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# Numerical Modelling of the PVF<sub>2</sub> Volume Strain with Carbon Dioxide

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**Résumé — Modélisation numérique de la déformation volumique du PVDF en présence de dioxyde de carbone** — Les polymères utilisés dans l'industrie pétrolière sont soumis à des fluctuations de pression de gaz et de température qui peuvent les endommager. Cette détérioration résulte de couplages entre phénomènes mécaniques, thermiques et de diffusion. Une loi modélisant ces couplages a été implémentée dans le logiciel Abaqus. En réalisant une étude numérique de certains de ces couplages, on montre la nécessité de modéliser par un coefficient de dilatation l'effet de la diffusion du CO<sub>2</sub> sur le comportement mécanique du PVDF. On montre que ce paramètre est indépendant de la pression appliquée et qu'il permet de prédire le gonflement maximum du matériau lorsque celui-ci est saturé en gaz.

**Abstract — Numerical Modelling of the PVF<sub>2</sub> Volume Strain with Carbon Dioxide** — In the oil industry, polymer materials are subjected to temperature and gas pressure fluctuations that can damage them. This degradation results from couplings between mechanical, thermal and diffusion phenomena. A law modelling these couplings was implemented in the Abaqus software. By making a numerical study of these couplings, we show that it is necessary to model by an isotropic expansion coefficient the effect of CO<sub>2</sub> diffusion on the mechanical behaviour of the PVF<sub>2</sub>. We show that this parameter is independent of the applied pressure. Moreover, with this coefficient we can predict the maximum swelling of the material when it is saturated by gas.

## INTRODUCTION

In the oil industry, polymer materials are used in gaseous medium at high temperature and pressure. Thus, there is an adsorption then a diffusion of gas such as methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>) or hydrogen sulphide (H<sub>2</sub>S) in the material. Due to thermo-diffuso-mechanical couplings, the polymer can swell and its mechanical properties are modified. When the pressure decreases brutally, the stresses acting on the polymer are very important and can damage it in the form of cracks or blisters. This phenomenon is called “explosive decompression” or “blistering”. For several years, the oil industry has been interested in this kind of process.

Various studies concerning the comprehension and the modelling of these coupled phenomena have already been carried out. For example, Gaillard-Devaux [1] studied the rupture of the polyethylene (PE) at temperature by decompression of methane. This study showed the existence of a strong coupling between mechanical, thermal and diffusion phenomena. Boyer [2] studied the damage mechanisms of semicrystalline thermoplastic polymers by explosive gas decompression. This author showed that the comprehension of these mechanisms requires the knowledge of the solubility and the diffusion coefficient of gases (CO<sub>2</sub>, CH<sub>4</sub>) in polymer materials (PE, polyvinylidene fluoride: PVF<sub>2</sub>). Moreover, studies of gas diffusion through polymer showed the influence of pressure, temperature and gas concentration on these coefficients [3-5]. Nevertheless, the volume strain of the polymer during sorption-desorption was rarely studied. Indeed, when a gas diffuses through a polymer the latter can swell. For example, the swelling of the PVF<sub>2</sub> at a pressure of one hundred MPa is about forty percent. So, this coupling between gas diffusion and volume strain must be modelled. Rambert introduced this coupling [6] by defining an isotropic expansion coefficient linked to mass transport noted  $\alpha_c$ . This coupling is equivalent to the thermo-mechanical coupling classically defined by an isotropic expansion coefficient linked to heat conduction noted  $\alpha_T$ .

The objective of this paper is to show the interest of taking into account the coupling between gas diffusion and volume strain during solubility tests. Calculations with particular finite elements are compared with CO<sub>2</sub> desorption in the PVF<sub>2</sub>. We show that this coupling is necessary to predict the swelling of the PVF<sub>2</sub> with carbon dioxide. We also show that the parameter  $\alpha_c$  is independent of the applied pressure (25, 50 and 100 MPa). In fact, the same parameter  $\alpha_c$  predicts to the maximum swelling of the sample when it is saturated by carbon dioxide.

