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A poroplastic model for hygro-chemo-mechanical damage of concrete

M. Cuomo & A. Nicolosi

Department of Civil and Environmental Engineering, University of Catania, Catania, Italy

ABSTRACT: The paper proposes an analytical model for calcium leaching of concrete due to water. The model is set in the framework of chemically active saturated porous media. Continuum damage mechanics is used in order to develop a phenomenological poroplastic model of concrete. Two forms of damaging processes are included: mechanical, modelled with two scalar damage internal variables; chemical, related to the decreasing calcium concentration in the matrix. Main ingredients of the model are: a damage-poroplastic mechanical model for concrete; a fluid motion mechanism with an explicit dependence of the permeability on the porosity and the damage variables; a diffusive-convective mechanism for ion transportation, governed by a diffusion coefficient function of porosity and of calcium concentration. The evolution of the state of the material is given by a set of internal variables including, in addition to mechanical and damage variables, porosity and calcium concentration in the solid skeleton. For them, evolution laws are provided by the relevant "elastic" mechanisms, governed by the internal energy, and dissipation mechanisms.

1 INTRODUCTION

1.1 Motivations

Greater and greater concern is being devoted by codes and building rules to the assessment of durability and to the prediction of long term response of concrete constructions. The crystalline and porous microstructure exposes concrete to slow degradation phenomena. Leaching of the cement paste is of particular relevance whenever it is expected that the material retains its mechanical and permeability properties for long time, as happens in barriers for contaminant underground storage or for radioactive waste disposal. Furthermore, chemical softening, reducing the stiffness of concrete, can induce loss of efficiency in prestressed structures. Even in less severe cases, it is unpractical and economically costly to neglect completely the contribution of leached parts. For all these reasons it appears appealing to try to characterise calcium leached cementitious materials with respect to mechanical, chemical and transport properties for concrete structures design.

A mass reduction of calcium, which is the main component of the solid phases in the concrete skeleton, entails a reduction of the mechanical properties at a macroscopic level; leaching can therefore be considered a further source of damage, acting together with the mechanical one. Unlike the latter, the chemical damage stems from processes taking place at a very smaller scale than that involved with cracking. Nev-

ertheless, its effects are distinctly measurable at the macroscopic level. The loss of calcium can be due to several chemical interactions. Among them, calcium leaching due to pure or low concentration calcium water is the most dangerous for its consequences. The leaching process is articulated in two phases, involving at first the migration of calcium ions towards the fluid phase (*dissolution*), then a *diffusive* motion of the ions within the material, coupled with the fluid motion, occurs. It is therefore necessary to take into account also the hydraulic processes and their interactions with the other phenomena, characterized by the *permeability* of concrete.

Fluid transport within the pores, ion transport and diffusion, chemical reactions in the cement paste, mechanical response are strongly coupled: deformations modify the internal structure of the pores and interact with the chemical equilibrium, for instance, but not only, for the increase of concrete surface exposed to chemical aggression caused by mechanical cracking; cracking induces also the growth of the permeability. Conversely, leaching produces an increase of the porosity, and therefore an increase of the liquid transportation. Finally, the presence of water into the porous channels modifies the stress state within the material.

1.2 Objectives

The main objective of the work is to provide a constitutive model that accounts for the phenomena involved in calcium leaching, so that the problem can be solved by the main field equations coupled at the constitutive level, through the introduction of proper internal variables. Particularly, the model is developed within the framework of the Generalized Standard Material Model.

Given the different size scales involved, a continuum-like representation of the material is required that takes into account its porous structure. Therefore the theory of active porous media is employed, in the extension to poroplasticity given by Coussy (Coussy 2004), that is here generalized in order to account also for damage. The fracture process is treated phenomenologically within the framework of continuum damage models; the drawbacks of the latter approach are well known, and can be found in the relevant literature, but it allows to use continuum formulations either for the equilibrium and for the transport equations, so that all coupling effects can be brought at the constitutive level.

Thermodynamic models for chemo-mechanical coupling with special reference to calcium leaching have been introduced in the works of Ulm (e.g. (Ulm et al. 2002)), who, however, restricted himself to poroelasticity. In other papers (see (Ulm and Coussy 1995)) he also studied the case of partial fluid saturation of the porous structure. No coupling with the fluid motion and with the mechanical damage was introduced. The latter were added in later works by Ulm (Ulm et al. 1999) and Meschke (Kuhl et al. 2000), who coupled the mechanical and the diffusion problem through the porosity, with the definition of a *chemical plasticity*, representing the pore volume increase due to the matrix loss in calcium mass. Also these models were restricted to poroelasticity and the coupling of ion transport with the fluid motion was not considered.

The model will be limited to small deformations. Since in the problems of interest the temperature does not usually rise above 65°C, isothermal conditions are assumed.

2 MECHANICAL MODEL

2.1 Porosity

The theory of porous media is used, considered as a superposition of several phases with distinct motions, being in mechanical, energetic and chemical interaction. The present work is restricted to the study of *fully saturated* concrete in isothermal conditions, in order to simulate the situation of a structural element completely immersed in groundwater. The porous structure is thus completely filled with water and the material can be regarded as *biphasic*. Therefore the

internal structure is fully defined by the porosity, representing the local average volume ratio occupied by connected voids, referred to the total RVE volume.

$$\phi = \frac{dV^p}{dV_0} \quad (1)$$

In the paper we use a Lagrangian description, so that porosity is referred to the initial volume.

