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### NUMERICAL STUDY OF THE CHEMO-PORO-MECHANICAL BEHAVIOUR OF THE CEMENT SHEATH DURING CO<sub>2</sub> INJECTION

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Abstract. This paper aims at describing the influence of carbonation on the poromechanical behaviour of a wellbore cement. Attention is paid to the estimation of the damage risk of the cement sheath in the context of  $CO_2$  geological storage. A chemoporomechanical model is presented. It accounts for the main chemical reactions occurring within the cement matrix and their consequences in terms of matrix dissolution and carbonates precipitation. These porosity changes are accounted for by introducing a chemical porosity associated to the cement matrix dissolution and the porous volume occupied by carbonate precipitates. The model has been implemented in a finite volume code. An axisymmetrical configuration is considered. Evolutions of transport characteristics and mechanical behaviour during carbonation process are predicted. The damage risk of the cement sheath is finally estimated through the calculation of the elastic energy stored within the solid matrix.

#### 1 INTRODUCTION

A possible solution to mitigate the impact of greenhouse gases emissions into the atmosphere relies on the geosequestration of carbon dioxide. This technology consists in injecting  $CO_2$  into a relatively deep geological formation through an injection well. Selected sequestration sites must ensure the perenity of the storage. To this end, a favourable geological configuration has to include a highly porous reservoir rock covered by a caprock characterised by low permeability and porosity.

The study presented in this paper deals with the chemo-poromechanical couplings occurring in wellbore cements in the context of  $CO_2$  geosequestration. The main objective is to follow the evolution of chemically induced mechanical alterations of the cement and to estimate the damage risk of the cement well. Indeed, the presence of  $CO_2$  within the injection site may affect the poromechanical behaviour of the cement and the rocks. This work concerns exclusively the behaviour of a cement well. The matrix of this latter is composed of several hydrated minerals such as lime hydrates (mainly Portlandite and calcium silicates). In presence of  $CO_2$ , cement will be submitted to dissolution and precipitation reactions, which will heavily affect its stiffness and strength. These chemical reactions can present a serious threat to the perenity of  $CO_2$  geosequestration.

A cylindrical cement well-bore submitted to the injection of  $CO_2$  is considered in this study. This boundary value problem is solved by considering axisymmetric conditions and assuming infinitesimal transformations. At any time, the porous medium is saturated by a single liquid phase.  $CO_2$  injection effects are simulated by the presence of  $CO_2$ -rich brine put in contact with the porous system.

In the first part of the paper, the chemo-poromechanical model is presented before describing its implementation within a finite volume code. Then, the simulated boundary value problem, corresponding to a possible leakage of  $CO_2$  between the caprock and the cement sheath, will be presented and numerically solved. Evolutions of pore overpressure, porosity, permeability and solid matrix modulii during cement carbonation process will be predicted. Finally, the damage risk of the cement sheath will also be estimated through the calculation of the elastic energy stored within the solid matrix.

#### 2 CHEMO-POROMECHANICAL MODEL FOR CEMENT CARBONATION

In all the study, we assume isothermal conditions and infinitesimal transformations. We consider a two-phase porous medium, composed of a solid phase and a fluid phase. Each of these phases is composed of several species. The solid phase, denoted by S, contains not only the solid cement matrix itself composed by several minerals  $M_i$  but also carbonate crystals C. The in-pore fluid phase F is made of water, the solvent, denoted w, and dissolved species denoted  $\alpha$  which partly come from the dissolution of the solid phase and  $CO_2$ . In presence of  $CO_2$  the main chemical alteration to which the cement is submitted corresponds to a carbonation process leading its matrix leaching and to the formation of carbonate crystals. Furthermore, it has been assumed that the carbonate crystals precipitate exclusively as calcite, given the relative stability of this polymorph as compared to other forms.

#### 2.1 Saturated poroelasticity

Mechanical behaviour of saturated porous solids can be efficiently accounted for using a sound thermodynamical framework. Such an approach, as demonstrated by Coussy [1], [2], is relevant because it allows the extension to porous media of the balance equations of continuum mechanics relative to mass, momentum, energy and entropy. Key points of this approach are recalled in the following.