## 1 DIFFUSO-ELASTIC MODELLING

In this article, we are interested only in the diffuso-elastic couplings of the thermo-diffuso-elastic Rambert's model, the thermal couplings are neglected. This model has been developed in the framework of the generalised standard media and therefore follows a classical approach. In this thermodynamic framework, the ERV (Elementary Representative Volume) has been described at a macroscopic scale as a bi-component, continuous, homogeneous medium: polymer and gas. A field of state variables represents the material at any given time. The introduction of a first potential (specific free energy) makes it possible to define laws linking thermodynamic forces (stress, chemical potential) to dual variables (strain, normalised concentration). Under the assumption of small perturbations, that is to say small strains and small difference of normalised concentration, the development of this potential to the second order leads to the linear constitutive equations (1) and (2).

The dissipations, which are only associated with diffusion phenomenon in an elastic behaviour case, were obtained using a second potential (dissipation potential) which depends on the coupling phenomena which are included. Once defined, under the assumption of uncoupling between dissipative phenomena, this leads to a complementary evolution law (3):

$$\underline{\underline{\sigma}} = \underline{\underline{\sigma}}_0 + \lambda \text{tr}(\underline{\underline{\varepsilon}}^e) \underline{\underline{I}} + 2\mu \underline{\underline{\varepsilon}}^e - (3\lambda + 2\mu) \alpha_c S_g (c - c_0) \underline{\underline{I}} \quad (1)$$

$$\mu_g - \mu_p = \mu_{g0} - \mu_{p0} + D S_g (c - c_0) - \frac{1}{\rho} (3\lambda + 2\mu) \alpha_c \text{tr}(\underline{\underline{\varepsilon}}^e) \quad (2)$$

$$\rho S_g \dot{c} = D \rho S_g \text{div}(\underline{\underline{\text{grad}}} c) - k_\mu \alpha_c \frac{3\lambda + 2\mu}{\rho} \text{div}[\underline{\underline{\text{grad}}}(\text{tr} \underline{\underline{\varepsilon}}^e)] \quad (3)$$

Among the eight coefficients of this model, two introduce couplings between mechanical and diffusion phenomena:  $\alpha_c$  is the isotropic coefficient of expansion linked to diffusion phenomenon;  $k_\mu$  is an undetermined parameter which is linked to the chemical potential gradient effect on the gas mass flux (kg.s.m<sup>-3</sup>). The other coefficients of the model are the average mixture density  $\rho$  (kg.m<sup>-3</sup>), the Lamé coefficients noted  $\lambda$  and  $\mu$  (Pa), the gas solubility in the polymer  $S_g$  (cm<sup>3</sup> STP.cm<sup>-3</sup>.Pa<sup>-1</sup>), the diffusion coefficient  $D$  (m<sup>2</sup>.s<sup>-1</sup>),  $D$  is defined as a function of  $\rho$ ,  $D$ ,  $k_\mu$ .

The tensor  $\underline{\underline{\sigma}}$  is the total Cauchy stress tensor (Pa) applied to the homogeneous gas-polymer mixture, which is equal to  $\underline{\underline{\sigma}}_0$  (Pa) at the initial state,  $\underline{\underline{\varepsilon}}^e$  the infinitesimal

elastic strain tensor and  $\underline{I}$  the identity tensor,  $\underline{f}$  being the body force per unit of mass (N/kg) at any point within the ERV. Moreover,  $\mu_g$  (J.kg<sup>-1</sup>),  $\mu_p$  (J.kg<sup>-1</sup>) and  $c$  (Pa) are respectively the mass chemical potentials for the gas and the polymer and the normalised concentration of the gas of the mixture, respectively given initially by  $\mu_{g0}$ ,  $\mu_{p0}$  and  $c_0$ .

These equations account for couplings between diffusion and elastic phenomena. The first term of Equation (1) is Hooke's law. In Equation (3) the product  $k_\mu \times \alpha_c$  shows the impact of the elastic volume strain on the evolution of the gas concentration in the material. In a reciprocal way the last term of Equation (1) shows the effect of the gas diffusion on the mechanical behaviour of the material.

