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A Model to Predict the Permeation of Type IV Hydrogen Tanks

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Abstract

In the frame of the certification process of the type IV hydrogen storage tanks MaHyTec aims to manufacture, this innovative SME is developing a numerical model dedicated to the study of permeation issues. Such an approach aims at avoiding complicated, time-consuming and expensive testing. Experimental results obtained under real conditions can moreover be significantly influenced by the scattering of material properties and liner dimensions. From simple testing on small-size flat membranes, the model allows to predict the gas diffusion flow through the whole structure by means of numerous parameters. On every step, theory can be compared with the results obtained from the samples.

This document presents a brief review of the mathematical theory describing gas diffusion and the different aspects of the study for better understanding the proposed approach.

1 Introduction

In a worldwide complex context of global warming, depletion of fossil fuel and increase of the general energy price, it is important to find new clean solutions. Hydrogen can be one of those future possibilities if we are able to produce, supply and storage it properly. Earth being full of this molecule, numerous solutions are available to extract it from water, gas or biological organisms… In different countries (Germany, Belgium, Netherlands, United States…), some installations or local production devices already exist to tank up vehicles. The actual real difficulty comes from its storage due to its low mass density. Among the three storage possibilities: solid (too heavy), liquid (too complicated and energy consuming to maintain -253°C), and gas, MaHytec believes in the high pressure tank of gaseous hydrogen. Four types of tanks exist, detailed on Fig.1, depending on utility and pressure wished.

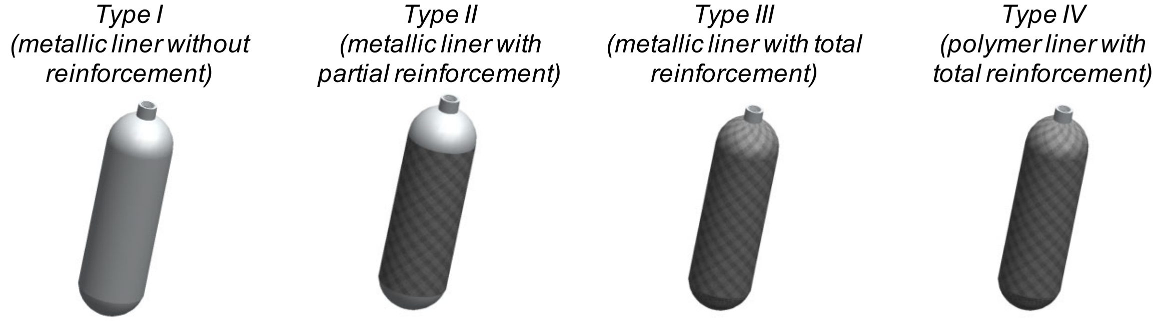

Figure1: Different types of gaseous hydrogen storage.

This study deals with the type IV hydrogen tank, which have the major drawback of a significant permeation. To be able to manufacture a good tank it is obligatory to respect legislation. In the perspective of being in compliance with the international standard ISO 11439:2000 defining the requirements for hydrogen tanks gastightness, it is of utmost importance to understand the gas transport phenomenon through polymers. Different mathematical theories have been proposed to represent the diffusion of a gas through a flat membrane but also through a cylinder or a sphere [1]. Inspired by Fourier's law on heat conduction, the Fick's first law is the most suitable theory for expressing the permeation of hydrogen :

$$J = -D\nabla C \tag{1}$$

J : hydrogen diffusion flow [cm^3(STP)/s.cm^3]

D : diffusion coefficient [cm²/s]

∇C : concentration gradient [cm/s.cm^3]

The minus sign represents the direction of the flow, from the highest pressure side to the lowest pressure side. This equation can be combined with the mass conservation to obtain the Fick's second law (2, 3, 4). Depending on the shape of the material that is investigated, the law can be expressed as:

Flat membrane
$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}(D\frac{\partial C}{\partial x}) \tag{2}$$

Cylinder
$$\frac{\partial C}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}(rD\frac{\partial C}{\partial r}) \tag{3}$$

Sphere
$$\frac{\partial C}{\partial t} = D(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}) \tag{4}$$

On the basis of these formulae, it is possible to develop a numerical model coupled with an experimental permeation system to predict the behavior of a type IV hydrogen tank.

2 Study

The permeation parameters of numerous materials can be readily found in the literature. However, the values of the diffusion, solubility and permeation coefficients are strongly influenced by the nature of the raw material, the production process or the conversion method, and the characteristics of a given polymer can vary from a specimen to another. The rigorous analysis of the permeation must rely on real parameters which must be determined experimentally rather than on unreliable theoretical values. On that purpose, a permeation vessel for the testing of flat membrane has been designed.