In this work, in-pore fluid solution is assumed to be a mixture composed of several species: the water being the solvent and several solutes such as the species coming from the dissolved matrix, dissolved carbonates and dissolved  $\text{CO}_2$ . Let  $n_i \times \Omega_0$  be the number of moles of the species *i* present in a unit volume of the porous medium  $\Omega_0$ , so that  $n_i$  is the apparent molar density of species *i*. The isothermal Gibbs-Duhem equality assuming chemical equilibrium can be written relatively to the in-pore solution and to the carbonate crystal so that:

$$-\delta_C \frac{\mathrm{d}p_C}{\mathrm{d}t} + n_C^S \frac{\mathrm{d}\mu_C^S}{\mathrm{d}t} = 0 \tag{1}$$

$$-\phi_F \frac{\mathrm{d}p_F}{\mathrm{d}t} + \sum_{i=\alpha,w} n_i^F \frac{\mathrm{d}\mu_i^F}{\mathrm{d}t} = 0$$
<sup>(2)</sup>

where  $p_C$  and  $p_F$  are the pressures of the carbonate crystal and the in-pore fluid respectively and  $\mu_C^S$  and  $\mu_{\alpha}^F$  stand for the molar chemical potentials of calcite and aqueous species  $\alpha$  respectively. In the equation 2, the energy transmitted through the shear stress is assumed to be neglected in front of that transmitted through the normal stress between carbonate crystals and solid matrix.

Let  $\phi_0$  be the initial porosity and  $\Omega_0$  be the initial volume of the infinitesimal representative element of the porous continuum so that the initial porous volume of the medium is  $\phi_0 \times \Omega_0$ . A difference is made between the effective porosity of the porous medium and the porosity of the solid matrix. The former, denoted  $\phi_F$ , corresponds to the porous volume occupied by the in-pore fluid per unit of porous medium. The latter denoted  $\phi$ corresponds to the space per unit of volume of porous medium which is not occupied by the cement phase. The difference between these two porosities is denoted  $\delta_C$ . By definition, the volume  $\delta_C \times \Omega_0$  equals the volume occupied by carbonate crystals. This distinction is relevant to follow precisely the processes of dissolution/precipitations of the cement matrix and the calcite. These porosities are linked through the following relation:

$$\phi = \phi_F + \delta_C \tag{3}$$

When a cementitious material is submitted to the presence of  $CO_2$ , it undergoes several variations on porosities. Some are due to chemical reactions, denoted  $\phi_L$  for leaching of cement matrix and  $\phi_P$  for carbonates precipitation. Others are related to the deformation of the porous medium. Let  $\varphi_F$  and  $\varphi_C$  be the deformation of the porosity filled respectively

by the fluid phase and by the calcite phase. The porosities involved in Eq. (3) can thus be rewritten as follows:

$$\phi_F = \phi_0 + \phi_L - \phi_P + \varphi_F \tag{4}$$

$$\delta_C = \phi_P + \varphi_C \tag{5}$$

Let now  $\boldsymbol{\epsilon}$  be the overall infinitesimal strain tensor of  $\Omega_0$  and  $\boldsymbol{\sigma}$  the overall stress tensor to which the considered system is subjected.  $\Omega_0$  being an open thermodynamic system,  $\Omega_0$  will exchange during its evolution moles of species  $\alpha$  with its surroundings. Finally, let introduce  $\Psi$  the free energy of the system. The first and the second laws of thermodynamics combine to provide the isothermal Clausius-Duhem inequality related to the system in the form (see [1]):

$$\boldsymbol{\sigma}: \dot{\boldsymbol{\epsilon}} - \sum_{i=\alpha,w} \mu_i^F \operatorname{div} \boldsymbol{w}_i^F - \frac{\mathrm{d}\Psi}{\mathrm{d}t} \ge 0$$
(6)

where  $\boldsymbol{w}_i^F$  is the vector of molar transport of the aqueous species *i*. Thus  $-\operatorname{div} \boldsymbol{w}_i^F$  is the rate of moles of aqueous species *i* externally supplied to the infinitesimal porous element  $\Omega_0$  by its contiguous elements. Considering Fick's diffusion law and Darcy's law for the diffusive and advective transport of species *i*, the vector  $\boldsymbol{w}_i^F$  can be expressed as:

$$\boldsymbol{w}_{i}^{F} = -d_{\text{eff}} \operatorname{\mathbf{grad}} C_{i}^{F} - C_{i}^{F} \frac{\kappa}{\eta_{\text{vis}}} \operatorname{\mathbf{grad}} p_{F}$$

