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Modeling the Poromechanical Behavior of Microporous and Mesoporous Solids: Application to Coal

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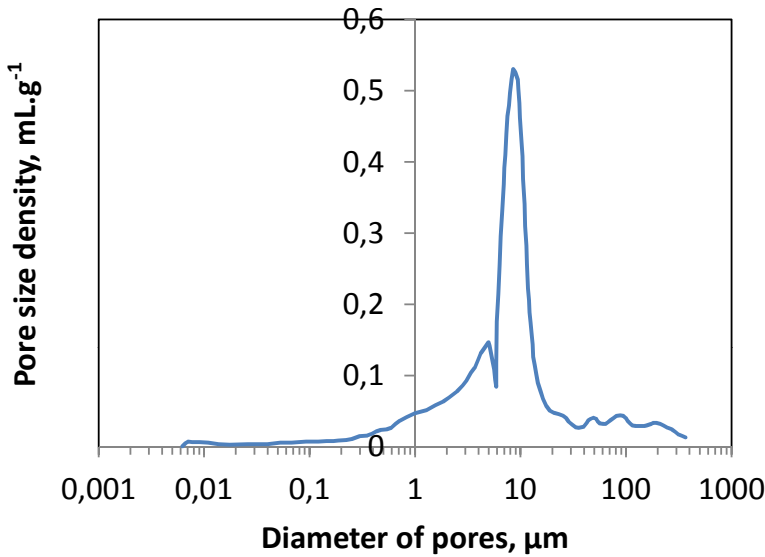


Abbildung 1 Pore size distribution of a loess, measured by mercury intrusion porosimetry (adapted from [1]).

This chapter focuses on poromechanical modeling of porous solids, i.e., of solids for which the mechanical behavior is significantly impacted by the presence of a fluid in its pore network. The size of the pores of such materials can vary on several orders of magnitude, as is observed in Fig. 1 for a loess. Other examples are that of cement pastes, coal, wood, soils, among other natural materials, for which pores can range from a millimeter size down to a sub-nanometer size.

According to their size, pores can be divided into subcategories: macropores (the diameter of which is above 50 nm), mesopores (the diameter of which is comprised between 2 nm and 50 nm), and micropores (the diameter of which is below 2 nm). This subdivision can be explained by the fact that the characteristic range of intermolecular forces is on the order of the nanometer in most cases, except when charged particles are involved (e.g., ions, colloids) [2]. Therefore, in a macroporous medium, almost all molecules of fluid are in a bulk state, i.e., behave as if they were surrounded by an infinite volume of fluid: only a negligible fraction of the molecules of fluid in the macroporous medium are in intermolecular interaction with the atoms of the solid. In contrast, micropores are so small that almost all molecules of fluid interact with the atoms of the solid skeleton, so that those molecules no more behave as if they were in a bulk state. Between those two extremes, one finds the mesopores, in which both a significant fraction of molecules of fluid in a bulk state and a significant fraction of molecules of fluid in intermolecular interaction with the atoms of the solid skeleton are present. Those latter molecules of fluid are located close to the walls of the mesopores, so that in this case we come back to the classical definition of adsorption, which, according to the International Union of Pure and Applied Chemistry,

is a surface phenomenon and, more precisely, ‘an increase in the concentration of a dissolved substance at the interface of a condensed and a liquid phase due to the operation of surface forces’ [3]. By extension, we consider adsorbed molecules to be those that are in intermolecular interactions with the atoms of the solid skeleton. Therefore, we will also refer to molecules of fluid in a microporous medium – which are in intermolecular interaction with the atoms of the solid skeleton – as being ‘adsorbed’, in spite of the fact that in such a case adsorption is not a surface phenomenon, but occurs more by pore filling.

This chapter is dedicated to describe how the mechanical behavior of such macroporous, mesoporous, or microporous media can be modeled in presence of fluids. For each type of medium, we will discuss its specificities and the simplifications that can be made. The modeling will be restricted to the case of porous media saturated with a pure fluid, i.e., to media for which the pore space is occupied by one pure fluid. The modeling here presented should therefore be extended if one aims at studying the behavior of partially saturated media such as, for instance, a chunk of soil upon drying, for which part of the pore space is occupied by air (at atmospheric pressure) and part of the pore space is occupied by liquid water at a pressure lower than the atmospheric pressure because of capillary effects. For those interested in the modeling of the mechanical behavior of partially saturated materials, we refer to the large amount of work available, both on porous solids in general [4] [5], or on specific porous media such as unsaturated soils for instance [6].

As an application, we will consider the case of underground coal seams. Accurately modeling the behavior of such seams is of prime importance for energy production, since those seams naturally contain methane that can be produced. In addition, coal seams are one of the types of reservoirs identified by the International Panel on Climate Change as potential sites for the underground storage of carbon dioxide [7]. Again, performing such a storage at an industrial level would require an accurate modeling of the behavior of the seam. But the pore network of such seams is complex and extends from macroporous cleats down to the micropores of the coal matrix. How to tackle the modeling of such material will be described and we will show how the derived equations can be used for reservoir simulations.

Teil I

Modeling of saturated porous media

Porous media being solids, their mechanical behavior can be well studied and modeled with the help of regular solid mechanics. For nonporous media, the aim of the modeling at the material level is to derive the constitutive equation that links the stresses $\underline{\underline{\sigma}}$ that can be applied to a small homogeneous volume of material with the resulting strains $\underline{\underline{\epsilon}}$ of this small volume. In contrast to nonporous media, porous media can also be injected with one or several fluids. In this chapter, we consider only the case of a porous medium saturated with a pure fluid: in addition to a stress or a strain, a given pressure p of the fluid (or a given molar chemical potential μ) can be applied or the number N_v of moles of fluid (per unit volume of undeformed medium) can be controlled. For such porous media, the aim of the modeling at the material level is to determine the constitutive equations that link stresses $\underline{\underline{\sigma}}$, strains $\underline{\underline{\epsilon}}$, pressure p of the fluid (or molar chemical potential μ), and number N_v of moles of fluid (per unit volume of undeformed medium).

One must note that the stresses $\underline{\underline{\sigma}}$ that can be applied to the medium can be independently controlled from the pressure p of the fluid. In many applications in civil engineering, those two parameters are indeed independent: for a piece of soil in the underground, the pressure of the water in its pores is governed by the height of the water table, while the vertical stress is basically due to the weight of the soil layers above. This is why, in geotechnical applications, the mechanical behavior of a sample must be characterized in function of both the pressure of the pore fluid and the stresses applied to the sample. Those stresses are usually called 'confining' stresses. An apparatus that enables to do so is the triaxial cell (see Fig. 2) which enables to control not only the pressure of the pore fluid, but also both the axial stress and the radial stress applied to the sample. In summary, for a porous medium, stresses and fluid pressure are parameters that are truly independent. A specific case is that of a porous sample immersed in a fluid at a given pressure p . This pressure p is the pressure of the fluid in the pore network of the sample, but also applies a stress on the boundaries of the sample: in such a very specific case, pressure p of the fluid and stresses $\underline{\underline{\sigma}}$ acting on the boundary of the sample are no more independent.