Materials such as concrete are characterized by an initial nonzero porosity, ϕ_0 , due to voids and defects consequent to the strengthening process. Because of the deformation of the solid matrix, the porous structure undergoes reversible and irreversible variations and rearrangements, depending on the intensity of the stress state. In addition, an increase of porosity due to calcium leaching (chemical porosity) has been considered. The following partition then holds

$$\phi - \phi_0 = \phi_m^e + \phi_m^p + \phi_c \quad (2)$$

2.2 Effective stress

Interstitial water is as usual assumed to be an *ideal* fluid, so that it exerts a static pressure on solid grains. Biot's approach is followed, that introduces a coupled set of elastic constitutive relations for a porous medium that, in isothermal conditions, are defined by

$$\begin{cases} \sigma_m = K \varepsilon^v - b p \\ s_{ij} = 2 G e_{ij} \\ \phi - \phi_0 = b \varepsilon^v + \frac{p}{N} \end{cases} \quad (3)$$

where $\sigma_m = \frac{1}{3} \text{tr } \boldsymbol{\sigma}$, $\varepsilon^v = \text{tr } \boldsymbol{\varepsilon}$, and \mathbf{s} and \mathbf{e} are the stress and strain deviators, respectively.

The model is defined by four elastic coefficients: the global bulk modulus K , the global shear modulus G , the Biot's coefficient b , and the Biot modulus N .

A rearrangement of the first of the (3) leads to

$$\sigma_m + b p = K \varepsilon^v \quad (4)$$

The quantity

$$\boldsymbol{\sigma}'' = \boldsymbol{\sigma} + b p \mathbf{I} \quad (5)$$

is called *Biot's effective stress*.

Using the linear constitutive equations for the solid matrix the following expressions for b and N are found:

$$b = 1 - \frac{K}{K_s} \quad \frac{1}{N} = \frac{b - \phi_0}{K_s} \quad (6)$$

where K_s is the intrinsic bulk modulus of the solid matrix.

The constitutive relations (3) can be rewritten in order to relate static variables to kinematic variables:

$$\begin{cases} \sigma_{ij} = C_{ijkl}^u \varepsilon_{kl} - b N (\phi - \phi_0) \delta_{ij} \\ p = -b N \varepsilon^v + N (\phi - \phi_0) \end{cases} \quad (7)$$

$$C_{ijkl}^u = (K + b^2 N) \delta_{ij} \delta_{kl} + 2G (\delta_{ik} \delta_{jl} - \frac{1}{3} \delta_{ij} \delta_{kl}).$$

2.3 Damage model

A phenomenological model based on continuum damage mechanics is used for concrete. Many proposals exist in the literature (see e.g. (Dragon et al. 2000) and the bibliography quoted therein), each one trying to better catch some peculiar aspects of concrete mechanical behavior. A ductile softening response in the compressive range is needed, affected by the confinement ratio, while in tension a brittle response has to be modelled. A coupled plastic-damage model has been shown to be able to reproduce most of these properties. For the purpose of this paper it is sufficient to consider an isotropic damage model (obviously restricted to cases that do not present abrupt rotation of the load direction). Of great importance is the numerical robustness of the model, in order to make possible its application to realistic structural problems. The framework proposed in (Contrafatto and Cuomo 2005) is used here.

The model is defined, in the framework of GSMM, by the specification of two functionals relative to the reversible and irreversible processes taking place in the material; the internal variables are additively decomposed in two components, the first one responsible for the internal energy stored by the body, the second one for the definition of the dissipation. Both the reversible and irreversible phenomena are fully coupled with damage. Two damage variables are introduced related to tensile and compressive stress states; a jump in the elastic stiffness is obtained through a decomposition of the strain space. The elastic domain is defined by three limit functions, accounting for fracture, ductile dissipation and compaction due to high confinement. The model is able, given the elastic limit (defined as the region of no damage), to predict the peak stress and its progressive degradation, as well the evolution of the secant moduli.

The following state variables and their dual mechanical counterparts are introduced:

ε	macroscopic strain	σ	stress
α	hardening	χ	hardening forces
ω_1, ω_2	damage variables	ζ_1, ζ_2	damage forces

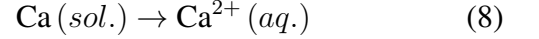
3 CHEMICAL LEACHING

3.1 Macroscopic aspects

In sound material there is equilibrium between the chemical species contained in the cement paste and the substances contained in the fluid phase (ions, water, etc.). When this equilibrium is disturbed, that is the case when the interstitial fluid has a calcium concentration lower than an equilibrium threshold, a flow of calcium ions occurs from the solid to the fluid phase, as a result of the dissolution of the solid constituents, in order to restore the equilibrium. This process has different phases: first the complete dissolu-

tion of portlandite and ettringite, then the progressive failure of the calcium bonds between the C-S-H sheets take place.

In this paper a macroscopic analysis of the chemical dissolution is proposed, so that no distinction is made between the dissolution reactions of the single constituents in the solid matrix, and the leaching process is thus simply modelled with a phenomenological reaction:



The equilibrium condition is expressed in the literature by means of $s - c$ curves, experimentally measured by Gérard ((Gérard et al. 1998), (Gérard 1996)) at different fluid calcium concentrations, after that equilibrium was restored (fig. 1). These curves start from the equilibrium at sound conditions between the average calcium concentration in the solid phase s_0 and the correspondent fluid concentration $c_0 = 20 \text{ mol/m}^3$. The two abrupt steps correspond to the onset of dissolution of portlandite and C-S-H, respectively.

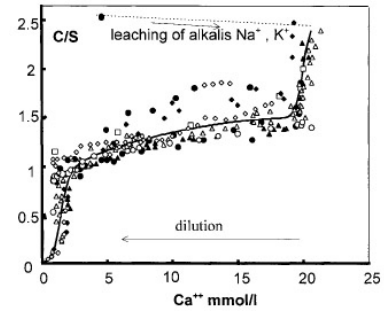


Figure 1: Chemical equilibrium curve

Since calcium leaching is a spontaneous process, from a thermodynamical point of view it has to be related to a decrease of the Gibbs free energy, so that, with reference to reaction (8)

$$\mathcal{A} = \mu_{Ca}(c) - \Gamma(s) \leq 0 \quad (9)$$

where s is the concentration of calcium in the solid phase (per total unit volume) and c is the calcium ion concentration in fluid phase (per fluid unit volume). The chemical potentials may depend on other state variables, as will be seen later.