$$\tag{7}$$

with  $d_{\text{eff}}$  the effective diffusion coefficient,  $\kappa$  the intrinsic permeability,  $\eta_{\text{vis}}$  the dynamic viscosity of the fluid phase,  $C_i^F$  the molar concentration of the species *i* and  $p_F$  the fluid pressure. From Gibbs-Duhem equalities (1) and (2) and Clausius-Duhem inequality (6), assuming isothermal conditions, the constitutive equations of isotropic linear poroelasticity can be deduced (see [1] for more details):

$$\boldsymbol{\sigma} - \boldsymbol{\sigma}_{\mathbf{0}} = \left(K - \frac{2}{3}G\right)(\varepsilon - \varepsilon_0)\mathbf{1} + 2G\left(\boldsymbol{\epsilon} - \boldsymbol{\epsilon}_{\mathbf{0}}\right) - \sum_{K=F,C} b_K(p_K - p_{K,0})\mathbf{1}$$
(8)

$$\varphi_J - \varphi_{J,0} = b_J \left(\varepsilon - \varepsilon_0\right) + \sum_{K=F,C} \frac{p_K - p_{K,0}}{N_{JK}} \quad ; \quad J = F,C \tag{9}$$

where  $\varepsilon = \operatorname{tr}(\boldsymbol{\epsilon})$  is the volumetric deformation. K and G respectively are the bulk modulus and the shear modulus of the empty porous solid and  $b_J$  and  $N_{JK}$  respectively are the generalised Biot coefficient and the generalised poroelastic coupling moduli.

In order to account for the effects of porosity variations and others parameters of the solid matrix on the mechanical modulii, the three-phase self-consistent micromechanical model under the assumption of local isotropy [5] is used. The effective bulk modulus of the porous medium thus writes:

$$K = \frac{4G_m K_m (1 - \phi)}{4G_m + 3K_m \phi}$$
(10)

where  $K_m$  and  $G_m$  are the bulk and shear modulii of the solid matrix. The effective shear modulus G can be obtained thanks to  $G_m$ , the effective porosity and Poisson's ratio  $\nu$  of the porous medium. Its expression is detailed in [5].

Finally, thanks to the linearity of poroelastic constitutive equations (8), the elastic energy W stored within the solid matrix simply writes in the following form:

$$W = \boldsymbol{\sigma}_{0} : \boldsymbol{\epsilon}_{0} + \frac{\left(\sigma - \sigma_{0} + \sum_{J=F,C} b_{J}(p_{J} - p_{J,0})\right)^{2}}{2K} + \sum_{I,J=F,C} \frac{(p_{I} - p_{I,0})(p_{J} - p_{J,0})}{2N_{IJ}} + \frac{(\boldsymbol{s} - \boldsymbol{s}_{0}) : (\boldsymbol{s} - \boldsymbol{s}_{0})}{4G} \quad (11)$$

where  $\sigma = \frac{1}{3}tr(\sigma)$  denotes the mean stress and  $s = \sigma - \sigma \mathbf{1}$  the deviatoric stress. The calculation of this energy W is relevant when evaluating the risk of damage to the solid matrix.

#### 2.2 Chemical reactions

In this work, we will only consider two hydrates of the cement : Portlandite  $(Ca(OH)_2)$ , noted CH in cement industry, and calcium silicate hydrates, noted C–S–H. Indeed, following [8], predominant mechanisms of the carbonation of cement are those related to these last two hydrates. The chemical mechanism associated to the carbonation of CH is simple whereas the evolution of the C–S–H during carbonation corresponds to a progressive loss of density linked to a decalcification of the structure until the formation of amorphous silica SiO<sub>2</sub>. In order to identify the reactions pathways of carbonation, a reactive transport simulation has been carried out using the reactive transport code TOUGHREACT, a software well suited for modelling multiphase geochemical reactive transport in porous and fractured media (cf [9]). The main chemical reactions which have been identified during these simulations are the following:

$$R_1 \quad \mathrm{CH} + \mathrm{CO}_2 \longrightarrow \mathrm{CaCO}_3 \downarrow + \mathrm{H}_2\mathrm{O} \tag{12}$$

$$R_2 \quad 2,5 \text{ C}-\text{S}-\text{H}_{1.6} + \text{CO}_2 \longrightarrow 2,5 \text{ C}-\text{S}-\text{H}_{1.2} + \text{CaCO}_3 \downarrow + 1,3 \text{ H}_2\text{O}$$
(13)

$$R_3 \quad 2,5 \text{ C}-\text{S}-\text{H}_{1,2} + \text{CO}_2 \longrightarrow 2,5 \text{ C}-\text{S}-\text{H}_{0,8} + \text{CaCO}_3 \downarrow + 1,3 \text{ H}_2\text{O}$$
(14)

$$R_4 \quad 1,25 \text{ C}-\text{S}-\text{H}_{0.8} + \text{CO}_2 \longrightarrow 1,25 \text{ SiO}_{2\,(\text{am})} + \text{CaCO}_3 \downarrow + 1,925 \text{ H}_2\text{O}$$
(15)