In order to derive the constitutive equations for the various porous media considered, we will use thermodynamics. Quantities defined per unit volume will be referred to with the subscript v . The volume considered for those quantities will be that of the undeformed system: all quantities defined per unit volume in this chapter will be

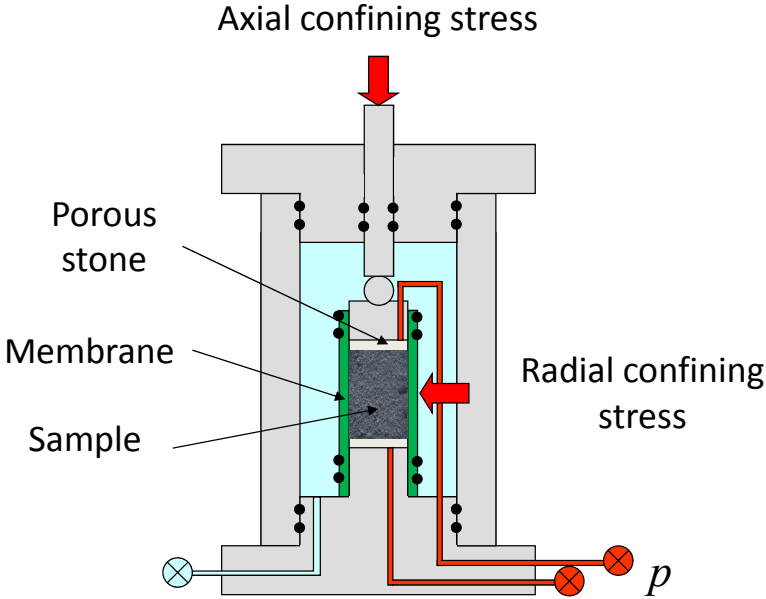


Abbildung 2 Triaxial cell classically used in soil or in rock mechanics (courtesy of D. N. Espinoza).

Lagrangian ones. The thermodynamic system considered is the porous medium of interest. We note F_v its Helmholtz free energy, thus per unit volume of undeformed porous medium. Work can be provided to the sample by straining it with stresses or, since it is an open system, by adding fluid molecules to it. Making use of the first two laws of thermodynamics yields

$$dF_v \leq \underline{\underline{\sigma}} : d\underline{\underline{\epsilon}} + \mu dN_v - S_v dT, \quad (1)$$

where μ is the molar chemical potential of the fluid in the system, N_v is the number of moles of fluid in the system (still per unit volume of undeformed porous medium), S_v is the entropy of the system (again per unit volume of undeformed porous medium), and T is the temperature. Under the assumption of isothermal reversible evolutions, this equation can be rewritten as

$$d\Omega_v = d(F_v - N_v\mu) = \sigma d\epsilon - N_v d\mu + s_{ij} de_{ij} \quad (2)$$

where $\Omega_v = F_v - N_v\mu$ is the grand potential of the system and where the stress tensor $\underline{\underline{\sigma}}$ and the strain tensor $\underline{\underline{\epsilon}}$ have been decomposed into their volumetric and deviatoric part, i.e., $\underline{\underline{\sigma}} = \sigma \underline{\underline{1}} + \underline{\underline{s}}$ and $\underline{\underline{\epsilon}} = \frac{1}{3}\epsilon \underline{\underline{1}} + \underline{\underline{e}}$, $\sigma = \frac{1}{3}\text{tr}(\underline{\underline{\sigma}})$ is the mean confining stress (also called volumetric confining stress) and $\epsilon = \text{tr}(\underline{\underline{\epsilon}})$ is the volumetric strain. $\underline{\underline{s}}$ and $\underline{\underline{e}}$ are the shear stresses and the shear strains, respectively. This energy balance will be at the heart of the subsequent derivations.

0.1

Macroporous media

The first case we consider is that of a medium that contains macropores only. Starting from the energy balance (2), one can use the Gibbs-Duhem relation for the fluid phase, which, under isothermal evolutions reads: $d\mu - V_b dp = 0$, where V_b is the bulk molar volume of the fluid, so that Eq. (2) reads:

$$d\Omega_v = \sigma d\epsilon - N_v V_b dp + s_{ij} de_{ij} \quad (3)$$

In a macroporous medium, the Lagrangian porosity Φ (i.e., the actual volume of the pores divided by the volume of the undeformed system) is well identified and the pore space is filled by a fluid in a bulk state, so that: $\Phi = N_v V_b$. The above energy balance can therefore be rewritten as

$$d\Omega_v = \sigma d\epsilon - \Phi dp + s_{ij} de_{ij} \quad (4)$$

From this energy balance, one concludes that small increments $d\sigma$ of volumetric confining stress, $d\Phi$ of porosity, and ds_{ij} of shear stresses are linked to small increments $d\epsilon$ of volumetric strain, dp of pressure of pore fluid, and de_{ij} of shear strain. In addition, under the assumptions of isotropy of the medium and of uncoupled volumetric and deviatoric behavior, $d\sigma$ and $d\Phi$ do not depend on a small increment de_{ij} of shear strain, while a small increment ds_{ij} only depends on this latter. Therefore, one can write

$$\begin{aligned} d\sigma &= A_1 d\epsilon + A_2 dp \\ d\Phi &= A_3 d\epsilon + A_4 dp \\ ds_{ij} &= A_5 de_{ij} \end{aligned} \quad (5)$$

for which, in addition, the Maxwell relation $\partial^2 \Omega_v / \partial \epsilon \partial p|_{e_{ij}} = \partial^2 \Omega_v / \partial p \partial \epsilon|_{e_{ij}} \Rightarrow \partial \sigma / \partial p|_{\epsilon, e_{ij}} = - \partial \Phi / \partial \epsilon|_{p, e_{ij}}$ imposes $A_2 = -A_3$. In the general case of a nonlinear poroelastic medium, the coefficients A_i depend on the state variables ϵ , p , and e_{ij} . However, in the simplest case of linear poroelasticity, one considers that all those coefficients are constant, so that the above set of equations can readily be integrated:

$$\begin{aligned} \sigma &= K\epsilon - bp \\ \Phi - \Phi_0 &= b\epsilon + p/N \\ s_{ij} &= 2Ge_{ij} \end{aligned} \quad (6)$$

where Φ_0 is the porosity in the undeformed state of reference. This set of equations is the set of classical poroelastic constitutive equations for a linear elastic isotropic

porous medium. The different poroelastic parameters are the bulk modulus K , the shear modulus G , the Biot coefficient b , and the Biot modulus N . The bulk modulus K and the shear modulus G can be identified on a dry medium, while the Biot coefficient b and the Biot modulus N are specific to the presence of the porous network. Micromechanical relations exist, that enable to express those coefficient and modulus in terms of the bulk modulus K_s of the solid skeleton [4]:

$$\begin{aligned} b &= 1 - K/K_s \\ 1/N &= (b - \Phi_0)/K_s \end{aligned} \tag{7}$$

Therefore, for a regular porous medium, the Biot coefficient b must verify $\Phi_0 \leq b \leq 1$, the Biot modulus N must verify $N \geq K_s/(1 - \Phi_0)$, and the bulk modulus K must verify $K \leq (1 - \Phi_0)K_s$.

0.2 Generic (and potentially microporous) media

We now consider a medium with a generic pore size distribution. Potentially, this medium could contain micropores that are so small that their volume is ill-defined, in the sense that trying to measure their volume by filling the micropores with a fluid will lead different values, depending on whether the molecule is small enough in order to penetrate within the micropore or not. The modeling of such a material should therefore restrain to refer to a pore volume. Moreover, the apparent density of adsorbed fluid is likely to differ from that of the bulk fluid. It is therefore no more possible to assert, as was done in the previous section for a macroporous medium, that the fluid occupies the whole porosity: the relationship $\Phi = N_v V_b$ no more holds. Therefore, in the previous derivations, the energy balance (4) no more holds. In contrast, the energy balances (2) and (3) still hold. We therefore start from this equation, which, with the help of Maxwell relations and under the assumptions of isotropy and of uncoupled volumetric and deviatoric behaviors, leads to the following constitutive equations in an incremental form:

$$\begin{aligned} d\sigma &= B_1 d\epsilon + B_2 d\mu \\ dN_v &= -B_2 d\epsilon + B_3 d\mu \\ ds_{ij} &= B_4 de_{ij} \end{aligned} \tag{8}$$

where the amount N_v of fluid in the system can be identified as the adsorption isotherm of the fluid considered on the porous medium of interest. In the general case, for an isotropic medium this adsorption isotherm can depend on both the molar chemical potential μ and the volumetric strain ϵ : $N_v = N_v(\epsilon, \mu)$. Considering that this adsorption isotherm amount $N_v = N_v(\epsilon, \mu)$ is known as a function of both its state

variables, the first of these constitutive equations can be rewritten as:

$$d\sigma = B_1 d\epsilon - \left. \frac{\partial N_v}{\partial \epsilon} \right|_{\mu} d\mu \quad (9)$$