When (9) is fulfilled as an equality, is the condition that triggers the dissolution. From the theory of mixtures, the chemical potential μ_{Ca} is related to calcium concentration by (see (Nicolosi 2005))

$$\mu_{Ca}(c) = \mu_{Ca}^0 + RT \ln \frac{c}{c_0} \quad (10)$$

3.2 Increase of porosity

The most immediate consequence of the leaching process is the strong increase of porosity.

We define a *chemical porosity* as

$$\phi_c(s) = \frac{\mathcal{M}_{Ca}}{\rho_{s,Ca}} \bar{s} = \frac{\mathcal{M}_{Ca}}{\rho_{s,Ca}} (s_0 - s) \quad (11)$$

being s_0 , s , \bar{s} , the initial, current and eroded solid calcium concentrations, respectively. The quantities \mathcal{M}_{Ca} and $\rho_{s,Ca}$ are the calcium ions molar mass and apparent density (with respect to the solid volume), respectively.

3.3 Decay of the mechanical properties

Experimental data related to the decay of the stiffness due to leaching are reported in the works of Ulm (Ulm et al. 1999) and Meschke (Kuhl et al. 2000) in terms of Young modulus vs. fluid calcium concentration ($E - c$) curves (fig. 2). These plots refer to a purely chemical damage process, with no interaction with mechanical cracking. Recent studies (Ulm (Heukamp et al. 2001)) seem to indicate that a residual stiffness and strength is preserved even with a total decalcified solid skeleton.

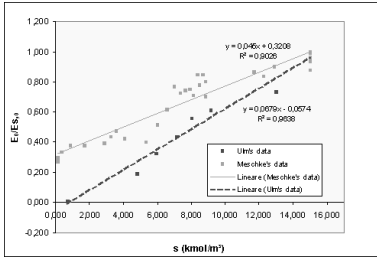


Figure 2: Adimensional Young modulus vs. solid calcium concentration - data obtained by means of the equilibrium curve from Ulm and Meschke

In order to extrapolate a relation between E and s , here used as a state variable measuring the internal chemical damage, the chemical equilibrium curve was used to obtain $E - s$ curves. The $E - s$ experimental data, as it can be seen from figure 2, are well interpolated by linear fitting lines. Consequently, a chemical degradation law for the elastic stiffness is proposed, of the type

$$E(s) = [1 - \phi_c(s)]E_0 = \left[1 - \frac{\mathcal{M}_{Ca}}{\rho_{s,Ca}}(s_0 - s)\right] E_0 \quad (12)$$

In (12), E_0 is the undamaged Young modulus and use of (11) has been made.

4 TRANSPORT PROCESSES

4.1 Hydraulic transport

Fluid motion through the pore channels arises from pressure gradients present in some zone of the porous

body.

A Darcy-like law links the *filtration vector* to the pressure gradient:

$$\mathcal{V} = -\mathbf{D}_w \cdot \text{grad } p \quad (13)$$

The *relative fluid volume flow vector* or *filtration vector* $\mathcal{V} = \phi(\mathbf{V}^w - \mathbf{V}^s)$ represents the elementary fluid volume flow through the area element dA during the time dt . The *fluid mass flow vector* \mathbf{w} relative to the solid velocity \mathbf{V}^s is defined as

$$\mathbf{w} = \rho_w \phi(\mathbf{V}^w - \mathbf{V}^s) \quad (14)$$

The *permeability tensor* \mathbf{D}_w is assumed in the form:

$$\mathbf{D}_w = \frac{\mathbf{k}}{\mu_w} \left[\frac{m^4}{N s} \equiv \frac{m^3 s}{kg} \right] \quad (15)$$

In (15), μ_w is the water dynamic viscosity, linking in a non ideal fluid the shear stress to the shear strain rate. The following form is adopted for the *intrinsic permeability tensor* \mathbf{k} :

$$\mathbf{k} = \mathbf{k}_0 k_\phi(\phi - \phi_0) + \mathbf{k}_d(\omega^e) \quad [m^2] \quad (16)$$

where \mathbf{k}_0 is the intrinsic permeability of the virgin material; in the present work we reasonably consider the material as originally isotropic, so that it is assumed $\mathbf{k}_0 = k_0 \mathbf{I}$.

Equation (16) shows that the permeability depends on the porosity variation and on the crack distribution within the material. Darcy's law is thus no more a linear law, since a strong dependence on the internal porosity variables and on the damage variable ω^e is introduced.

Nyame and Illston (Nyame and Illston 1981) proposed the expression

$$k_\phi(\phi - \phi_0) = 10^m \quad m = \frac{6(\phi - \phi_0)}{0.3 - 0.4\phi_0} \quad (17)$$

for the adimensional corrective factor of the intrinsic permeability accounting for the variation of porosity. Since ϕ is the total porosity, a strong coupling of permeability with mechanical and chemical phenomena arises.

For the cracking dependence of permeability it is followed the proposal of Meschke (Grasberger and Meschke 2000), who assimilated the flow through a crack to a Poiseuille flow between two planar faces at distance w (the crack opening), empirically corrected to take into account the roughness of the real crack surfaces and the consequent turbulent water flow:

$$\mathbf{w} = -\frac{w_h^2}{12\nu_w} \text{grad } p \quad \left[\frac{kg}{m^2 s} \right] \quad w_h = \frac{w^2}{\bar{R}^{2.5}} \quad (18)$$

where \bar{R} is a roughness parameter.