The first reaction  $R_1$  corresponds to the carbonation of CH, whereas the others describe the carbonation of C-S-H by successive decalcifications, from C-S-H<sub>1.6</sub> to SiO<sub>2</sub>. The subscripts 1.6, 1.2, and 0.8 reflect the loss of density of the C-S-H and correspond to the C/S density ratio. Based on the simulations performed with TOUGHREACT, we will assume that all the reactions  $R_i$  are instantaneous, complete and successive. In other words, reaction kinetics are neglected. We can write these four reactions in the following synthetic form:

$$\mathbf{a}_{1,\mathrm{R}_{i}}\mathbf{M}_{1,\mathrm{R}_{i}}^{\mathrm{S}} + \mathrm{CO}_{2} \longrightarrow \mathbf{a}_{2,\mathrm{R}_{i}}\mathbf{M}_{2,\mathrm{R}_{i}}^{\mathrm{S}} + \mathbf{a}_{\mathrm{H2O},\mathrm{R}_{i}}\mathbf{H}_{2}\mathrm{O} + \mathrm{CaCO}_{3}\downarrow, \qquad i \in \{1,4\}$$
(16)

where  $a_{j,R_i}$  is the stoechiometric coefficient of the mineral  $M_{j,R_i}^S$  in the reaction  $R_i$ , with j = 1 for a reactant and j = 2 for a product in the same reaction.

Chemical equilibrium conditions between fluid, crystals and cement matrix components are now recalled. The reaction of precipitation of calcium carbonates is assumed to be instantaneous. This assumption can be made because the kinetics of dissolution/precipitation is really faster than diffusive transport of  $CO_2$  in the liquid phase (cf [7]). Doing so, the thermodynamical equilibrium between dissolved species in the fluid and precipitated carbonate crystals is true at any time and in each infinitesimal representative volume. This amounts to say that the chemical potential of carbonate crystals is in equilibrium with the one of dissolved crystal:

$$\mu_C = \mu_{\rm Ca^{2+}} + \mu_{\rm CO_3^{2-}} \tag{17}$$

Finally, during the molar transport of  $CO_2$  and during chemical reactions, each molar quantity of species, denoted  $\frac{dn_i}{dt}$  is not only due to exchanges of matter with surrounding elementary volumes but also to chemical reactions. Assuming that molar transport of solid minerals is not significant, conservation equations can be expressed such as:

$$\frac{\mathrm{d}n_{M_i,C}^S}{\mathrm{d}t} = \mathring{n}_{M_i,C}^S \tag{18}$$

$$\frac{\mathrm{d}n_{\alpha,w}^{F}}{\mathrm{d}t} = -\mathrm{div}\boldsymbol{w}_{\alpha,w}^{F} + \mathring{n}_{\alpha,w}^{F}$$
(19)

with  $\mathring{n}_{M_i,C}^S$  and  $\mathring{n}_{\alpha,w}^F$  the molar variations of solid and dissolved species due to the chemical reactions and  $\boldsymbol{w}_{\alpha,w}^F$  the molar transport given by equation (7).

#### 2.3 Chemo-poromechanical behaviour

To conclude on the coupling between the chemical reactions and the poromechanical behaviour, we express the overall mass conservation of the in-pore fluid:

$$\frac{1}{\rho_F} \frac{\mathrm{d}(\phi_F \rho_F)}{\mathrm{d}t} = \frac{1}{\rho_F} \sum_{i=\alpha,w} \mathcal{M}_i \frac{\mathrm{d}n_i}{\mathrm{d}t}$$
(20)