Moreover, the diffusion coefficient strongly depends on the gas concentration for high pressures. For polymers such as PVF<sub>2</sub> above their glass temperature, an exponential model is classically used:

$$D(C) = D_0 e^{\beta C} \quad (4)$$

$D_0$  being the limit of  $D$  when  $C$  tends towards zero and  $\beta$  a constant parameter at fixed  $T$ , characterising this dependence. In the case  $\beta = 0$ , the model corresponding to a constant  $D$  value is obtained. In the work of Benjelloun-Dabaghi [7] this model was also considered for the PVF<sub>2</sub> at high pressures.

Thus in this paper, we considered this dependence with gas concentration using Rambert's model.

The numerical implementation of the linear diffusio-elastic model in the software Abaqus<sup>TM</sup> was implemented here in a user subroutine called User Element (UEL). A library of various elements (6 node linear triangular prism, 8 node linear brick, 20 node quadratic brick etc.) is available in this UEL.

## 2 SOLUBILITY TEST

### 2.1 Experimental Results

The solubility tests studied in this document was carried out at the *Institut français du pétrole (IFP)*. During these tests the solubility of the PVF<sub>2</sub> for CO<sub>2</sub> pressures of 25, 50 and 100 MPa was calculated. The polymer samples are ring shaped.

The solubility test can be broken up into two stages: the sorption and the desorption. For the sorption phase, the temperature and pressure are gradually increased for a sample in a particular system named pressure cell and left in this state until it is saturated with gas. For all pressures this temperature is equal to 403 K. The system is quenched with water to 298 K, maintaining the pressure. For the desorption phase, a fast decompression to the atmospheric

pressure is realised, then the sample left the experimental system. During this last stage its volume is measured over time at atmospheric pressure and ambient temperature. It is noted that the sorption phase is carried out by heating the pressure cell in order to decrease the saturation period. Indeed, for a given temperature, many authors have showed that the diffusion coefficient is generally related to the temperature by an Arrhenius' law [8, 9].

The evolution of the volume during desorption for the three applied pressures is illustrated in Figure 1. The first point of each curve, in grey, corresponds to extrapolation at time zero of the curve of desorption, and thus at the beginning of the decompression. These measurements show that the PVF<sub>2</sub> swells strongly with CO<sub>2</sub>.

These results show that the samples recover their initial size very slowly. One cannot conclude as to a residual volume strain of the sample because the total time of measurement is insufficient to determine if the material reaches a volume strain threshold.

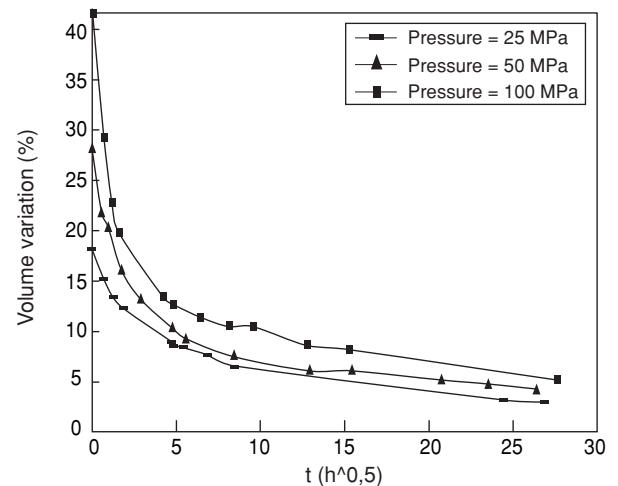


Figure 1

Experimental curves: volume variation during CO<sub>2</sub> desorption in PVF<sub>2</sub>.

### 2.2 Numerical Results

To simulate the couplings suggested by Rambert, 9000 finite elements, defined in the UEL, with twelve nodes and twenty seven integration points are used.

Figure 2 illustrates the geometry of the sample used experimentally, that is to say a PVDF ring of interior radius  $R_i$ , external radius  $R_e$  and thickness  $e$  (along axis  $Z$ ).

Its initial mass  $m_i$  and its initial volume  $V_i$  are given in Figure 2. One hundred elements are defined in the radial direction, one in the ortho-radial direction and ninety in the thickness; moreover to optimize the computing time we chose  $\theta = \pi/180$ .