Like in Sec. 0.1, the functions B_1 and B_4 can then be identified as being the tangent bulk modulus $K(\epsilon, \mu)$ and twice the shear modulus G , respectively. Maxwell relations show that the shear modulus G depends neither on the volumetric strain ϵ , nor on the molar chemical potential μ of the fluid and is therefore constant. Note that, if one assumes that the tangent bulk modulus $K(\epsilon, \mu)$ does not depend on the molar chemical potential of the pore fluid, i.e., if one assumes $\partial B_1 / \partial \mu|_{\epsilon} = 0$, the Maxwell relation $\partial B_1 / \partial \mu|_{\epsilon} = \partial B_2 / \partial \epsilon|_{\mu}$ inferred from Eq. (8) imposes that, at constant molar chemical potential, the adsorption isotherm $N_v(\epsilon, \mu)$ must depend linearly on the volumetric strain. In the general case, an integration of the same Maxwell relation enables to express the tangent bulk modulus $K(\epsilon, \mu)$ as:

$$K(\epsilon, \mu) = K_0 - \int_{-\infty}^{\mu} \left. \frac{\partial^2 N_v}{\partial \epsilon^2} \right|_{\tilde{\mu}} d\tilde{\mu} \quad (10)$$

where $K_0(\epsilon)$ is the bulk modulus of the dry medium, i.e, $K_0(\epsilon) = K(\epsilon, \mu \rightarrow \infty)$.

We now assume that, when the molar chemical potential of the pore fluid (and thus its pressure) is kept constant, the porous medium behaves linearly with respect to stresses. Under such an assumption, the set of incremental equations (8) can be integrated in order to yield the constitutive equations of a porous medium with a generic pore size distribution:

$$\sigma = K_0 \epsilon - \int_{-\infty}^{\mu} \left. \frac{\partial N_v}{\partial \epsilon} \right|_{\tilde{\mu}} (\epsilon, \tilde{\mu}) d\tilde{\mu} \quad (11)$$

$$N_v = N_v(\epsilon, \mu)$$

$$s_{ij} = 2G e_{ij}$$

Those equations, can be rewritten as a function of the bulk pressure p of the fluid, which is linked to the molar chemical potential μ of the fluid through the Gibbs-Duhem relationship already mentioned above:

$$\sigma = K_0 \epsilon - \int_0^p \left. \frac{\partial N_v}{\partial \epsilon} \right|_{\tilde{p}} V_b d\tilde{p} = K_0 \epsilon - \int_0^p b(\epsilon, \tilde{p}) d\tilde{p} \quad (12)$$

The pressure p that intervenes in this equation, also obtained by Coudert et al. [8] and Gor and Neimark [9], is the thermodynamic pressure of the fluid, i.e., the pressure of the fluid in a bulk reservoir in thermodynamic equilibrium with the system. In the general case, this pressure differs from the mechanical pressure that the fluid can apply on the walls of the pores. Thermodynamic and mechanical pressures are only equal in macroporous media.

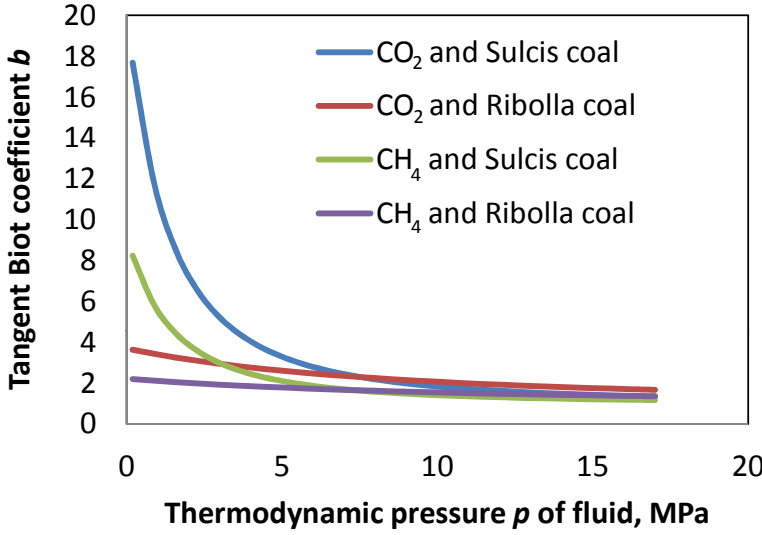


Abbildung 3 Tangent Biot coefficients for two types of coals (Ribolla and Sulcis coals, both from Italy) immersed in methane or in carbon dioxide (adapted from [11]). The calibration was performed on swellings measured upon immersion of coal samples in the fluids of interest [12].

One observes that the constitutive equation (12) can be written in terms of a tangent Biot coefficient $b = -\partial\sigma/\partial p|_{\epsilon} = \partial N_v/\partial\epsilon|_p V_b$. In the general case, this tangent Biot coefficient depends on both the thermodynamic pressure p of the fluid and the volumetric strain ϵ of the medium, i.e., $b = b(\epsilon, p)$. For linear elastic isotropic microporous media however, this coefficient is constant, so that the microporous constitutive equations (6) are recovered. For a generic (and potentially microporous medium), the dependence of the tangent Biot coefficient b on both ϵ and p must be characterized. Indeed, as explained in details in [10] with the help of molecular simulation, for crystalline microporous media this tangent Biot coefficient b can significantly depend on those two state variables. For more disordered media however, i.e., for media with a more spread pore size distribution, it seems that the adsorption isotherm N_v can be well approximated by a first-order expansion in terms of the volumetric strain ϵ of the medium, so that the tangent Biot coefficient depends no more on the strain: $b = b(p)$. With the Maxwell relation $\partial B_1/\partial\mu|_{\epsilon} = \partial B_2/\partial\epsilon|_{\mu}$ already used above, one concludes that the tangent bulk modulus K no more depends on the molar chemical potential μ of the fluid. Under such a simplification, the tangent Biot coefficient b can be calibrated on an experiment in which the swelling of a sample upon an immersion in a fluid would be measured, or in which one would measure the swelling pressure that a sample would exert in an isochoric cell (i.e., a cell which keeps the volume of the sample constant) upon an increase of pressure of the pore fluid.

Such a calibration can be performed on coal. For instance, we display in Fig. 3 the tangent Biot coefficients of Ribolla and Sulcis coal samples in presence of methane

and carbon dioxide. The calibration was performed by using experimental data gathered by Pini [12], who measured the swellings of coal samples upon immersion in the fluids of interest. One observes that this tangent Biot coefficient indeed depends significantly on the pressure of the fluid. Moreover, especially at low pressure, this coefficient can be greater than unity, while this latter value is an upper bound for macroporous media. Physically, a tangent Biot coefficient b greater than unity means that, for a sample kept at constant volume, a small increment Δp of pressure of fluid leads to an increase $b\Delta p$ of confining stress (in absolute value) which can be much greater than the small increment Δp of pressure of fluid. Such an unexpected behavior is a direct consequence of the microporous feature of coal.

