partial g/\partial \sigma$ and $\partial h/\partial \zeta$ taken by the plastic increments $d\varepsilon^p$ and $d\chi$, satisfying non-negative dissipation related to plastic phenomena

$$\Phi_1 dt = d\lambda \left(\sigma \frac{\partial g}{\partial \sigma} + \zeta \frac{\partial h}{\partial \zeta} \right) \geq 0. \quad (49)$$

Note clearly the different time scales of chemical and plastic evolution. The evolution of the reaction extent ζ is related to the time scale of the reaction kinetics, while plastic increments $d\varepsilon^p$ and $d\chi$ occur simultaneously with any variation in loading, provided that the chemical reaction does not alter the hardening state, i.e. $\zeta = \zeta(\chi)$. In this case, writing the consistency condition $df = 0$ in the form

$$\frac{\partial f}{\partial \zeta} d\zeta = -\frac{\partial f}{\partial \sigma} d\sigma = -d\lambda H, \quad (50)$$

the hardening modulus H and the plastic multiplier $d\lambda$ read

$$H = \frac{\partial f}{\partial \zeta} \left(-\frac{\partial \zeta}{\partial \chi} \right) \frac{\partial \chi}{d\lambda} = \frac{\partial f \partial^2 U \partial h}{\partial \zeta \partial \chi^2 \partial \zeta} \quad \text{and} \quad d\lambda = \frac{1}{H} \frac{\partial f}{\partial \sigma} d\sigma. \quad (51)$$

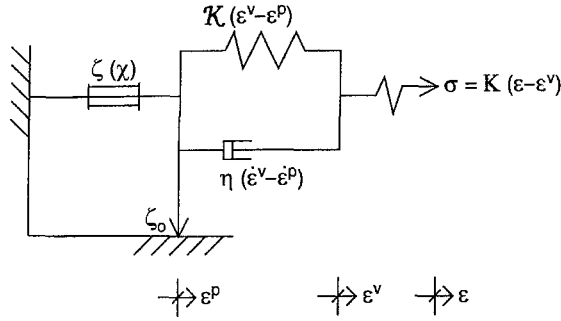


Fig. 1. Rheological model corresponding to the chemically reactive plastic porous material

Here, use has been made of hardening rule (47) and the state equation of relations (39) which links the hardening force ζ to the frozen energy $U(\chi)$. The hardening modulus H is positive for hardening, and negative for softening, which corresponds to an expansion or a shrinkage of the elasticity domain C_e , respectively.

Constitutive equations (44), (46) and (47) correspond to a viscoelastic material, now coupled with plasticity, as illustrated in Fig. 1, which undergoes both a time-dependent deformation governed by the kinetics of the chemical reaction, and a permanent strain in an instantaneous manner when reaching a threshold. It may be coupled with a second reaction as shown in Sec. 3 to account for ageing, i.e. the variation of elastic characteristics in time. Also the threshold may vary in time, due to chemo-mechanical couplings, the modelling of which will be shown hereafter.

6

Chemical hardening

In the previous section, hardening phenomena due to chemical effects were neglected. In other words, at constant stress, the progress of the reaction has no effect upon the elasticity domain of the material. Consequently, the hardening/softening state of the material depends only upon plastic variables χ , which, according to hardening rule (47), evolve in an instantaneous manner, if a loading point σ is at the boundary of the elasticity domain C_e which it deforms while carrying it along. Recalling, in particular, that

$$\zeta = -\frac{\partial \psi}{\partial \chi}, \tag{52}$$

expression (38) of the free energy ensures the independence of the hardening force ζ with regard to the chemical reaction and its kinetics, and thus with regard to the physical time independent of stress application. However, a time-dependent evolution of the threshold (material strength) can play an important role for some geomaterials, where the evolution of the material strength cannot be considered as instantaneous with respect to the time scale of observation (maturing concrete, dissolution process etc.). To model such a phenomenon, we consider again the ageing reaction of extent x . Combining free energy expressions (27) and (38), the following expression for free energy $\psi = \psi(\varepsilon, \varepsilon^p, \chi, \xi, x)$ is adopted:

$$\psi = \frac{1}{2} K(x) (\varepsilon - \varepsilon^p - \beta \xi)^2 - \mathcal{H}(x) (\beta \xi)^2 + U(\chi, x) - A_{x_0} x + \frac{1}{2} \kappa x^2, \tag{53}$$

and constitutive equations (28) become

$$\sigma = K(x)(\varepsilon - \varepsilon^p), \quad \sigma - \mathcal{H}(x) \beta \xi = \eta_d \beta \dot{\xi} \quad \text{or} \quad \sigma - \mathcal{H}(x) \beta \xi = \eta_d \beta \dot{\xi} \exp\left(\frac{E_a}{\mathcal{R}T}\right), \tag{54}$$

with ε^v given by Eq. (43), and \mathcal{H} and η_d by Eq. (26). Substituting expression (53) in Eq. (52) shows that the hardening force ζ now depends on reaction extent x through the function $U(\chi, x)$. In the first approach, a linear coupling of reaction extent x with the hardening phenomenon can be assumed

$$U(\chi, x) = U(\chi) - xA_\chi(\chi), \tag{55}$$

leading to the following expression of hardening force ζ :

$$\zeta = -\frac{\partial U(\chi)}{\partial \chi} + x \frac{\partial A_x(\chi)}{\partial \chi}. \quad (56)$$

Kinetic law (33), linking affinity A_x and reaction rate \dot{x} , now reads in the modified form

$$A_x = A_{x_0} + A_x(\chi) - \kappa x = \eta_x \dot{x} \exp\left(\frac{E_x}{\mathcal{R}T}\right), \quad (57)$$

which allows to identify $A_x(\chi)$ as the thermodynamic imbalance induced by plastic evolutions and thus by mechanical loading. Hence, it is worth noting that maturity μ , as defined by Eq. (36), can be used as an equivalent state variable for reaction extent x only if plastic effects do not significantly affect the thermodynamic imbalance between the chemical constituents involved in the ageing reaction, i.e. $|A_x(\chi)| \ll |A_{x_0} - \kappa x|$. In return, plastic affinity $A_x(\chi)$ concerns only the amplitude of reaction extent x . Plastic evolution may, however, also influence the kinetics of the reaction. In this case, the function η_x will depend on the hardening variable χ , i.e. $\eta_x = \eta_x(\chi)$.

Furthermore, the elasticity domain is still expressed by Eq. (45). Even when no plastic loading occurs, and, consequently, the hardening variable χ keeps its current value the hardening force ζ may change. This occurs according to Eq. (56) when a variation $dx = \dot{x}dt$ of the reaction extent x within the time interval dt takes place according to kinetic law (57). Hence, the elasticity domain C_E changes as well. This phenomenon corresponds to a pure chemical hardening.

Assuming again non-negative dissipation Φ associated with plastic effects, i.e. Eq. (49), the flow rule and the hardening rule are still given by Eqs. (46) and (47), while the plastic multiplier $d\lambda$ and hardening modulus H are now expressed in slightly different forms. In fact, the consistency condition (50) reads now

$$\frac{\partial f}{\partial \zeta} \frac{\partial \zeta}{\partial \chi} d\chi = -d_\chi f = -d\lambda H, \quad (58)$$

where $d_\chi f$ stands for differentiating function f at constant hardening variable χ . Substituting Eq. (56) in (45) and using hardening rule (47), the plastic multiplier $d\lambda$ and the hardening modulus H can be expressed explicitly in the form

$$d\lambda = \frac{d_\chi f}{H} = \frac{1}{H} \left(\frac{\partial f}{\partial \sigma} d\sigma + \frac{\partial f}{\partial \zeta} \frac{\partial A_x(\chi)}{\partial \chi} dx \right), \quad (59)$$