The intrinsic *isotropic* permeability tensor is then obtained as

$$\mathbf{k}_d = \begin{bmatrix} \frac{w_h^3}{12l_c} & 0 \\ 0 & \frac{w_h^3}{12l_c} \end{bmatrix} = \frac{w_h^3}{12l_c} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = k_d \mathbf{I} \quad [m^2] \quad (19)$$

where the total flow (18) has been corrected as

$$\bar{\mathbf{w}} = \mathbf{w} \frac{w_h}{l_c}$$

since within the context of a continuum-like approach, the crack is assumed as smeared over a "damage process zone" wide l_c , as a result of homogenization procedures.

The crack width w is related to the damage variable ω^e ; with reference to an uniaxial tensile test over a bar, in the context of continuum-like models, the average localized strain in the cracked zone is given by

$$w(\omega^e) = \bar{\varepsilon}^d l_c = (\varepsilon - \varepsilon^p - \varepsilon_{rel}^e) l_c \quad (20)$$

where the elastic release strain (related to the uncracked parts of the bar) and the permanent strain have been subtracted from the total average strain. The localized strain is again referred to the length of the "damage process zone" l_c .

4.2 Calcium ions transport

As a consequence of the leaching process, a diffusive and a convective flow of calcium ions occurs through the fluid phase: the diffusive process is activated by concentration gradients within the fluid. Furthermore, since interstitial water is in motion through the pores, the calcium ions are also subjected to this convective transportation mechanism.

Like permeability, the *diffusivity* (i.e. the ion conductivity) is strongly influenced by variations in porosity and, in addition, by the fluid calcium ion concentration itself.

The driving force of the *diffusion process* is the gradient of the fluid calcium chemical potential μ_{Ca} (J mol^{-1}), so that the *relative calcium diffusion velocity* is given by

$$\bar{\mathbf{V}}_{Ca}^{diff} = -D \text{grad } \mu_{Ca} \quad \left[\frac{m}{s} \right] \quad (21)$$

The quantity D ($\text{m mol N}^{-1} \text{s}^{-1} \equiv \text{mol s kg}^{-1}$) is called *molar conductivity*. By means of expression (10), and considering that calcium ion density w.r.t. the fluid volume is related to the concentration by the relation $\rho_{w,Ca} = \mathcal{M}_{Ca} c$, the ion mass flow is given by

$$\mathbf{w}_{Ca}^{diff} = -\mathcal{M}_{Ca} \phi D RT \text{grad } c \quad (22)$$

where \mathcal{M}_{Ca} is the molar mass of calcium ions.

Equation (22) introduces a linear dependence of calcium flow on porosity; this choice is made among others for the sake of simplicity.

According to experimental evidences, the higher the fluid calcium concentration, the lower is the molar conductivity. This is due to the increasing mutual interference between the ions, with a consequent reduction of the global flow. In order to model this phenomenon, an explicit dependence of D on the calcium concentration c is introduced:

$$D(c) = D_0 - D_c \sqrt{c} \quad (23)$$

according to the approach followed in (Kuhl et al. 2004).

The convective term is immediately obtained by thinking the ions as attached to the water particles, and thus subjected to their velocity field (recall eqn. (13)):

$$\mathbf{w}_{Ca}^{conv} = \rho_{w,Ca} \mathbf{V} = -\mathcal{M}_{Ca} c \mathbf{D}_w \cdot \text{grad } p \quad (24)$$

The total ion mass flow is finally obtained as a summation of (22) and (24):

$$\mathbf{w}_{Ca} = \mathbf{w}_{Ca}^{diff} + \mathbf{w}_{Ca}^{conv} \quad (25)$$

5 CHEMO-MECHANICAL MODEL

5.1 Review of the balance equations

The boundary problem for a damaging poroplastic body subjected to calcium leaching is ruled by the set of linear momentum, fluid mass, calcium ion mass and energy balance equations. It can be proved that, in isothermal conditions, the energy balance equation is automatically fulfilled (see (Nicolosi 2005)).

The general form of the mass balance equation, for small transformations, is:

$$\dot{m}_i + \text{div } \mathbf{w}_i = \dot{m}_i^{\rightarrow} \quad (26)$$

where the term \dot{m}_i^{\rightarrow} at the right-hand side represents the source mass term of the i -th component.

For the problem at hand we have the set

$$\begin{aligned} \overline{\rho_s(1-\phi)} + \text{div } \mathbf{w}_s &= -\mathcal{M}_{Ca} \dot{\bar{s}} \\ \overline{\rho_w \phi} + \text{div } \mathbf{w} &= 0 \\ \overline{\rho_{w,Ca} \phi} + \text{div } \mathbf{w}_{Ca} &= \mathcal{M}_{Ca} \dot{\bar{s}} \end{aligned} \quad (27)$$

In (27) we have indicated with \mathbf{w}_s the mass flow vector relative to the solid phase, i.e. $\mathbf{w}_s = \rho_s(1-\phi)(\mathbf{V}^g - \mathbf{V}^s)$, being \mathbf{V}^g the velocity of the solid grains.

The first expression of (27) can be dropped from the problem since, considering a pure leaching process, one has

$$-\rho_s \dot{\phi} = -\mathcal{M}_{Ca} \dot{\bar{s}} \quad \Rightarrow \quad \dot{\phi}_c = \frac{\mathcal{M}_{Ca} \dot{\bar{s}}}{\rho_s} \quad (28)$$

so that the definition of chemical porosity is recovered.