0.3

Mesoporous media

We now aim at deriving the constitutive equations that govern the mechanical behavior of a mesoporous medium. In such a medium, the pore volume Φ is well identified, as is the surface area A_{v0} of the pore walls in the state of reference per unit volume of material. In contrast to what is observed for a macroporous medium, in a mesoporous medium energy can be stored at the interfaces, so that the grand potential of the porous medium is the sum of the grand potential of the solid skeleton, of the bulk fluid in the pores, and of the interfaces. In the energy balance (3) derived for a macroporous medium, the grand potential Ω_v was only that of the bulk fluid in the pores and of the solid skeleton, since a negligible amount of fluid could be adsorbed on the pore walls and thus no energy could be stored at interfaces. To avoid any confusion, we will now refer to this grand potential of the macroporous medium as to $\Omega_{v,macro}$. Therefore, in order to adapt the energy balance for macroporous media to the case of a mesoporous medium, to the grand potential $\Omega_{v,macro}$ must be added the grand potential of interfaces, which by definition is γA_{v0} , where γ is the surface energy (also called commonly surface tension), here defined in a Lagrangian manner, i.e., with respect to the surface area A_{v0} in the state of reference. Thus, the grand potential of the mesoporous medium is equal to $\Omega_{v,macro} + \gamma A_{v0}$. Therefore, the energy balance (3) must be adapted as

$$d(\Omega_{v,macro} + \gamma A_{v0}) = \sigma d\epsilon - N_v V_b dp + s_{ij} de_{ij} \quad (13)$$

where $\Omega_{v,macro}$ is the grand potential of the solid skeleton and of the bulk fluid only, i.e., the grand potential of a macroporous medium.

The amount N_v of fluid in the system can be divided into fluid molecules that are in a bulk state and fill the whole pore space at their bulk molar volume V_b and into molecules adsorbed at the surface of the pores. The amount of adsorbed molecules per unit volume is ΓA_{v0} , where Γ is the Lagrangian amount of adsorbed molecules per unit area of the undeformed pore walls. Therefore, the energy balance can be

rewritten as:

$$d(\Omega_{v,macro} + \gamma A_{v0}) = \sigma d\epsilon - (\Phi + \Gamma A_{v0} V_b) dp + s_{ij} de_{ij} \quad (14)$$

so that:

$$d\Omega_{v,macro} = \left(\sigma - A_{v0} \frac{\partial \gamma}{\partial \epsilon} \Big|_p \right) d\epsilon - \left(\Phi + A_{v0} \Gamma V_b + A_{v0} \frac{\partial \gamma}{\partial p} \Big|_\epsilon \right) dp + s_{ij} de_{ij} \quad (15)$$

In the system here considered, energy can be stored at the surface of the pores, in a very similar manner to how energy can be stored in a stretched membrane by elastic deformation. Therefore, like a membrane force, there exists a force which opposes an elastic deformation of the surface of the pores: we call this force the surface stress $\tilde{\sigma}^s$. How such a surface stress $\tilde{\sigma}^s$ can be related to the surface energy γ and to adsorption effects is due to Gibbs [13] and Shuttleworth [14]. The Shuttleworth equation [14] governs how the surface stress $\tilde{\sigma}^s$ evolves with the surface energy γ :

$$\tilde{\sigma}^s = A_{v0} \frac{\partial \gamma}{\partial A_v} \Big|_p \quad (16)$$

where A_v is the surface area of the pore walls per unit volume of undeformed material, while the Gibbs adsorption isotherm [13] governs how the surface energy γ evolves with the amount Γ of fluid adsorbed at the surface of the pores:

$$\Gamma = - \frac{\partial \gamma}{\partial \mu} \Big|_{A_v} = - \frac{1}{V_b} \frac{\partial \gamma}{\partial p} \Big|_{A_v} \quad (17)$$

In both the Shuttleworth equation and the Gibbs adsorption isotherm, the surface energy γ is a function of the surface area A_v and of the pressure p of the fluid. However, for the mesoporous medium considered here, the state variables of interest are the volumetric strain ϵ and the pressure p of the fluid. With respect to this latter set of state variables, the energy balance (15) can be rewritten as follows:

$$d\Omega_{v,macro} = \left(\sigma - \tilde{\sigma}^s \frac{\partial A_v}{\partial \epsilon} \Big|_p \right) d\epsilon - \left(\Phi + \tilde{\sigma}^s \frac{\partial A_v}{\partial p} \Big|_\epsilon \right) dp + s_{ij} de_{ij} \quad (18)$$

in which the partial derivatives of the surface energy γ combine as follows: $\partial \gamma / \partial p|_\epsilon = (\tilde{\sigma}^s / A_{v0}) (\partial A_v / \partial p|_\epsilon) + \partial \gamma / \partial p|_{A_v}$.

In both the energy balance above for mesoporous media and the energy balance (4) for macroporous media, the grand potentials Ω_v or $\Omega_{v,macro}$ are the sum of the grand potential of the solid skeleton with that of the bulk fluid. In those two energy

balances, those grand potentials Ω_v and $\Omega_{v,macro}$ must therefore be identical, and so must be their first derivatives. Consequently, by comparison with the constitutive equations (6) for macroporous media, we can readily obtain the constitutive equations of an isotropic linear elastic mesoporous medium:

$$\begin{aligned} \sigma - \tilde{\sigma}^s \left. \frac{\partial A_v}{\partial \epsilon} \right|_p &= K\epsilon - bp \\ \Phi - \Phi_0 + \tilde{\sigma}^s \left. \frac{\partial A_v}{\partial p} \right|_\epsilon &= b\epsilon + p/N \\ s_{ij} &= 2Ge_{ij} \end{aligned} \tag{19}$$

where the evolutions of the surface stress $\tilde{\sigma}^s$ with adsorption are governed by a combination of the Gibbs adsorption isotherm (17) with the Shuttleworth equation (16). The coefficients $\partial A_v / \partial \epsilon|_p$ and $\partial A_v / \partial p|_\epsilon$ that weigh the effect of the surface stress are material properties with a physical meaning: the former is determined by how the surface area A_v evolves with the volumetric strain ϵ of the medium at fixed pressure p of the fluid, while the latter is determined by how the surface area A_v evolves with the pressure p of the fluid at fixed volumetric strain ϵ of the medium. Those coefficients can be related to microstructural features for specific microstructures [15].

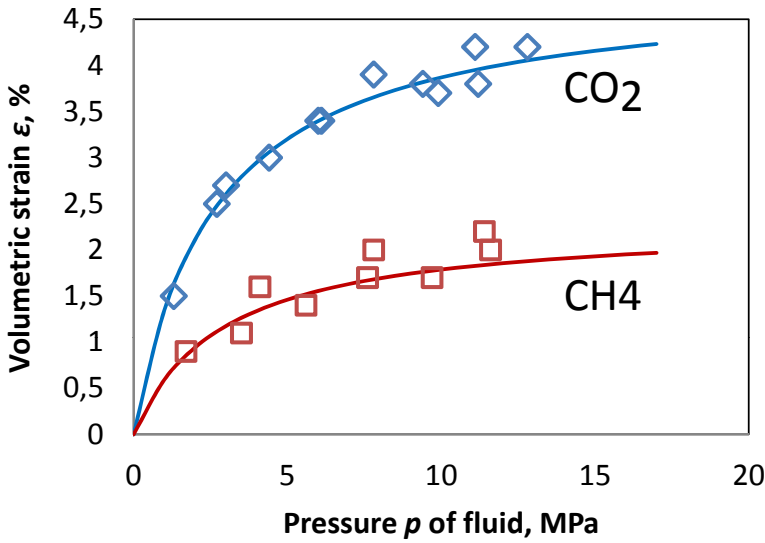


Abbildung 4 Volumetric strain of a coal sample immersed in methane or in carbon dioxide (adapted from [12]).

Teil II

Application to coal seams

This part is dedicated to applying the framework presented in Part I to coal seams. Indeed coal seams are complex natural porous materials with pores the size of which goes down below the nanometer. Because of its microporosity, the coal of which those seams are made exhibits a very peculiar poromechanical behavior. In particular, when immersed in methane or in carbon dioxide, a swelling of the coal sample is observed with an increasing pressure of the pore fluid (see Fig. 4), while poromechanical equations for macroporous media (6) predict that, in the saturated case, the coal sample should shrink upon an increase of the pressure of the fluid. This swelling is a consequence of adsorption in the micropores of the coal.