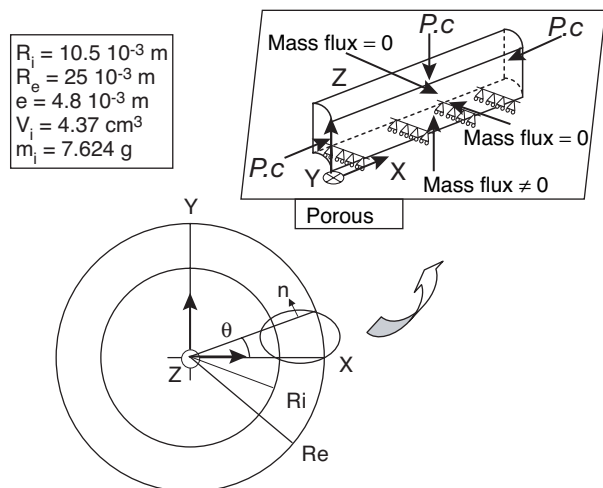


Figure 2  
Geometry and loads.

Moreover, in order to optimise the computing time, only a part of the ring was modelled by taking into account of the appropriate symmetries. With regard to the loading and the boundary conditions, it were defined in order to reproduce the experimental test conditions.

Properties of material are those of a PVF<sub>2</sub> at ambient temperature: 0.38 for the Poisson’s ratio, 1743 MPa for the Young modulus and 1745 kg/m<sup>3</sup> for the density.

For the diffusion coefficient (Equation 4), we choose  $1.5 \cdot 10^{-12}$  m<sup>2</sup>/s as  $D_0$  and the following law for  $\beta$ :

$$\beta = -10^{-5} \ln(P) + 10^{-4}, \quad \forall 25 \leq P \leq 100 \text{ MPa}$$

The value obtained experimentally is used for the solubility coefficient. In the Abaqus software the solubility is expressed in ppm/Pa. It is thus necessary to correct the experimental values that are given in cm<sup>3</sup> STP.cm<sup>-3</sup>.MPa<sup>-1</sup>.

TABLE 1

Solubility coefficient (ppm.Pa<sup>-1</sup>) of CO<sub>2</sub> in PVF<sub>2</sub>

Pressure (MPa)	25	50	100
Sg (ppm.Pa <sup>-1</sup> ) (×10 <sup>-2</sup> )	0.405	0.311	0.229

Consequently, it remains to determine the parameters of the direct coupling ( $\alpha_c$  and  $\kappa_\mu$ ).

### 2.2.1 Evolution of the Volume without Diffuso-Elastic Coupling

The numerical simulation without diffuso-elastic coupling is equivalent to Hooke’s law.

The volume evolution of the sample during a solubility test at a pressure of 25 MPa taking the parameter  $\alpha_c$  equal to zero and using a constant diffusion coefficient is illustrated on Figure 3.

In the absence of coupling, the strain of the material is completely hydrostatic during the sorption, no swelling appears under the effect of the gas diffusion. Indeed, at the end of the decompression, the sample recovers its initial volume whereas experimentally the sample shows important swelling.

Thus, Hooke’s law is insufficient to characterise the kinetics of the volume strain of PVF<sub>2</sub> with CO<sub>2</sub>.

It should be noted that these results are independent of the diffusion law because the diffusion coefficient does not appear in the mechanical behaviour.

### 2.2.2 Evolution of the Volume with a Diffuso-Elastic Coupling in the Mechanical Behaviour

Figure 3 gives also the volume evolution of the sample during a solubility test at a pressure of 25 MPa taking the  $\alpha_c$  parameter not equal to zero, the  $\kappa_\mu$  parameter equal to zero and a constant diffusion coefficient.

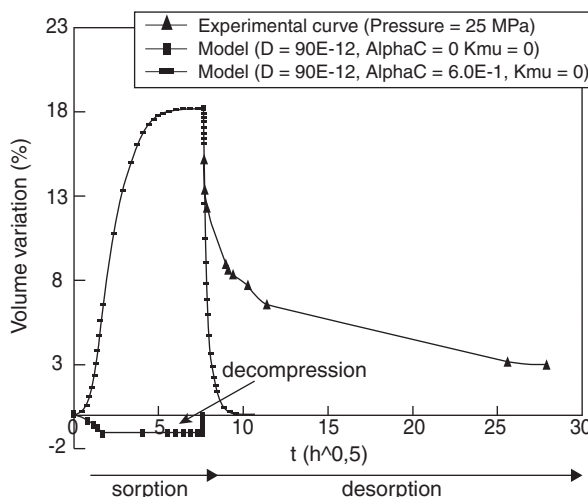


Figure 3

Volume evolution during CO<sub>2</sub> sorption-desorption in PVF<sub>2</sub> with and without diffuso-elastic coupling in the mechanical behaviour and D constant.