2.1 Experimental part

The system has been developed in view of simplicity and reliability (see Fig. 2). It makes it possible to test a polymer disc (a) under low or high pressure. The risk of bulging is overcome thanks to a reinforcement disk (c) made from a porous material. Hydrogen tightness between the two vessel blocks and the membrane is achieved by means of O-rings (b) to ensure that all the permeated gas is measured.

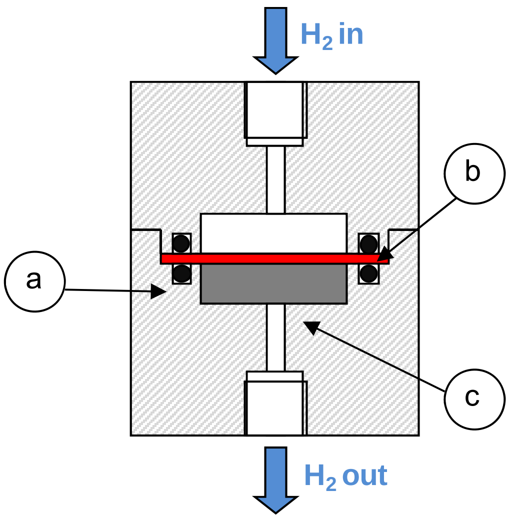

Figure 2: Schematic of the permeation vessel (refer to text for details).

The permeation testing is realized in a thermostatted environment to perfectly control the temperature, whose impact on diffusion kinetics is non-negligible. The low hydrogen flow is measured by a pressure sensor coupled with an acquisition device allowing us to obtain its evolution over time. With the help of equations obtained from the analytical analysis of a flat membrane, the permeation properties of the material can be assessed. This experimental qualification of the polymer should then contribute to estimate the permeation which may occur through a liner of type IV hydrogen storage tank.

2.2 Analytical analysis

Some publications [2-3] provide simplified methods for quantification of flat membranes permeation

$$Q(t) = eC_1\left(\frac{Dt}{e^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{i=1}^{\infty}\frac{(-1)^i}{i^2}exp\left(-\frac{Di^2\pi^2t}{e^2}\right)\right) \quad (5)$$

$Q(t)$: amount of gas [cm^3 (STP)/cm^3]

e : thickness of the membrane [cm]

C_1 : gas concentration on the most pressurized side [cm^3(STP)/cm^3]

D : diffusion coefficient [cm^2/s]

t : time [s]

Equation (5) gives a relevant approximation of gas permeation in a simple unidirectional case, where gas concentration C_1 is assumed to be constant and C_2, concentration on the lowest pressure side, is assumed to be null. These hypotheses turn out to be satisfactory as long as the outlet pressure is relatively low.

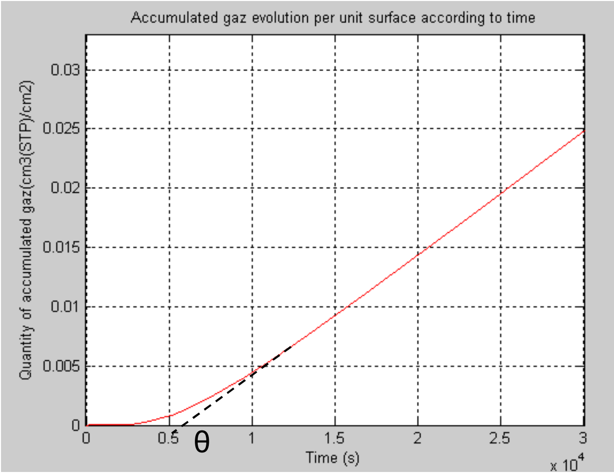

Figure 3: Typical permeation curve.

Fig. 3 shows the typical permeation curve obtained whether it be from experimental or theoretical investigations. It is then possible to determine material parameters like diffusion coefficient or gas concentration by using the evolution of Q over time. Thus, once the permeation has reached a steady state, the curve is a straight line which equation is:

$$Q(t) = \frac{DC_1}{e}\left(t - \frac{e^2}{6D}\right) \tag{6}$$

The intersection with the time axis of the submentioned line gives the “time lag” θ.

$$\theta = \left(\frac{e^2}{6D}\right) \tag{7}$$

The three main permeation parameters of a flat membrane made of any material can then be assessed.

- **Diffusion coefficient D**, obtained with equation (7) after having found θ experimentally.
- **Solubility coefficient S** [cm^3(STP)/cm^3.cmHg], obtained with Henry’s law $C = S.P$, where P [cmHg] is the pressure and C the gas concentration from (6) on the same side.
- **Permeation coefficient Pr** [cm^3(STP).cm²/cm^3.s.cmHg], obtained by multiplying D and S.