Being able to accurately model those variations of volume is of prime interest for reservoir engineers. Indeed, coal seams naturally contain methane that can be extracted for energy production. This process is known as Coal Bed Methane (CBM)

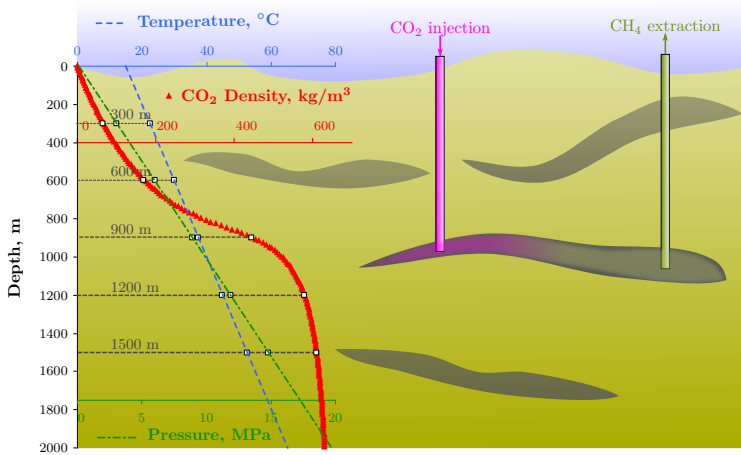


Abbildung 5 CO₂-enhanced Coal Bed Methane recovery process (ECBM).

production. In order to increase the economic viability of the process, one wants to enhance the amount of methane that can be produced in a given period of time. To do so, an injection well can be used, through which carbon dioxide is injected (see Fig. 5 : carbon dioxide occupies the pore space and is being adsorbed in the coal preferentially to methane, so that more methane can eventually be recovered. This process is known as CO₂-Enhanced Coal Bed Methane recovery (CO₂-ECBM). Moreover, given the actual concerns regarding global warming, injecting carbon dioxide into underground formations to have it stored over hundreds or thousands of years might be paid for in the future.

However, large-scale pilot projects of injection of carbon dioxide in coal seams around the world have shown an unexpectedly fast decrease of permeability of the seam close to the injection well, which hinders further injection. The reasons for this decrease of permeability are the following: coal seams are naturally fractured, and their permeability is mostly governed by their set of small natural fractures (called cleats), which are spaced by a few centimeters from each other. Upon injection, the diffusion of carbon dioxide from the cleats to the coal matrix makes the coal matrix swell, which, in the confined conditions that prevail in the underground, leads to a closure of the cleats and thus to a decrease of permeability. In order to estimate the economic viability of CO₂-ECBM projects, accurately modeling the poromechanical behavior of the seam and how adsorption leads to a decrease of permeability is required. In addition, modeling is a first step toward remediation.

The coal seams that are deemed viable for ECBM applications are generally located at depths comprised between 300m and 2000m. The pressures of fluid of interest are therefore in the range of 3MPa up to 20MPa. The confining stresses, which result from the weight of the geological layers above, are of about half a dozen of MPa up to a few dozens of MPa. At depths larger than 2000m, the permeability of the seam is too low because of the high confining stresses resulting from the geological layers

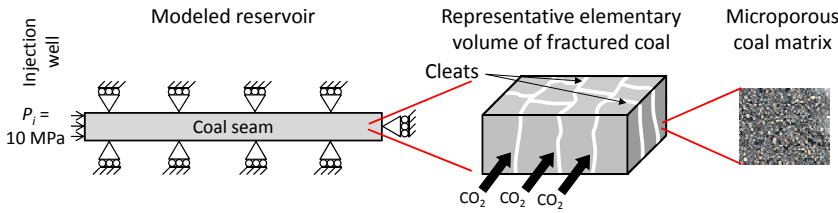


Abbildung 6 Various scales involved in the problem of an injection of carbon dioxide into a coal seam.

above.

The goal of Sec. 0.4 is to model the behavior of a small chunk of fractured coal. The derived constitutive equations will be used in Sec. 0.6 in order to simulate an injection of carbon dioxide into a coal seam. The constitutive equations of the fractured coal will be derived by following the same approach as the one presented in Sec. I for various porous media. We will however take into account that the pore network of fractured coal is made of two very distinct types of pores, i.e., the cleats and the pores of the coal matrix: the derived model will therefore be a dual-porosity one. We will show in Sec. 0.5 that the presence of those two types of porosity can be a source of hysteresis.

0.4

Modeling of a representative elementary volume of a coal seam

A coal seam is considered to be the juxtaposition of a large number of small representative volumes of fractured coal, to which we will refer as to ‘representative elementary volumes’ (see Fig. 6). The aim of the modeling at the material scale is therefore to derive the constitutive equations that govern the behavior of such representative elementary volumes. The simulation of a whole coal seam will be performed by juxtaposing numerically a large number of those representative elementary volumes of fractured coal. To each representative elementary volume is associated one set of state variables, considered to be homogeneous in the volume.

Here we consider a representative elementary volume of fractured coal, representative of a small part extracted from the seam (see the center part of Fig. 6). Given the centimeter spacing between cleats, the characteristic size of a representative elementary volume would be on the order of a dozen of centimeters. In this volume, we consider that the pressure p_c of the fluid in the cleats, the thermodynamic pressure p_m in the coal matrix, the volumetric confining stress σ , and all other state variables are homogeneous. The pore network of fractured coal can be divided into two distinct types of pores: the pores of the coal matrix and the cleat system. Given their size, cleats are considered as macropores, which occupy a well-defined porosity Φ_c . In those cleats, fluid is therefore considered to be in a bulk state. In contrast, no assumption is made on the pore size distribution of the coal matrix: the coal matrix

is considered as a generic porous medium. Therefore, adsorption may take place in the coal matrix, but not in the cleats. The coal matrix and the cleats are permanently exchanging fluid molecules and, accordingly, at thermodynamic equilibrium, the chemical potential of the fluid must be the same in both types of porosity. But the transfer of fluid in the coal matrix takes some time, so that, in practice, fluid molecules in the cleats and in the coal matrix may not be in thermodynamic equilibrium. Therefore, from a modeling point of view, we consider the thermodynamic pressure p_m of the fluid in the coal matrix and the pressure p_c of the fluid in the cleats to be independent state variables.

Our modeling starts from Eq. (2), and by recognizing that the amount N_v of fluid in a small representative elementary volume of fractured coal can be divided into the amount $N_{v,c}$ of fluid in the cleats (at a molar chemical potential μ_c) and the amount $N_{v,m}$ of fluid in the coal matrix (at a molar chemical potential μ_m):

$$d\Omega_v = \sigma d\epsilon - N_{v,c} d\mu_c - N_{v,m} d\mu_m + s_{ij} de_{ij} \quad (20)$$

As stated above, cleats are considered as macropores which occupy a well defined porosity Φ_c filled by bulk fluid (i.e., $\Phi_c = N_{v,c} V_b$), so that the above energy balance can be rewritten as:

$$d(\Omega_v + p_c \Phi_c) = \sigma d\epsilon + s_{ij} de_{ij} + p_c d\Phi_c - N_{v,m} d\mu_m \quad (21)$$

From this equation, again by assuming that the material is isotropic, we end up with the constitutive equations of the fractured coal in an incremental form:

$$\begin{aligned} d\sigma &= C_1 d\epsilon + C_2 d\Phi_c - C_3 d\mu_m \\ dp_c &= -C_2 d\epsilon + C_4 d\Phi_c - C_5 d\mu_m \\ dN_{v,m} &= C_3 d\epsilon - C_5 d\Phi_c + C_6 d\mu_m \\ ds_{ij} &= C_7 de_{ij} \end{aligned} \quad (22)$$

The amount $N_{v,m}$ of fluid in the coal matrix must depend only on state variables at the scale of the coal matrix: those variables can be for instance the volumetric strain ϵ_m of the matrix and the chemical potential μ_m of the fluid in the coal matrix, i.e., $N_{v,m}(\epsilon, \Phi_c, \mu_m) = N_{v,m}(\epsilon_m, \mu_m)$. This volumetric strain ϵ_m is related to state variables at the scale of a representative elementary volume of coal seam through the relation [5]:

$$\epsilon_m = \frac{\epsilon - \Phi_c + \Phi_{c0}}{1 - \Phi_{c0}} \quad (23)$$

so that we readily find out that $C_3 = C_5$.