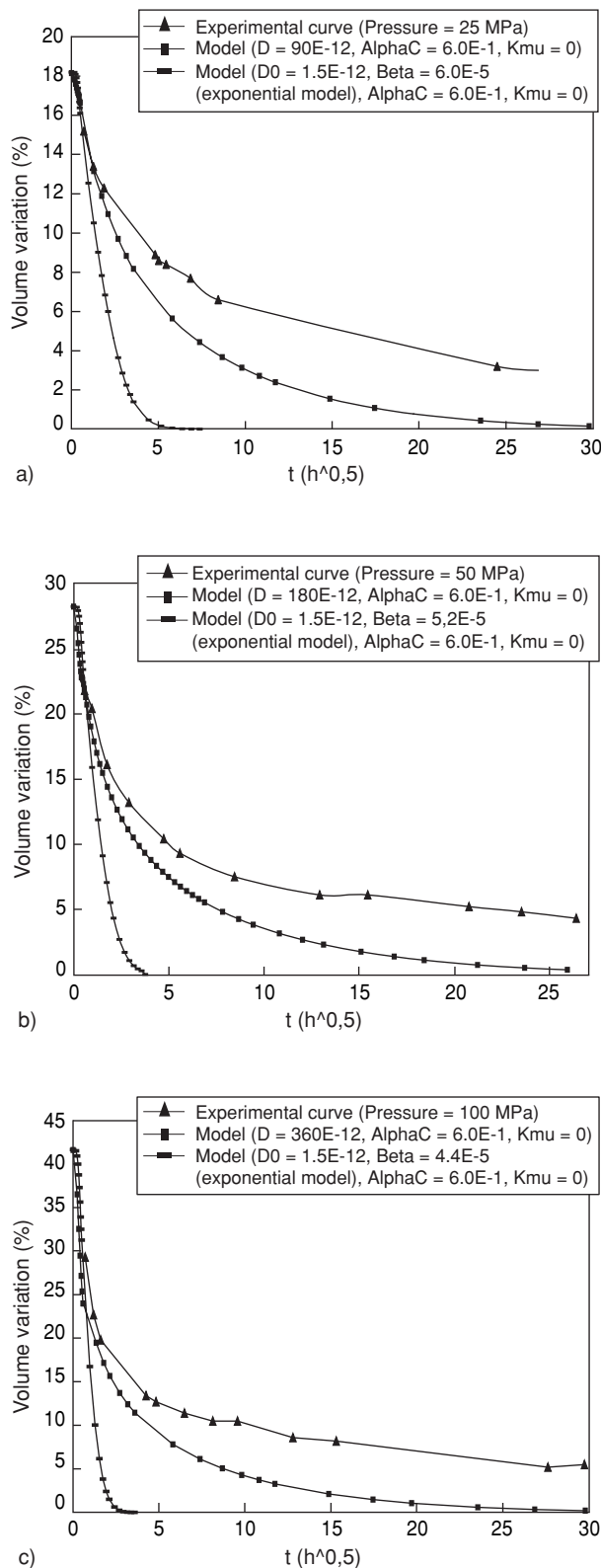


Figure 4

Volume evolution during  $CO_2$  desorption in PVF<sub>2</sub> with a diffuso-elastic coupling in the mechanical behaviour and different models for D.

The coupling imposed by the expansion coefficient linked to the diffusion of gas in the sample induces a swelling during the sorption phase. The swelling reaches a threshold when the material is saturated by gas. This threshold does not depend on the coefficient of coupling  $\kappa_\mu$  but only on  $\alpha_c$ . Then, during decompression, there is a competition between two phenomena: the deflation of the sample due to gas desorption induced by the concentration gradient, and the expansion of volume related to the external pressure drop. If the diffuso-elastic coupling in the diffusion equation is neglected ( $\kappa_\mu = 0$ ) and if the diffusion coefficient is high, such as in the beginning of the desorption, this competition is clearly in favour of the first phenomenon.