Thus, within the context of this restriction, the boundary problem is completely ruled by the reduced set of equations:

$$\begin{cases} \operatorname{div} \boldsymbol{\sigma} + \rho \mathbf{f} = \mathbf{0} \\ \dot{m}_w + \operatorname{div} \mathbf{w} = 0 \\ \dot{m}_{Ca} + \operatorname{div} \mathbf{w}_{Ca} = \mathcal{M}_{Ca} \dot{s} \end{cases} \quad (29)$$

System (29) is a set of five equations to be solved for five field variables. Following a mixed irreducible formulation, the primary field variables are:

$$\begin{aligned} \mathbf{u}^s & \text{ displacement field} \\ p & \text{ pressure field} \\ c & \text{ fluid Ca}^{2+} \text{ ion concentration} \end{aligned}$$

A numerical procedure can be obtained from a weak formulation of (29). A solution can be sought once the constitutive equations are added. In the remaining of the chapter, the constitutive model will be formulated in terms of internal variables.

5.2 State variables

The state variables, within the context of small transformations, additively split in a reversible and an irreversible component; together with their dual mechanical counterparts they are:

$$\begin{aligned} \boldsymbol{\varepsilon} &= \boldsymbol{\varepsilon}^e + \boldsymbol{\varepsilon}^p & \boldsymbol{\sigma} \\ \phi_m - \phi_0 &= \phi_m^e + \phi_m^p & p \\ \alpha &= \alpha^e + \alpha^p = 0 & \chi \\ \omega_i &= \omega_i^e + \omega_i^p = 0 & \zeta_i \\ s &= s^e + s^p = s_0 & \Gamma \end{aligned} \quad (30)$$

The total values of α and ω_i are zero, since they do not contribute to internal energy in a closed system, while the total value of the solid calcium concentration is the sound material calcium content s_0 , split into the current calcium content s^e and the eroded calcium content s^p . For porosity decomposition, use of (2) has been made. We will attempt to set the whole constitutive model within the framework of GSMM. Thus, for each component, the *elastic constitutive relations* will be obtained by differentiating the free energy functional with respect to the state variables. The irreversible processes are described introducing a dissipation functional in the space of the generalized state variables; this approach is equivalent to the introduction of suitable limit surfaces in the space of the generalized static variables, from which the *plastic flow rules* are derived for the evolution of the internal variables of the model.

5.3 Reversible processes: free energy functional

The free energy functional of the medium is given by a function of the kinematic variables:

$$\begin{aligned} \psi &= m_w \psi_w \left(\frac{1}{\rho_w} \right) + m_{Ca} \psi_{Ca}(c) + \\ &+ \bar{\psi}_s(\boldsymbol{\varepsilon}^e, \phi_m^e, \alpha^e, \omega^e, s^e) \end{aligned} \quad (31)$$

where the single contributions related to the solid and fluid phases and to the ions have been explicitly indicated.

The fluid is assumed to be *incompressible*, i.e.

$$\frac{1}{\rho_w} = \text{const} \quad (32)$$

The free energy functional of the solid phase, depending on the elastic components of the state variables, is chosen in the form

$$\begin{aligned} \bar{\psi}_s &= \frac{1}{2} \boldsymbol{\varepsilon}^e : \mathbf{C}^u(\omega^e, s^e) : \boldsymbol{\varepsilon}^e + \frac{1}{2} N(\omega^e, s^e) \phi_m^e{}^2 + \\ &- b(\omega^e, s^e) N(\omega^e, s^e) \varepsilon_v^e \phi_m^e + \frac{1}{2} H(\omega^e, s^e) \alpha^e{}^2 + \\ &+ \int_{s_0}^s \bar{\Gamma}(s^e) ds^e + \Gamma_0 s^e \end{aligned} \quad (33)$$

where $\bar{\Gamma}(s^e)$ is the solid calcium chemical potential in conditions of purely chemical interaction between solid and fluid phases, when no interactions with the mechanical and hydraulic phenomena are considered. Its expression can be immediately obtained from the equilibrium condition:

$$\bar{\Gamma}(s^e) = \mu_{Ca}(c(s^e)) \Rightarrow \bar{\Gamma}(s^e) = \mu_{Ca}^0 + RT \ln \frac{c(s^e)}{c_0} \quad (34)$$

where use of the inverse of the equilibrium curve has been made.

The elastic coefficients are affected by chemical and mechanical damage. A multiplicative dependence on mechanical and chemical damage is assumed for the global bulk modulus K only. This assumption is based on the hypothesis that the global stiffness is damaged because of the erosion of the solid matrix, but the latter preserves its intrinsic elastic properties.

As a consequence, it is assumed

$$K(\omega^e, s^e) = (1 + \omega^e)^n [1 - \phi_c(s^e)] K_0 \quad (35a)$$

$$G(\omega^e, s^e) = (1 + \omega^e)^n [1 - \phi_c(s^e)] G_0 \quad (35b)$$

$$K_s = \text{const} \quad (35c)$$

Again, equation (6) provides the consequent expressions for b and N :

$$b(\omega^e, s^e) = 1 - \frac{K_0}{K_s} (1 + \omega^e)^n [1 - \phi_c(s^e)] \quad (36a)$$

$$N(\omega^e, s^e) = \frac{K_s^2}{K_s - K_0 (1 + \omega^e)^n [1 - \phi_c(s^e)] - \phi_0 K_s} \quad (36b)$$