For coal, which is amorphous, Brochard et al. [10] identified that the amount of methane adsorbed in the coal matrix depends linearly on the volumetric strain of the

matrix. Considering that this first-order expansion remains valid for any fluid, the amount $N_{v,m}$ of fluid adsorbed in the matrix can be expressed as:

$$N_{v,m} = C_3(\mu_m)(\epsilon - (\Phi_c - \Phi_{c0})) + N_{v,m}^0(\mu_m) \quad (24)$$

where $N_{v,m}^0(\mu_m)$ is the adsorbed amount of fluid in the coal matrix when the coal matrix is kept at constant volume. Under the assumption of validity of such a first-order expansion, the coefficient C_3 depends on the molar chemical potential μ of the fluid, so that $\partial C_3 / \partial \epsilon |_{\mu_m, \Phi_c} = 0$. By making use of the Maxwell relation $\partial C_1 / \partial \mu_m |_{\epsilon, \Phi_c} = -\partial C_3 / \partial \epsilon |_{\mu_m, \Phi_c}$ related to the first constitutive equation of the set of equations (22), we infer that the coefficient C_1 is independent of the molar chemical potential μ_m and thus of the thermodynamic pressure p_m of the fluid in the coal matrix. Likewise, one shows that the coefficients C_2 and C_4 do not depend on the molar chemical potential μ_m of the fluid in the coal matrix.

If we assume that the relationships between the state variables (σ, p_c, s_{ij}) and $(\epsilon, \Phi_c, e_{ij})$ are linear, we end up with the following state equations:

$$\begin{aligned} \sigma &= C_1 \epsilon + C_2 (\Phi_c - \Phi_{c0}) - p^a & (25) \\ p_c &= -C_2 \epsilon + C_4 (\Phi_c - \Phi_{c0}) + p^a \\ N_{v,m} &= N_{v,m}(\epsilon_m, \mu_m) \\ s_{ij} &= C_7 e_{ij} \end{aligned}$$

or equivalently:

$$\begin{aligned} \sigma &= K \epsilon - b_c (p_c - p^a) - p^a & (26) \\ \Phi_c - \Phi_{c0} &= b_c \epsilon + (p_c - p^a) / N_c \\ N_{v,m} &= N_{v,m}(\epsilon_m, \mu_m) \\ s_{ij} &= 2G e_{ij} \end{aligned}$$

where the volumetric strain ϵ_m of the coal matrix is given by Eq. (23), and where the adsorption-induced pressure $p^a(\mu_m) = p^a(p_m)$ satisfies:

$$dp^a = \frac{\partial N_{v,m}}{\partial \epsilon} \Big|_{\Phi_c, \mu_m} d\mu_m = (1 - \Phi_{c0}) \frac{\partial N_{v,m}}{\partial \epsilon_m} \Big|_{\mu_m} V_b dp_m \quad (27)$$

This equation leads to the following expression for the adsorption-induced pressure:

$$p^a = \int_0^{p_m} b_m d\tilde{p}_m = \int_0^{p_m} (1 - \Phi_{c0}) \frac{\partial N_{v,m}}{\partial \epsilon_m} \Big|_{\mu_m} V_b d\tilde{p}_m \quad (28)$$

In this expression, the quantity $(1 - \Phi_{c0})N_{v,m}$ is the amount of fluid in the coal matrix per unit volume of undeformed coal matrix.

We now have a set of constitutive equations to model the poromechanical behavior of a representative elementary volume of fractured coal, seen as dual-porosity medium: a set of cleats considered as macropores which occupies a well defined porosity Φ_c , and a microporous coal matrix with an ill-defined porosity and subjected to adsorption phenomena. We can now make use of this set of equations in order to tackle various processes. Before considering the scale of a whole coal seam and simulating an injection of carbon dioxide in the seam (see Sec. 0.6), we will first consider in the following section the scale of a representative elementary volume of fractured coal and bring to light one possible source of hysteresis for this system.

0.5

A source of hysteresis: the kinetics of transfer between cleats and coal matrix

In the set of constitutive equations for a representative volume of fractured coal derived in the previous section, the pressure p_c of the fluid in the cleats is considered to be a state variable that is independent of the thermodynamic pressure p_m of the fluid in the coal matrix. Indeed, but at thermodynamic equilibrium, those two pressures have no reason to be equal to each other. In practice, upon an injection of fluid in the seam for instance, what can be directly controlled is the pressure p_c of the fluid in the cleats. The thermodynamic pressure p_m of the fluid in the coal matrix evolves over time, mainly governed by the transfer of fluid from the cleats to the coal matrix and vice versa.

We can derive a simple model to govern the kinetics of this transfer based on Darcy's law, from which follows that the molar amount transferred from the cleat system to the coal matrix per unit time is directly proportional to the difference of pressures, i.e.:

$$-\frac{\partial N_{v,c}}{\partial t} = \frac{\partial N_{v,m}}{\partial t} = \frac{k_m}{V_b \eta l^2} (p_c - p_m) \quad (29)$$

where k_m is the intrinsic permeability of the coal matrix, η is the viscosity of the fluid, and l is the characteristic spacing between cleats (here chosen equal to $l = 1$ cm). Dimensional analysis provides a characteristic time τ_d for the transfer of fluid between cleats and coal matrix:

$$\tau_d = \frac{\eta l^2}{p_f k_m} \quad (30)$$

where p_f is a characteristic pressure of the fluid, chosen equal to $p_f = 1$ MPa.

We now consider a representative elementary volume of fractured coal, confined so that its volume can not vary (therefore $\epsilon = 0$). This volume will be exposed to carbon dioxide. The poromechanical behavior of this representative elementary volume

is governed by the set of constitutive equations (26) derived in Sec. 0.4, while the kinetics of transfer of fluid between cleats and coal matrix is governed by Eq. (29). The coal sample is considered to be made of Sulcis coal, characterized by Pini [12] experimentally and with the results of which we can calibrate the different parameters of the model, among which the tangent Biot coefficient b_m (see Fig. 3) and the amount $N_{v,m}^0$ of fluid adsorbed by the undeformed coal matrix. The bulk modulus of the sample is considered to be $K = 0.78$ GPa, its shear modulus is $G = 0.44$ GPa, its Biot coefficient is $b_c = 0.25$, its Biot modulus is $N = 4.77$ GPa, the initial porosity associated to the cleats is $\Phi_{c0} = 3.2\%$. The viscosity of the fluid is chosen equal to $\eta = 1.79 \times 10^{-5}$ Pa.s, which is the viscosity of carbon dioxide at a temperature $T = 318$ K and a pressure $p = 6$ MPa.

The pressures p_c of the fluid in the cleats and p_m of the fluid in the coal matrix are initially equal to zero. The pressure of the fluid in the cleats is increased linearly with time from 0 MPa up to 17 MPa in a duration τ_l and decreased linearly with time back to 0 MPa in the same duration τ_l . The response of the system is therefore going to be governed by the dimensionless ratio τ_d/τ_l of the characteristic time τ_d of transfer between cleats and coal matrix to the characteristic time τ_l of loading. For various dimensionless ratios τ_d/τ_l , the constitutive equations are solved numerically.