$$H = -\frac{\partial f}{\partial \zeta} \frac{\partial \zeta}{\partial \chi} \frac{d\chi}{d\lambda} = \frac{\partial f}{\partial \zeta} \left(\frac{\partial^2 U(\chi)}{\partial \chi^2} - x \frac{\partial^2 A_x(\chi)}{\partial \chi^2} \right) \frac{\partial h}{\partial \zeta}, \quad (60)$$

which are to be compared with Eqs. (51). It is worth noting, that the previous definitions are consistent with the habitual definition of the hardening modulus H , which is positive for hardening (for which plastic loading occurs when $d_\chi f > 0$) and negative for softening (for which plastic loading occurs when $d_\chi f < 0$). In fact, replacing the hardening force ζ in the loading function $f = f(\sigma, \zeta)$ by expression (56), thus obtaining $f = f(\sigma, \chi, x)$, and using Eq. (55) for $df = 0$ yields

$$f(\sigma, \chi + d\chi, x) = f(\sigma, \chi, x) + \frac{\partial f}{\partial \chi} d\chi = f(\sigma, \chi, x) - Hd\lambda. \quad (61)$$

Consider an initial loading state defined by stress σ_0 and chemical hardening state x_0 at the boundary of the elasticity domain, satisfying $f(\sigma_0, \chi_0, x_0) = 0$. If plastic loading occurs ($df = 0$), the hardening variable χ undergoes an infinitesimal change $d\chi$. According to Eq. (61), and since $Hd\lambda > 0$ for hardening, the initial loading point σ_0 satisfies $f(\sigma_0, \chi_0 + d\chi, x_0) < 0$. Thus, it lies inside the new elasticity domain associated with the new hardening state which is defined by $\chi_0 + d\chi$ and the reaction extent x_0 prior to the plastic loading. The same reasoning applies to softening for which $H < 0$ and $d_\chi f < 0$. In this case, initial loading point σ_0 lies outside the new elasticity domain. As an intermediary case, ideal plasticity is defined by a zero hardening modulus ($H = 0$), while the plastic multiplier $d\lambda$ remains undetermined during plastic loading.

Finally, the previous modelling can be easily extended to the case where plastic evolution leads to a degradation of the elastic moduli of the material; i.e. to the case of a damaged material. In this case free energy ψ reads

$$\psi = \frac{1}{2}K(x, \chi) (\varepsilon - \varepsilon^p - \beta \xi)^2 - \mathcal{H}(x, \chi) (\beta \xi)^2 + U(\chi) - (A_{x_0} + A_\chi(\chi))x + \frac{1}{2}\kappa x^2, \quad (62)$$

and the constitutive equations become

$$\sigma = K(x, \chi) (\varepsilon - \varepsilon^v) \quad \text{with} \quad \varepsilon^v = \varepsilon^p + \beta \xi$$

$$\sigma - \mathcal{H}(x, \chi) \beta \dot{\xi} = \eta_d \beta \dot{\xi} \quad \text{or} \quad \sigma - \mathcal{H}(x, \chi) \beta \xi = \eta_d \beta \xi \exp\left(\frac{E_a}{\mathcal{R}T}\right). \quad (63)$$

Furthermore

$$\dot{\xi} \cong -\frac{\partial U(\chi)}{\partial \chi} + x \frac{\partial A(\chi)}{\partial \chi}, \quad A_x \cong A_{x_0} + A_\chi(\chi) - \kappa x = \eta_x \dot{x} \exp\left(\frac{E_x}{\mathcal{R}T}\right), \quad (64)$$