The hardening function has been chosen to depend on ω^e and s^e similarly to the elastic constants:

$$H(\omega^e, s^e) = (1 + \omega^e)^n (1 - \phi_c(s^e)) H_0$$

From equation (33), the elastic constitutive equations are immediately obtained. Stress and pressure are given by (7), and

$$\begin{aligned} \zeta &= \frac{\partial \bar{\psi}_s}{\partial \omega^e} = \frac{1}{2} \boldsymbol{\varepsilon}^e : \frac{\partial \mathbf{C}^u}{\partial \omega^e} : \boldsymbol{\varepsilon}^e + \frac{1}{2} \frac{\partial N}{\partial \omega^e} \phi_m^e{}^2 + \\ &\quad - \frac{\partial(bN)}{\partial \omega^e} \varepsilon_v^e \phi_m^e + \frac{1}{2} \frac{\partial H}{\partial \omega^e} \alpha^{e2} \\ \Gamma &= \frac{\partial \bar{\psi}_s}{\partial s^e} = \Gamma_0 + \frac{1}{2} \boldsymbol{\varepsilon}^e : \frac{\partial \mathbf{C}^u}{\partial s^e} : \boldsymbol{\varepsilon}^e + \frac{1}{2} \frac{\partial N}{\partial s^e} \phi_m^e{}^2 + \\ &\quad - \frac{\partial(bN)}{\partial s^e} \varepsilon_v^e \phi_m^e + \frac{1}{2} \frac{\partial H}{\partial s^e} \alpha^{e2} + \bar{\Gamma}(s^e) \end{aligned} \quad (37)$$

where Γ_0 is the chemical potential of the sound concrete ($s^e = s_0$). Due to the energetic approach, equations (37) exhibit cross-effects between mechanical and chemical phenomena, as a consequence of the Maxwell symmetries of the energy functional (33). In particular, it can be noted that strains and porosity coupling terms arise in the definition of the chemical potential Γ due to the dependence of the elastic constants on chemical damage.

5.4 Irreversible processes: dissipation functional

In (Nicolosi 2005) the expression of the dissipation functional for isothermal conditions has been derived:

$$\Phi = \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \text{div}(g_w \mathbf{w} + g_{Ca} \mathbf{w}_{Ca}) + \mathbf{f} \cdot \mathbf{w} - \dot{\psi} \quad (38)$$

where g_i represents the Gibbs free energy of the i -th component.

After suitable transformations, equation (38) turns into

$$\Phi = \Phi_m + \Phi_c + \Phi_w + \Phi_{Ca} \quad (39)$$

where:

- $\Phi_m = \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}}^p + p \dot{\phi}_m^p + \chi \dot{\alpha}^p + \zeta \dot{\omega}^p \geq 0$ is the *mechanical dissipation*, related to the solid skeleton
- $\Phi_c = \left(\Gamma + \frac{\mathcal{M}_{Ca}}{\rho_{s,Ca}} p - \mu_{Ca} \right) \dot{s}^p \geq 0$ is the *chemical dissipation*, related to the leaching process. The quantity $\mathcal{A} = \Gamma + \frac{\mathcal{M}_{Ca}}{\rho_{s,Ca}} p - \mu_{Ca}$ is again called *chemical affinity*
- $\Phi_w = \left(-\frac{1}{\rho_w} \text{grad } p + \mathbf{f} \right) \cdot \mathbf{w} \geq 0$ is the *fluid dissipation*, related to the fluid motion
- $\Phi_{Ca} = (-\text{grad } g_{Ca} + \mathbf{f}) \cdot \mathbf{w}_{Ca} \geq 0$ is the *diffusive dissipation*, related to the diffusion of the ions within the medium

Note that each of these contributions to the dissipation is assumed to be separately non negative.

To describe the *mechanical dissipation* term, a plastic domain is introduced in the space $(\boldsymbol{\sigma}, p, \chi, \zeta)$. An equivalent procedure consists in defining the domain into a $(\boldsymbol{\sigma}', \chi, \zeta)$ space, being $\boldsymbol{\sigma}' = \boldsymbol{\sigma} + b^p p \mathbf{I}$ a *plastic effective stress*. The *plastic Biot's coefficient* b^p has been introduced, according to (Meschke and Grasberger 2003), (Grasberger and Meschke 2000), (Coussy 2004), that can be shown to range between ϕ_0 and 1. We thus introduce the mechanical admissible domain

$$g_m(\boldsymbol{\sigma}', \chi, \zeta) = \bar{g}_m(\boldsymbol{\sigma}, p, \chi, \zeta) \leq 0 \quad (40)$$

so that the associated flow rules are formally obtained in the extended form

$$\begin{aligned} \dot{\boldsymbol{\varepsilon}}^p &= \dot{\lambda} \frac{\partial \bar{g}_m}{\partial \boldsymbol{\sigma}} & \dot{\phi}_m^p &= \dot{\lambda} \frac{\partial \bar{g}_m}{\partial p} \\ \dot{\alpha}^p &= \dot{\lambda} \frac{\partial \bar{g}_m}{\partial \chi} & \dot{\omega}^p &= \dot{\lambda} \frac{\partial \bar{g}_m}{\partial \zeta} \end{aligned} \quad (41)$$

In (Nicolosi 2005) it has been shown that convex domains in the $(\boldsymbol{\sigma}', \chi, \zeta)$ space correspond to convex domains in the $(\boldsymbol{\sigma}, p, \chi, \zeta)$, so that it is possible to describe the mechanical dissipation of a porous medium by simply re-defining the classical yield domains commonly used in the theory of plasticity in terms of plastic effective stresses.

The *chemical dissipation* is described by means of a viscoplastic flow rule, since the leaching process is a slow time-dependent phenomenon. The *admissible chemical domain* is defined by the chemical affinity:

$$g_c(p, \Gamma) = \mathcal{A} = \Gamma + \frac{\mathcal{M}_{Ca}}{\rho_{s,Ca}} p - \mu_{Ca} \leq 0 \quad (42)$$

The presence of an explicit pressure-dependent term in the definition of the chemical affinity that stems directly from (39) is fully consistent with the findings

of Ulm (Ulm et al. 2003), who developed a two-scale level model for leached concrete.