By introducing the bulk modulus of the in-pore fluid,  $K_F$ , the variation of the density of the fluid in isothermal conditions can be written in the form:

$$\frac{1}{\rho_F}\frac{\mathrm{d}\rho_F}{\mathrm{d}t} = \frac{1}{K_F}\frac{\mathrm{d}p_F}{\mathrm{d}t} + \sum_{i=\alpha,w}\gamma_i^F\frac{\mathrm{d}n_i^F}{\mathrm{d}t} \qquad \text{with} \quad \gamma_i^F = \left[\rho_F\frac{\mathrm{d}(1/\rho_F)}{\mathrm{d}n_i}\right]_{p_F,n_{j,j\neq i}} \tag{21}$$

where  $\gamma_i^F$  is the variation of the density of the fluid which takes into account the effects of chemical reactions on the porous medium behaviour due to the modification of the chemical composition of the in-pore fluid. Moreover, with the assumption of no transmission of shear between calcite and cement matrix (see section 2.1), the mechanical behaviour of the crystal can be written as:

$$\frac{1}{\rho_C} \frac{\mathrm{d}\rho_C}{\mathrm{d}t} = \frac{1}{K_C} \frac{\mathrm{d}p_C}{\mathrm{d}t} \tag{22}$$

where  $K_C$  is the bulk modulus of the carbonate crystal,  $\rho_C$  its density and  $p_c$  its pressure. Thanks to equations (4), (5), (20) and (21) and by assuming a dilute in-pore fluid (that is to say that water is in excess as compared to dissolved species), the conservation of fluid mass can be expressed as follows:

$$\frac{\phi_F}{K_F}\frac{\mathrm{d}p_F}{\mathrm{d}t} + \frac{\mathrm{d}\varphi_F}{\mathrm{d}t} = (\nu_C^S - \nu_{C,dis}^F)\mathring{n}_C^S - \sum_{M_i} ((\nu_{M_i}^S - \nu_{M_i,dis}^F)\mathring{n}_{M_i}^S) + \mathrm{div}\left(\frac{\kappa}{\eta_{\mathrm{vis}}}\mathbf{grad}p_F\right)$$
(23)

According to the assumptions related to reactions kinetics previously introduced, the advancement rate  $\mathring{\xi}_{R_i}$  of each reaction  $R_i$  can directly be estimated from the quantity of CO<sub>2</sub> supplied to the system by diffusion and advection:

$$\mathring{\xi}_{R_i} = \begin{cases} \operatorname{div}\left(d_{\operatorname{eff}}\operatorname{\mathbf{grad}}\left(\frac{n_{CO_2}}{\phi_F}\right) + \left(\frac{n_{CO_2}}{\phi_F}\right)\frac{\kappa}{\eta_{\operatorname{vis}}}\operatorname{\mathbf{grad}}p_F\right) & \text{if } M_{1,R_i} \neq 0 \text{ and } M_{1,R_{i-1}} = 0\\ 0 & \text{otherwise} \end{cases}$$
(24)

Finally, the variation of the molar quantity of  $CO_2$  corresponds to the gas quantity brought by advection and diffusion minus the quantity consumed by chemical reactions:

$$\frac{\mathrm{d}n_{\mathrm{CO}_2}}{\mathrm{d}t} = \mathrm{div}\left(d_{\mathrm{eff}}\,\mathbf{grad}\left(\frac{n_{\mathrm{CO}_2}}{\phi_F}\right) + \left(\frac{n_{\mathrm{CO}_2}}{\phi_F}\right)\frac{\kappa}{\eta_{\mathrm{vis}}}\mathbf{grad}p_F\right) - \sum_{R_i}\mathring{\xi}_{R_i}$$
(25)

Equation (8) submitted to the momentum balance condition and equations (23), (24) and (25) define the chemo-poromechanical model that has to be solved. Its implementation into a finite volume code is described in the following section.

#### **3 COMPUTER CODE**

The chemo-poromechanical model introduced so far is now implemented into a numerical code in order to solve a realistic boundary value problem, corresponding to the modelling of wellbore cement subjected to  $CO_2$  injection under deep reservoir conditions. As a preliminary study, a simplified geometry is considered by assuming axial symmetry and plane strain conditions. In these conditions, the different unknowns only depend on the radial space variable (distance to the well). Assuming also that the material is isotropic, the strain and stress tensors are diagonal. The cement studied here corresponds

$\phi_0$	$\kappa_0$	$\eta_{\rm vis} \ ({\rm m^2/s})$	$K_m$ (MPa)	$G_m$ (MPa)	$K_F$ (MPa)
30%	$1 \cdot 10^{-19}$	$1.79 \cdot 10^{-9}$	17500	10575	2200
$ u_{CH}^S $	$ u^S_{CSH1.6}$	$\nu^S_{CSH1.2}$	$\nu^S_{CSH0.8}$	$\nu^S_{SiO2}$	$ u_C^S$