2.3 Numerical model for a type IV hydrogen storage tank

This model aims at predicting the diffusion behavior of hydrogen through a real liner of type IV tank as well as through a flat membrane. For the last, numerical and experimental results will be compared to check the model. The long-term objective is a full-numerical validation of the tanks permeation behavior. The model programming is based on the finite difference method with dimensionless quantities :

Flat membrane $$\frac{\partial \bar{C}_i}{\partial \bar{t}} = \frac{2}{h_i + h_{i-1}} \left(\frac{\bar{C}_{i+1} - \bar{C}_i}{h_i} - \frac{\bar{C}_i - \bar{C}_{i-1}}{h_{i-1}} \right) \quad (9)$$

Cylinder $$\frac{\partial \bar{C}_i}{\partial \bar{t}} = \frac{2}{h_i + h_{i-1}} \left(\frac{\bar{C}_{i+1} - \bar{C}_{i-1}}{2\bar{r}_i} + \frac{\bar{C}_{i+1} - \bar{C}_i}{h_i} - \frac{\bar{C}_i - \bar{C}_{i-1}}{h_{i-1}} \right) \quad (10)$$

Sphere $$\frac{\partial \bar{C}_i}{\partial \bar{t}} = \frac{2}{h_i + h_{i-1}} \left(\frac{\bar{C}_{i+1} - \bar{C}_{i-1}}{\bar{r}_i} + \frac{\bar{C}_{i+1} - \bar{C}_i}{h_i} - \frac{\bar{C}_i - \bar{C}_{i-1}}{h_{i-1}} \right) \quad (11)$$

Where $\bar{C}_i$ refer to the dimensionless concentration at point i, $\bar{r}_i$ is the dimensionless radius position of point , and h_i refer to the variable mesh size between point i and point $i + 1$.

According to the analysis presented by Scheichl [4], a formulation which only considers a derivation in space is proposed. Then, using the commercial software matlab and dedicated functions (ode15s, quad) make it possible to have an assessment of the concentration through the thickness. Regarding the geometry of a type IV hydrogen tank, it can be assumed that its permeation behavior is obtained by combining the numerical results obtained separately for a cylinder and for a sphere. This hypothesis is only acceptable for ordinary totally closed hydrogen tanks (without filler cap).

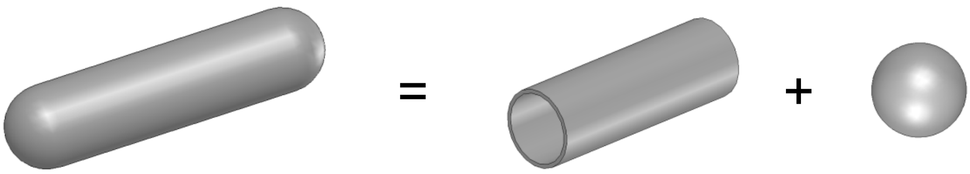

Figure 4: Geometrical decomposition of a type IV hydrogen tank.

The model is implemented in an easy-to-use program that allows to predict the permeation behavior of a structure depending on the shape, the material properties and the loading conditions. The results can be obtained numerically and graphically, under the form of a graph (Fig. 3) or cartography (Fig. 5). The latter represents the hydrogen concentration in regard of the time and wall thickness. On the figure here below, the blue color corresponds to the lowest concentration while the red color is used for the highest values.

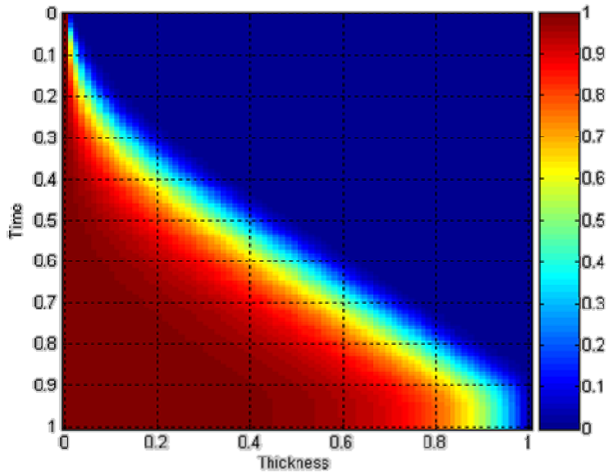

Figure 5: Evolution of concentration versus time and thickness.

3 Conclusion

Based on experimental investigations on flat membrane compared with both analytical modeling and numerical modeling, this study aims at predicting the permeation occurring in a type IV hydrogen storage tank which liner is made of polymer. Considering the first results that have been obtained up to now, the model turns out to be very promising. A good correlation was observed between theoretical, numerical and experimental approaches. Further developments will be carried out in order to improve the efficiency and accuracy of the program. The next step will consist in adding a mechanical aspect to take into consideration the free volume decrease under high pressure. It will be achieved by implementing the Cohen-Turnbull relationship [5] that will allow using non-constant diffusion coefficient.

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