The results of the calculations performed on this representative elementary volume are displayed in Fig. 7. We observe two limit cases. The first limit case corresponds to a ratio τ_d/τ_l that tends toward zero, i.e., to a case for which the transfer of fluid between cleats and coal matrix is much faster than the imposed variations of pressure p_c of fluid in the cleats. At any time during the process, cleats and coal matrix are in thermodynamic equilibrium, so that, as is observed in Fig. 7b, at any time $p_c = p_m$. The increase of thermodynamic pressure p_m that accompanies the increase of pressure p_c in the cleats translates into a swelling of the coal matrix and into a decrease of the porosity Φ_c associated to the cleat system (see Fig. 7a) since the volume of the system is constrained. The second limit case corresponds to a ratio τ_d/τ_l that tends toward infinity, i.e., to a case for which the transfer of fluid between cleats and coal matrix is much slower than the imposed variations of pressure p_c of the fluid in the cleats. In such a case, the thermodynamic pressure p_m of the fluid in the coal matrix remains equal to zero at any time during the process (see Fig. 7b): fluid has no time to penetrate into the matrix. Consequently, the representative elementary volume behaves like a linear elastic macroporous medium: the porosity Φ_c increases linearly with the pressure p_c of the pore fluid, as can be observed in Fig. 7a.

Between those two limit cases, the process was simulated for ratios τ_d/τ_l that ranged between 10^{-2} and 10^2 . For those intermediate cases, we observe that, while the pressure p_c of the fluid in the cleats is increased, the thermodynamic pressure p_m of the fluid in the cleats increases as well but remains lower than p_c . In contrast, when the pressure p_c of the fluid in the cleats is decreased, the thermodynamic pressure p_m of the fluid in the cleats decreases as well but remains larger than p_c . Those delayed variations of p_m lead to complex variations of the porosity Φ_c associated to the cleat system (see Fig. 7b). Since the permeability of fractured coal is mostly governed by the cleat system, we would therefore expect that, consequently, the permeability would evolve over time in a complex manner.

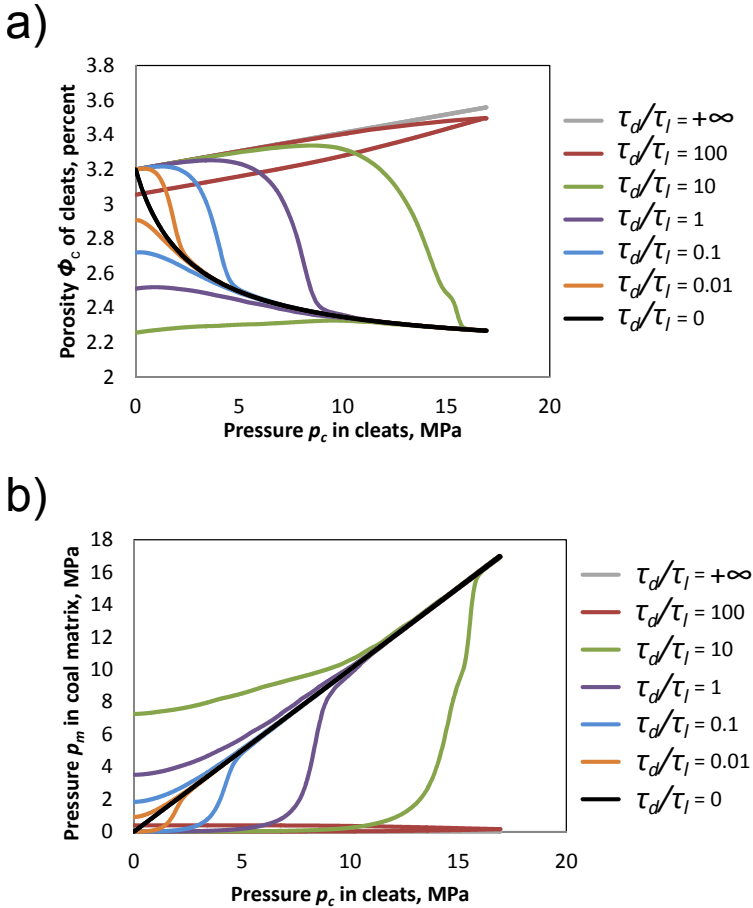


Abbildung 7 Representative elementary volume confined to a constant volume and for which the pressure p_c in the cleats is increased linearly with time up to a maximal value and decreased back to zero: (a) porosity Φ_c of the cleats and (b) pressure p_m in the coal matrix.

On all intermediate cases simulated, a hysteresis is observed. In contrast, no hysteresis is observed for the two limit cases. This difference is due to the fact that, in the simulated process on this representative elementary volume, the only potential dissipation is associated with the transfer of fluid between cleats and coal matrix. For the limit case $\tau_d/\tau_l \rightarrow \infty$, no fluid is transferred to the coal matrix, so that no dissipation and thus no hysteresis is observed. In contrast, for the limit case $\tau_d/\tau_l \rightarrow 0$, the variations of pressure p_c in the cleats are so slow that cleats and coal matrix are in thermodynamic equilibrium at all times: transfer of fluid occurs, but so slowly that no dissipation is associated to this transfer; therefore, for this limit case also, no hysteresis is observed.

0.6

Simulating an injection of carbon dioxide in a coal seam

In this last section, we aim at performing simulations at the scale of a whole coal seam (see the left part of Fig. 6). To do so, we discretized the seam and used the finite element method to solve the equilibrium equation, $\sigma_{ij,j} = 0$, and the two mass balance equations associated to the CO_2 gas of the cleats (at the pressure p_c) and that of the matrix coal (at the pressure p_m). These mass balance equations include, as source term, the rate of transferred mass given by Eq. (29). The other set of constitutive equations was derived in Sec. 0.4 and given in Eqs. (26). In addition, the transport of gas, which occurs only in the cleats, is governed by Darcy's law. After discretization, the system of nonlinear algebraic equations is solved by using an implicit time discretization and Newton iterative method until a convergence criterion is met under the form

$$\frac{u^{n+1} - u^n}{\Delta u_{\text{obj}}} < \varepsilon \quad (31)$$

where u_{obj} is a given objective variation of the unknown u (as a displacement or pressure) and ε a positive number small compared to unity, typically 10^{-4} . Practically, this model was implemented in the open-source software 'Bil' developed at Laboratoire Navier¹⁾.

The case considered is that of a coal seam from which all methane initially present in the seam would have been produced thanks to a former injection of carbon dioxide. At the beginning of the simulation, some carbon dioxide is therefore already present in the seam and the simulated injection is performed into a saturated medium. This case is hypothetical but can be treated with the constitutive equations here derived, which are only valid in the saturated case.

The coal seam is considered to be axisymmetric with a radius of 500 m. In the center of the seam is located the injection well, the radius of which is 10 cm. The performed simulations are axisymmetric plane-strain one-dimensional (see the left

1) Software and documentation available at <http://perso.lpc.fr/dangla.patrick/bil>

part of Fig. 6). We impose no displacement of the edge of the reservoir and no flow through the edge of the reservoir. The initial pressure of carbon dioxide in the system is considered to be equal to 1 MPa, and the pressure P_i of injection is kept constant and equal to $P_i = 10$ MPa for a year. The seam is considered to be made of Sulcis coal, the parameters of which have already been given in the previous section.

In addition to the constitutive equations, the equation that governs the transport of fluid must be given. We consider that this transport occurs mostly through the cleats and that it is governed by Darcy's law: $\underline{q} = -(k/\eta)\nabla p_c$, where \underline{q} is the volume flow vector of the fluid, and η is its viscosity, here equal to $\eta = 1.79 \times 10^{-5}$ Pa.s. The intrinsic permeability k of a small representative elementary volume of fractured coal is assumed to be governed by the porosity Φ_c associated to the cleat system only: this intrinsic permeability is considered to depend on this porosity Φ_c through the Kozeny-Carman relation $k \propto \Phi_c^3/(1 - \Phi_c^2)$. In the state of reference, the intrinsic permeability of the medium is considered to be equal to 10 mD. Simulations are performed by considering various kinetics of transfer of fluid between cleats and coal matrix: the characteristic time τ_d of transfer introduced in the previous section is assumed to be equal to zero, to 10^8 s, and to tend toward infinity.