Table 1: Table	e of parameters	(with molar	volumes in	$cm^3/$	(mol)
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to a class G cement. According to [6], for such cements, the permeability and the diffusivity coefficients depend on porosity changes according to:

$$\kappa = 1, 2 \left(\frac{\phi_F}{0, 26}\right)^{11} \cdot \kappa_0 \quad [m^2] \tag{26}$$

$$d_{\rm eff} = 100 \exp(9.95\phi_F - 29.08) \quad [m^2/s] \tag{27}$$

where  $\kappa_0$  is a material constant. A table of the parameters is presented in the table 1.

In order to solve numerically the problem, we implement the previous equations into a finite volume code. This code has been initially developped by M. Mainguy [7] and extended by A. Fabbri [3] to account for crystallisation phenomena. As seen from carbonation experiments on cement samples (see [4] for instance), a quite sharp separation exists between the carbonated and healthy parts of the samples. Furthermore, this front remains sharp during the carbonation process. As a consequence, it can reasonably be assumed that a sharp carbonation front exists at any time in the sample.

Based on the assumptions made in this study, it appears that the use of the finite volume discretization is pertinent for the numerical resolution since it prevents from the occurrence of numerical instabilities or divergence problems because of this sharp carbonation front.

In the finite volume method, we discretize the modelled domain in a given number of control volumes associated by central nodes and interfaces. We choose to keep a constant radius step between nodes of volumes, and thus between interfaces. The unknowns of the problem, as fluid pressure, advancement rate of reaction,  $CO_2$  concentration and displacements, are localized on the nodes (and thus constant per control volume). To fix the boundary conditions, two half-control volumes are added at the boundaries of the structure. In our program, an implicit Euler scheme is used for the temporal discretization. Then, the resolution of our problem is ensured by the Newton-Raphson method.

The cement is composed of 50% of Portlandite and 50% of C–S–H in volume. With the hypothesis of the sharp carbonation front, we consider that for a given control volume,  $CO_2$  reacts with all the reactants in presence before entering into the next control volume. Finally, given that the water bulk modulus  $K_F$  is sensibly lower than the bulk modulii of the cement matrix K and the carbonate crystal (70 GPa), we neglect the term  $\frac{\mathrm{d}\varphi_F}{\mathrm{d}t}$ in equation (23). To simplify the problem, calcite is assumed to be equilibrated with the fluid ( $p_C = p_F$ ).

#### 4 RESULTS AND DISCUSSION

#### 4.1 Statement of the problem

Before presenting the results of the simulations, we will make explicit initial and boundary conditions used.

We consider a cylindrical sample of cement with an internal radius of 89 mm, an external radius of 108 mm and an unit height. Since we are interested in the simulation of the leakage of gas dissolved in water through the interface between the caprock and the well cement seen as a preferential path, CO<sub>2</sub> will be assumed to reach the cement through its external surface. We consider a uniform fluid pressure of 13 MPa at the beginning, which roughly corresponds to the injection pressure of CO<sub>2</sub> at around 1000m depth. Moreover, the initial state being considered as a reference, null displacement ( $u_r = 0$ ) and deformation ( $\epsilon_r = \epsilon_{\theta} = 0$ ) are supposed in the well. The in situ stress field is uniform and isotropic. The mean total stress is 25 MPa. In addition, the cement is healthy and without any carbonate crystal before the injection of CO<sub>2</sub>. The initial porosity is 30%, a realistic value encountered in class G cements. The in-pore water does not contain dissolved CO<sub>2</sub> at the initial state.

At the beginning of the injection stage (t = 0s), the fluid pressure of 13 MPa is keeped constant on the outside face of the cylinder and, with the arrival of CO<sub>2</sub>-rich fluid, a CO<sub>2</sub> concentration corresponding to the saturated concentration of CO<sub>2</sub> in water is fixed on this surface. On the inside face, because of the presence of the metallic casing, an impermeable boundary is assumed. Finally, concerning the mechanical problem, we choose to apply a radial stress of compression of 25 MPa on the external surface and of 13 MPa on the internal surface of the well, which corresponds to the stress induced by injection pressure.