where the second-order terms of total strain ε and strains of plastic and chemical origin have been neglected in accordance with the hypothesis of infinitesimal strains, i.e. $\varepsilon \ll 1$, $\varepsilon^v \ll 1$, see Eq. (29) and (30). The previous constitutive equations together with the flow and hardening rules (46) and (47) correspond to those of a plastically degrading or plastically damaged ageing viscoelastic material. The elasticity domain C_E is still expressed by Eq. (45), and the plastic multiplier $d\lambda$ and hardening modulus H by Eqs. (59) and (60), respectively. In contrast to damage models found in literature (see for instance [7, 8, 10, 11, 12 and 13]), the plastic variable χ used herein models the plastic hardening/softening behaviour, i.e. the dependence of the elasticity domain C_E upon plastic evolution, as well as the damage behaviour i.e. the loss of elastic rigidity $\partial K(x, \chi)/\partial \chi < 0$, provided that both hardening/softening and damage can actually be associated with permanent irreversible evolutions in the porous material, for instance due to cracking, *cf.* [14]. In this way, two competing physical phenomena determine the instantaneous elastic behaviour of the material, one associated to the ageing reaction and defined by its kinetics, i.e. the second of Eq. (64), the other to plastic evolution undergone by the material throughout the loading history of the chemically hardening material, i.e. hardening rule (47) together with the first of Eq. (64).

7

Concluding remarks

The objective of this paper was to show how a chemical reaction can be integrated in the constitutive modelling at the macro-level of material description. It is worthwhile recalling the sequence of identification: first, starting from the open porous continua and considering the mass conservation for the involved fluid phases, Eq. (2), the intensive thermodynamic force (affinity A_m) is identified, Eq. (10), and linked to the chemical reaction rate through a complementary evolution law, for instance, Eqs. (12) or (13), representing the reaction kinetics. Second, considering the system as closed, Eq. (14), a chemical reaction can be considered as an internal process, and the reaction extent ξ as an internal state variable with a spontaneous evolution not controlled by external flow. For the closed porous continua, the modelling can then be worked out by specifying the expression of free energy ψ of the closed reactive porous medium on account of chemo-mechanical couplings between the observable strain and the reaction extent. In this way, an apparent macroscopic creep and/or ageing phenomenon can be caused by a chemical reaction. The term “reaction” as employed throughout this paper must be understood in a broad sense. It equally applies to a matrix dissolution, adsorption phenomena, etc., see [1]. More generally, when applying an external stress to a sample, a creep process will occur whenever a coupling of the strain with a physical phenomenon is involved, of which the kinetics cannot be considered as instantaneous with respect to the time scale of observation. Due to the chemo-mechanical coupling, an application of stress induces a thermodynamic imbalance, starting the “reaction” at the micro-level of material description, which imposes its kinetics on the apparent macroscopic creep phenomenon: the sample undergoes a time-dependent deformation, restoring thermodynamic equilibrium. If the stress reaches a threshold, permanent evolution may occur. The material undergoes a permanent straining leading to irreversible creep, which is not recovered after a complete unloading, while approaching thermodynamic equilibrium.

For the sake of clarity, shear effects have been set aside, allowing for a formulation of chemo-mechanical couplings with scalar quantities, which can easily be extended to the general case. For instance, Eq. (24) is to be replaced by $\boldsymbol{\varepsilon} = \mathbf{B} \zeta$ where \mathbf{B} is the second-order tensor of chemical dilatation coefficients, relating reaction extent ζ to the viscous strain tensor $\boldsymbol{\varepsilon}^v$ caused by chemomechanical couplings, and $\beta = \mathbf{B} : \mathbf{1}$ for an isotropic viscous behaviour. Furthermore, standard loading functions and hardening models (isotropic, kinematic, etc., see [4, 5, 9, and 11], can be used within the theoretical framework developed in this paper, when replacing scalar quantities (σ , ζ) and (ε^p , χ) by their tensorial counterparts ($\boldsymbol{\sigma}$, ζ) and ($\boldsymbol{\varepsilon}^p$, ζ), from which they derive.

Finally, the application of the presented modelling to the particular case of engineering geomaterials starts by identifying the microscopic physical origin which *lends* its kinetics to the apparent macroscopic creep phenomenon, the kinetics being the linkage between microscopic and macroscopic scale of material description.

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