The related flow rules for the eroded calcium s^p and for the chemical porosity are formulated by means of Perzyna-like viscoplastic laws:

$$\dot{s}^p = \frac{\beta}{\mu_{Ca}^0} \langle g_c \rangle \frac{\partial g_c}{\partial \Gamma} \quad \dot{\phi}_c = \frac{\beta}{\mu_{Ca}^0} \langle g_c \rangle \frac{\partial g_c}{\partial p} \quad (43)$$

where β is the *viscosity parameter* of the model, linked to the characteristic relaxation time of the leaching process and μ_{Ca}^0 is here used as a threshold value for μ_{Ca} . It can be easily shown that a combination of flow rules (43) leads to an expression of $\dot{\phi}_c$ consistent with the definition (11) of the chemical porosity.

6 APPLICATIONS AND FINAL REMARKS

In this section tests referred to steady-state chemical equilibrium conditions are presented, so that they show the response of the material after the time-dependent leaching process has taken place. Therefore the results have been obtained assuming an inviscid flow rule associated to the chemical admissible domain g_c .

Since the model has been developed within the framework of GSMM, it is possible to set the local problem as a non linear constrained optimization, so that standard numerical methods can be applied. The Multiplier Method has been adopted, that is, the plastic multipliers are kept fixed during the iterations until an optimal value for the static variables has been reached that satisfy admissibility conditions;

then the multipliers are updated as $\lambda_{i+1} = \lambda_i + cg_i$, $c \in \mathbb{R}$. The algorithm is more robust than the classical Lagrange Method, and allows to impose in a simple way the value of the water pressure p that is obtained from the field equations.

6.1 Drained tests

Some simple tests in drained and undrained conditions will be simulated. During a drained test, the interstitial fluid within the specimen is free to flow through the pore channels and, as a consequence, it is also able to reach equilibrium with the external environment, assumed to be at atmospheric pressure, so that $p = 0$.

Four compressive tests in nearly triaxial compression are compared, carried out at imposed deformation such that $\varepsilon_2 = \varepsilon_3 = -\nu \varepsilon_1$, with ν equal to its elastic value. The following mechanical and chemical test conditions have been considered:

- a *poroelastic test*, with an infinite compressive strength f_c and $c \gg c_0$

- a *poroelastic test coupled with leaching*, with an infinite compressive strength f_c and $c < c_0$, so that a pure chemical leaching damage process before the loading test is simulated
- a *poroplastic test* with a finite value of the compressive strength ($f_c = 16.40$ MPa) and $c \gg c_0$
- a *poroplastic test coupled with leaching*, with $f_c = 16.40$ MPa and $c < c_0$

The material data used are listed in table 1.

$E_0 = 29000$ MPa	$\nu = 0.25$
$H_0 = 1000$ MPa	$\phi_0 = 0.20$
$s_0 = 15000$ mol/m ³	$\frac{M_{Ca}}{\rho_{s,Ca}} = 4.484 \cdot 10^{-5}$ m ³ /mol
$\alpha = 0.48$	$k_0 = 1.135$ MPa
$f_c = 16.40$ MPa	$f_t = 2$ MPa
$c_0 = 20$ mol/m ³	$K_s = 40000$ MPa
$a = 30$	$\beta_p = \phi_0$

Table 1: Material data for the chemo-mechanical analyses

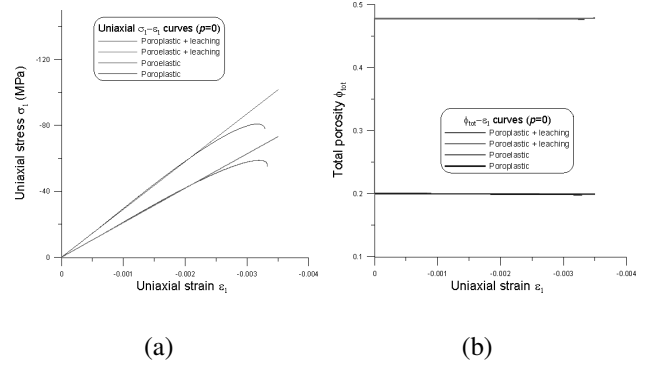


Figure 3: (a) Uniaxial stress vs. uniaxial strain - drained tests; (b) Total porosity vs. uniaxial strain - drained tests

From the results of figure 3(a), it is evident the reduction of Young modulus for the leached samples, but also the reduction of the peak stress, equal to about 20%. The latter aspect is a remarkable result, since it is not the consequence of a direct position, but it is due to the fully coupled character of the constitutive model.

The increase of porosity due to chemical leaching is much greater than the mechanical one (fig. 3(b)). This may indicate a small mutual influence between the chemical and the mechanical processes.

It is fundamental to be able to predict the reduction of the stress state due to the progressive erosion of the solid matrix. In order to highlight such an aspect of the chemical leaching, a *chemical softening* test has been simulated. Firstly, a purely uniaxial mechanical load has been applied, until a prefixed stress state was reached. Two tests have been carried out: in

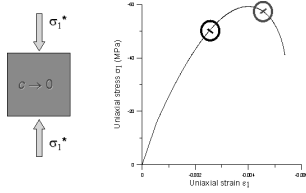


Figure 4: Initial softening test stresses

the first one, the target stress state was a pre-peak one, in the second one, the mechanical loading was carried out until the post-peak zone was reached (see fig. 4). Then, the fluid calcium concentration c has been progressively decreased in order to simulate an aggressive environmental situation. Once again, steady-state conditions are supposed, so it is imagined that after each step increment of c the specimen is allowed to reach its chemical equilibrium with the interstitial solution. The mechanical and chemical parameters are those listed in table 1