#### 4.2 Results

The results are now presented. We choose to simulate the injection of  $CO_2$  into a cement sample during 180 days. First, we can follow the evolutions of the chemical reactions as a function of space at several times by looking at the evolutions of the molar quantities of the CH, C-S-H and CaCO<sub>3</sub> in figure 1.

We recall that the incoming of  $CO_2$  is imposed by the external surface of the sample (at  $r = r_{ext} = 108$  mm). As we can see on figure 1(a), after 30 days of exposure, the zone of the sample between r=100mm and r=108 mm does not contain CH and C-S-H. So that, the first 8mm are totally carbonated. The limit between the part containing no CaCO<sub>3</sub> and the one containing only CaCO<sub>3</sub> (apart from SiO<sub>2</sub> coming from C-S-H carbonation) corresponds to the carbonation front. Figure 1(b) shows that all the sample is fully carbonated after 161 days of exposure to CO<sub>2</sub>. After this time, all the CH and C-S-H have been consumed, letting place to the carbonate cristals. As seen previously, these modifications of constitution of the cement matrix involve evolutions of the porosity of the porous media. Figure 2(a) shows how the chemical reactions affect the fluid porosity  $\phi_F$  of the sample during the 180 days of exposure.



Figure 1: Evolutions of molar quantities of the CH, C–S–H and  $CaCO_3$  under  $CO_2$  injection according to the distance from the cylinder axis and the time

When the cement sample is healthy (that is before being carbonated), its porosity is 30%, whereas in the part completely carbonated, its porosity decreases down to 24.4%. This important loss of porosity involves, as seen from equations (26) and (27), a real alteration of transport characteristics of the cement such as a real decrease of the permeability which is divided per 10 and of the diffusivity coefficient of the CO<sub>2</sub> in water which is divided by 2 in alterated zones.

Moreover, as a consequence of the decrease of the fluid porosity when the carbonate cristals are forming, the in-pore fluid pressure increases and can not be immediatly evacuated because of the low permeability. So, from the graph 2(c), we can see a peak of in-pore fluid pressure localized at the carbonation front and which creates a water flow directed towards the external surface of the cement sample. However, even though the fluid porosity decreases with the carbonation, the dissolution of the cement matrix due to its leaching leads to an increase of the effective porosity of the matrix  $\phi$  (see figure 2(b)). The porosity  $\phi$  (that is excluding carbonates) of the cement matrix varies between 30% and 82% in our case. Consequently and according to Eq.(10), the cement matrix stiffness is highly degraded: the bulk modulus is divided by 9 and the shear modulus per 3 in the carbonated zones. This indicates a potential risk for the durability of  $CO_2$ storage. The risk of damage of the cement can be evaluated by the estimation of the matrix elastic free energy stored in the cement matrix. As seen in Figure 2(d), the elastic free energy increases and damage could be expected . But this risk is really increased when the permeability decreases. Indeed, by comparing figures 3(a) and 3(b), the elastic free energy of the matrix reaches almost 600 MPa for  $\kappa = 6 \cdot 10^{-22} \text{ m}^2$  whereas when  $\kappa =$  $6 \cdot 10^{-21}$  m<sup>2</sup>, W does not exceed 3 MPa. Moreover, we can highlight that the carbonation front induces a peak of the stored elastic free energy. The carbonation process could thus create an important risk of damage into the cement matrix.



Figure 2: Evolutions of the porosities, the fluid pressure and the matrix elastic free energy in the cement sample during 180 days of exposure to the  $CO_2$ 

#### 5 CONCLUSIONS

Thanks to the development of a chemo-poromechanical model implemented into a finite volume code adapted to an axisymmetrical problem, we have simulated the behaviour of a cylindrical cement wellbore during the injection of  $CO_2$ . Taking into account the chemical reactions related to the cement carbonation enables to predict the modifications of the transport properties and the mechanical behaviour of the cement. Given that the leaching of the cement matrix and the precipitation of carbonates lead to important variations of the fluid and matrix porosities, permeability, diffusivity and elastic modulii are highly impacted by the carbonation process. Obtained results show a significant risk of damage in the cement that is mainly the result of the important excess pore pressures generated at the carbonation front.

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Figure 3: Evolution of the matrix elastic free energy in the cement sample during 180 days of exposure to the CO<sub>2</sub> when the permeability is equal to  $6 \cdot 10^{-21}$  m<sup>2</sup> and to  $6 \cdot 10^{-22}$  m<sup>2</sup>

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