The results of the simulation are displayed in Fig. 8. Figure 8a shows non monotonic variations of the permeability of the seam for the various cases. Such phenomenon is due to two competing effects: on one hand the increase of the pressure of fluid in the cleats increases the permeability, while on the other hand the increase of the thermodynamic pressure of fluid in the coal matrix leads to a swelling and to a decrease of permeability (see Fig. 7). We show in Fig. 8b the variations of injectivity (i.e., the ability of an injection well to receive injected fluid, here characterized by the rate of injection) over a year for the various characteristic times τ_d of transfer of fluid between cleats and coal matrix. The greater this characteristic time, the more pronounced the loss of injectivity (i.e., the decrease of rate of injection) in the reservoir. Those variations of rate of injection result also from a competition: on one hand, for smaller values of τ_d , swelling happens faster and the permeability of the reservoir is smaller (see Fig. 8a), which tends to lower the rate of injection; but on the other hand, smaller values of τ_d lead to faster adsorption in the coal matrix, which provides additional accessible pore volume and tends to increase the amount of fluid that is injected in a given period of time.

The simulations here performed were repeated for a characteristic time τ_d of diffusion equal to $\tau_d = 4.11 \times 10^3$ s, which corresponds to a realistic intrinsic permeability $k_m = 4.34 \times 10^{-4}$ mD for the coal matrix. Results obtained with such a value for τ_d coincide with results obtained with $\tau_d = 0$, i.e., when assuming thermodynamic equilibrium between cleats and coal matrix. Therefore, for the reservoir and the profile of injection of interest, it appears that assuming an infinitely fast transfer of fluid between cleats and coal matrix is a very reasonable assumption.

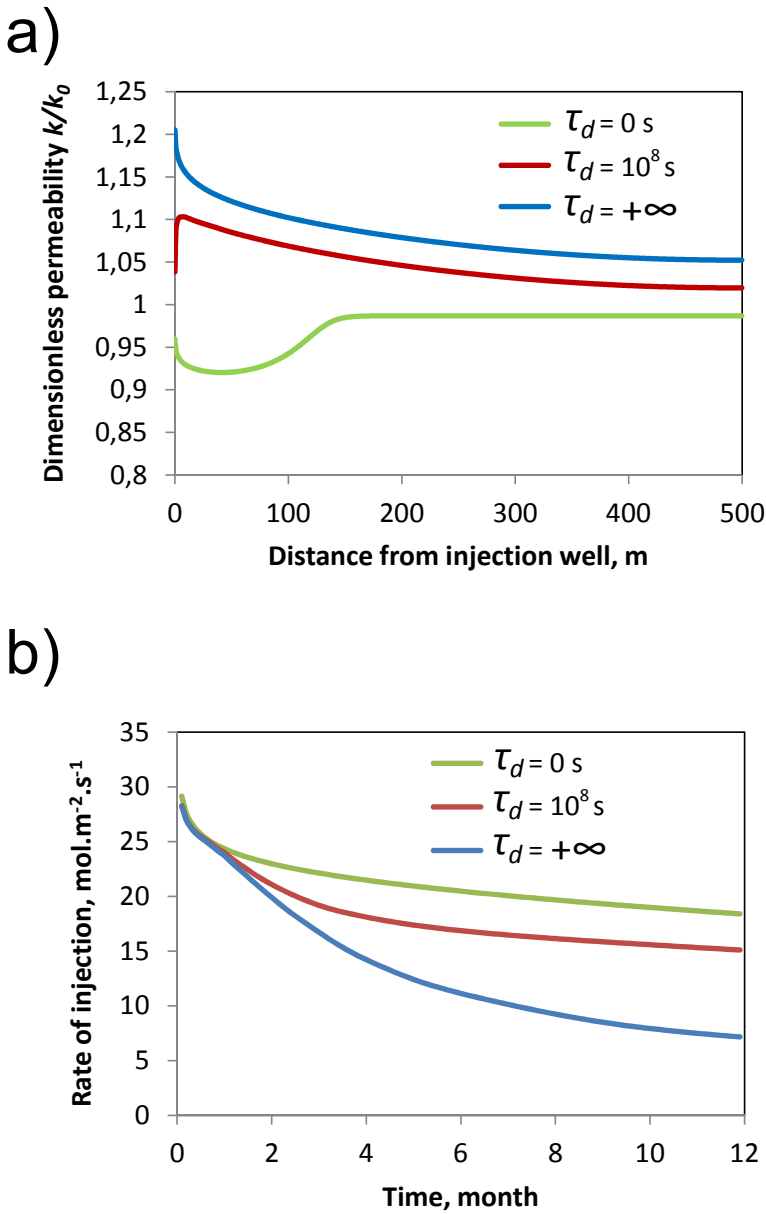


Abbildung 8 Results of finite-element simulations of a methane-free coal seam injected with carbon dioxide, for various characteristic times τ_d of transfer of fluid between cleats and coal matrix: (a) dimensionless permeability along the reservoir after a month of injection and (b) rate injection over a year of injection.

Teil III

Conclusions and perspectives

This chapter focused on poromechanical modeling of porous solids, i.e., of solids for which the mechanical behavior is significantly impacted by the presence of a fluid in its pore network. We considered various types of porous solids: macroporous ones, mesoporous ones, and microporous ones. For each type of porous solid, we detailed what simplifications could be made and derived specific constitutive equations. The derivations were rigorously based on thermodynamic principles.

We then showed that, based on the same approach, we could tackle more complex problems, such as the one of a representative elementary volume of coal seam: this porous solid is a dual-porosity one, made of macroporous cracks (i.e., cleats) and of the micropores of the coal matrix. For this coal, we derived constitutive equations that take into account the fact that the thermodynamic pressures in the cleats and in the micropores could be different. Choosing a law of transfer between the two pore spaces, we then studied hysteretic effects at the material scale induced by the application of a cycle of the pressure of fluid in the cleats. At a scale above, we showed that the derived constitutive equations can be implemented in a finite-element/finite-volume software, in order to treat numerically the problem of an injection of carbon dioxide in a coal seam.

We identify three limitations of the approach, that would require further work. The first limitation is that, here, constitutive equations were derived in the saturated case, i.e., when the pore space is occupied by only one type of fluid. In practice, such formulation needs to be extended to the partially saturated case, i.e., to the case where the pore space is occupied by several fluids. The second limitation is that, here, constitutive equations were derived in the reversible case. Therefore, those equations are not suited to capture irreversible processes such as creep or fracture, although it is known that such processes are modified by adsorption. The last limitation is that the generic constitutive equations derived in Sec. 0.2 do not allow, in their present form, to make use of any knowledge regarding the pore size distribution (also called PSD). This PSD is somewhat hidden in how the amount of fluid in the system depends on its chemical potential and on the strain of the solid (see the second equation in the set of equations (11)). However, we saw that we could take advantage of more information on this PSD in order to obtain more simple or more relevant constitutive equations: for instance, in Sec. 0.1, we obtained simple constitutive equations valid for macroporous solids only, the pores of which are only occupied by the bulk fluid. Also, any

explicit use of information on the PSD could be of value for the study of transport properties, which are often mostly governed by the largest pores. Therefore, noting that many natural geomaterials contain micropores, mesopores, and macropores simultaneously (see Fig. 1), deriving constitutive equations that make use of as much information as possible on the wide pore size distributions encountered in natural geomaterials remains a challenge.

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