Thus, in the PVF<sub>2</sub>- $CO_2$  system, the mechanical behaviour of the polymer during sorption and desorption is directly influenced by the diffusion of gas in the material.

A parametric study was performed in order to determine the  $\alpha_c$  parameter for the different pressures applied. The diffusion coefficient is taken constant in a first simulation and function of the gas concentration (4) in a second simulation.

We show Figure 4 that unique value of the  $\alpha_c$  parameter for the different pressures applied equal to 0.6 is sufficient to obtain the maximum swelling when the material is saturated by gas.

Moreover, on this Figure 4 we show that a strong dependence with gas concentration for the diffusion coefficient is insufficient to predict correctly all the deflating of the material during desorption. This result is more particularly due to the hypothesis of the diffuso-elastic coupling of Rambert. Indeed, the desorption occurs above the glass temperature of the PVF<sub>2</sub>, so a diffuso-viscoelastic or a diffuso-viscoplastic coupling would certainly be more in agreement with the behaviour of the material.

Figures 5 and 6 illustrate respectively the distribution of the concentration of  $CO_2$  and of the displacement of the sample at the end of the decompression for the solubility test to 50 MPa. We point out that the end of decompression corresponds to the end of time necessary to reach the atmospheric pressure, outside the sample, in the experimental cell.

At the end of decompression, the gas concentration in the sample is still raised, this moment thus does not coincide at the end of desorption.

### 2.2.3 Evolution of the Volume with a Diffuso-Elastic Coupling in the Mechanical Behaviour and in the Diffusion Law

A parametric study was carried out in order to estimate the maximum diffuso-elastic coupling in the diffusion



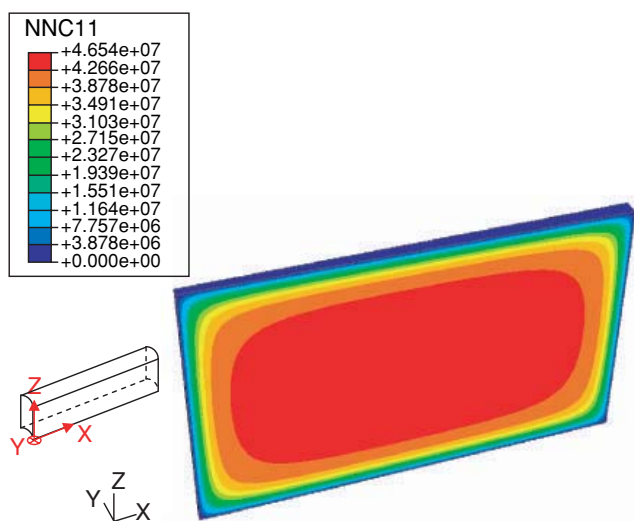


Figure 5

Distribution of the concentration in the sample at the end of the decompression for the solubility test to 50 MPa.

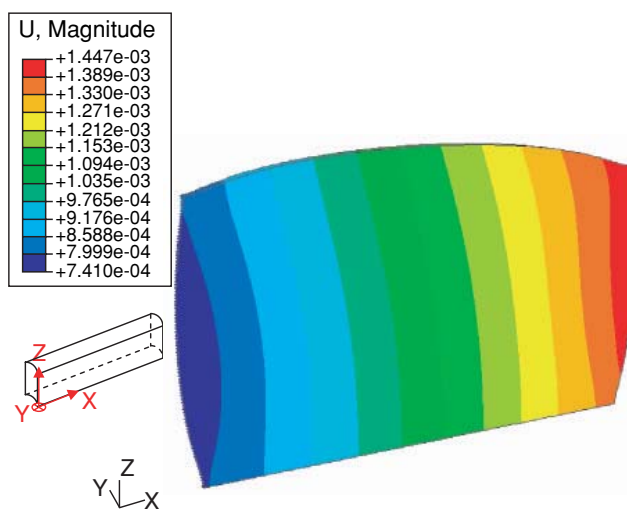


Figure 6

Distribution of the total displacement  $U$  in the sample at the end of the decompression for the solubility test to 50 MPa.