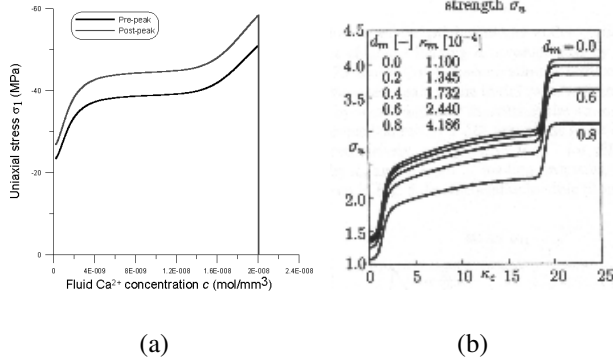


Figure 5: Peak stress vs. fluid calcium concentration: (a) present model; (b) experimental data from Meschke

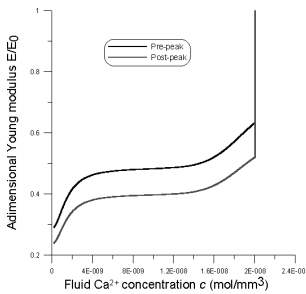


Figure 6: Adimensional Young modulus vs. fluid calcium concentration

Figure 5(a) is a chemical stress relaxation curve. It has to be read from right to left, in the sense that the test starts from the highest calcium concentration (c_0), and then proceeds towards lower concentrations. The stress relaxation response in the pre- and post-peak regime are quite similar, except in the region of C-S-H dissolution. Similar results were obtained by

Meschke (Kuhl et al. 2000) (fig. 5(b)). For the two stress levels used in the test, a damage of about 0.25 and 0.45 was reached.

The reduction of Young modulus (fig. 6) follows a similar trend.

6.2 Undrained tests

In order to study the effect of the internal pressure on the material response, the results of *undrained* tests are now presented. Since water is here assumed to be incompressible and fully saturating the porous structure, the pore volume does not change during the mechanical processes experienced by the material; thus, it will be assumed that $\phi = \phi_0$ during all the applications presented in this section.

The same four tests performed in section 6.1, are here presented in undrained conditions. The material data are those reported in table 1.

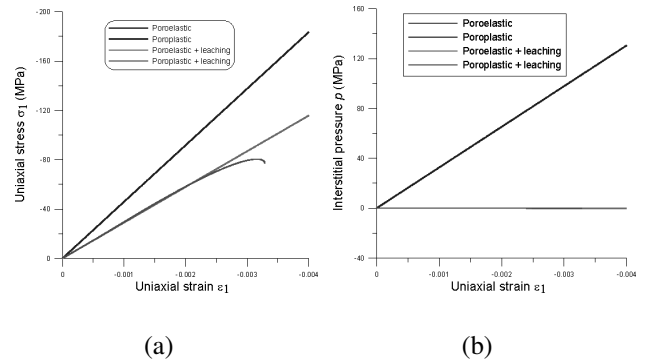


Figure 7: (a) Uniaxial stress vs. uniaxial strain - undrained tests; (b) Interstitial pressure vs. uniaxial strain - undrained tests

Comparing the $\sigma_1 - \epsilon_1$ curves 3(a) and 7(a), it is observed that the unleached elastic and plastic curves in the undrained case are coincident, unlike the drained case. This is a direct consequence of the internal pressure developed within the fluid phase (that is reported in figure 7(b)); because of this pressure, the effective stress experienced by the solid matrix is considerably lower than in the drained case (in this case the effective stress coincides with the total applied stress).

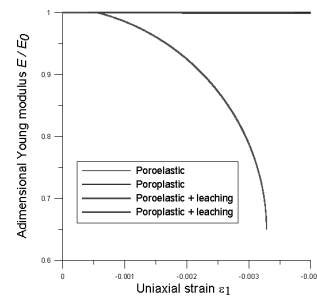


Figure 8: Adimensional Young modulus vs. uniaxial strain - undrained tests

When the full coupled chemo-plastic model is considered, the $\sigma_1 - \varepsilon_1$ curve becomes similar to the one obtained for the drained cases. This is due to the strong increase of porosity consequent to the leaching process, that prevents the build-up of pressure. Figure 8 confirms the faster decay of the Young modulus when both mechanical and chemical damage processes are at work.

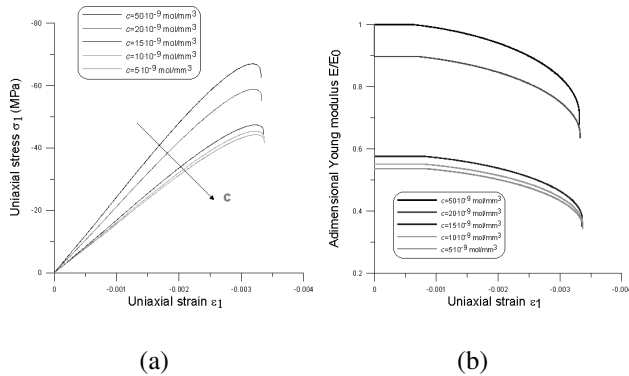


Figure 9: (a) Uniaxial stress vs. uniaxial strain; (b) Dimensional Young modulus vs. uniaxial strain

Finally the reduction of peak stress due to different degrees of calcium leaching for an High Strength Concrete is presented in figure 9(a). The unleached strength of the HSC was about 85 MPa. For the greatest degree of erosion ($c = c_0/4 = 5 \text{ mol/m}^3$) a reduction of 45% of the peak stress is observed. The decay of Young modulus (fig. 9(b)) highlights that damage in the material starts much before that the peak stress is reached. It is significant to stress that the curves of figure 9(b) are not superposable, thus indicating a high degree of nonlinear interaction.

The results presented illustrate the versatility of the proposed model for the long-term durability analysis of concrete. Further applications will be presented in forthcoming works.

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