equation, what corresponds to the highest value of the parameter  $\kappa_\mu$ . Figure 7 shows the volume evolution of the sample during a solubility test with a pressure of 25 MPa by taking the precedent value for the  $\alpha_c$  parameter, a value of the parameter  $\kappa_\mu$  inducing an important coupling and a constant diffusion coefficient. In the case of the solubility test, the gradient of the volume strain is very small during desorption due to the sample geometry and the loads applied during the test. So, in order to obtain a not neglected effect of the coupling it is necessary to use a high value of the parameter  $\kappa_\mu$ .

It is clear that, with a constant diffusion coefficient, the coupling with the gradient of the volume strain in the diffusion equation cannot be neglect. Indeed, during decompression the volume of the sample increases whereas the quantity of gas starts to decrease. This is due to the deflation of the sample during desorption that does not compensate for the expansion related to the external pressure drop. Thus, when this coupling is important the competition between the hydrostatic pressure drop and the diffusion of the gas towards the exterior of the material is in favour of the first phenomenon.

After the end of the decompression, desorption at atmospheric pressure induces a contraction of the sample.

In the case of the solubility test this coupling is not realistic for modelled correctly the mechanical behavior of the PVF<sub>2</sub> during CO<sub>2</sub> desorption. Nevertheless, this coupling must be considered in the pressure sheath of the

pipes used in petroleum industry because the gradient of the volume strain is not negligible.

The same study was carried out using a diffusion coefficient that depends on the gas concentration in the material (4). The diffuso-elastic coupling previously considered becomes negligible comparatively to the effect of the dependency with the gas concentration. Indeed, at the end of the sorption the gas concentration in the material is high, inducing a high diffusion coefficient ( $D = 3.10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$ ) due to the law of dependence in concentration. So, at the beginning of the decompression the first term of Equation (3) is preponderant comparatively to diffuso-elastic coupling.

## CONCLUSION

For high CO<sub>2</sub> pressures, numerical study of Rambert's model during CO<sub>2</sub> sorption-desorption in PVF<sub>2</sub> shows that it is necessary to take into account the effect of gas diffusion on the mechanical behaviour. This effect is expressed by an isotropic expansion coefficient, which is independent of the applied pressure for pressures ranging between 25 and 100 MPa. Moreover, with this coefficient we can predict the maximum swelling of the material when it is saturated by gas.

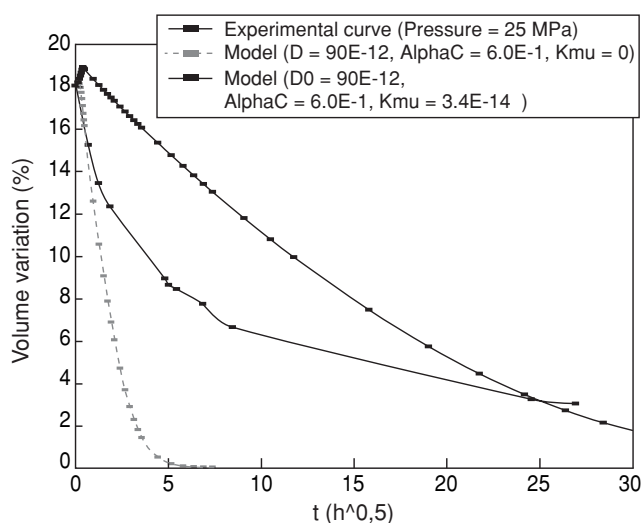


Figure 7

Volume evolution during CO<sub>2</sub> desorption in PVF<sub>2</sub> with and without diffuso-elastic coupling and a constant D.

However, this diffuso-elastic coupling appears insufficient to completely characterise the PVF<sub>2</sub> volume strain during a desorption at ambient temperature. For more accurate modelling the behaviour of the PVF<sub>2</sub> subjected to CO<sub>2</sub> pressure fluctuations, a diffuso-viscoelastic or diffuso-viscoplastic coupling must be considered.

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