Computer simulation of hydrogen permeability of structural materials through protective coating defect

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Abstract. In the context of problems of hydrogen and thermonuclear power engineering intensive research of the hydrogen isotopes properties is being conducted. Mathematical models help to specify physical-chemical ideas about the interaction of hydrogen isotopes with structural materials, to estimate the limiting factors and to significantly reduce the expenses of experimental research by means of numerical simulation for different parameters and experimental conditions (including extreme ones). Classical diffusion models are often insufficient. The paper is devoted to the models and numerical solution of the boundary-value problems of hydrogen permeability taking into account nonlinear sorption-desorption dynamics on the surface. Algorithms based on difference approximations. The results of computer simulation of the hydrogen flux from a structural material sample are presented.

1. Introduction

Interaction of hydrogen and its isotopes with solids has many applications [1–8]. It is sufficient to mention power engineering, protection of metals from hydrogen corrosion, design of chemical reactors, rocket and missile engineering. Hydrides help to retain substantial amounts of hydrogen: environmental-friendly energy source. Hence the high expectations are attached to hydrogen batteries and motors that avoid using high pressures or low temperatures. Some special topics are considered in [9–12]. Enthusiasts speak not only of hydrogen energy but also of hydrogen economy [5]. Reduction of hydrogen permeation through protective walls of structural materials is the most important objective when solving complex problems of hydrogen storage, hydrogen transport, and reduction of tritium content in protective systems of future thermonuclear reactors (the ITER project). Barrier of a structural material provides the necessary mechanical resistance of the construction, while superimposed protective coating is supposed to block migration of hydrogen atoms. Some areas of the material might face hydrogen and its isotopes directly due to defects in the protective coating. In [10], the model of hydrogen permeability through a cylindrical membrane with radius of the base L and height H was examined under assumption that diffusion is the only limiting process. The inlet surface $z = 0$ was covered with thin protective coating with a small (radius $r_0 < L$) defect called "pinhole defect". Hydrogen was able to permeate through it. The remainder of the inlet surface and the lateral surface of the cylindrical membrane were impermeable for hydrogen. Vacuum was created on the output side $z = H$. At the initial time the membrane contained no hydrogen. Pressure p of molecular hydrogen was instantly created at the inlet side. Relatively fast interjacent process was neglected (its speed depends on p, the material, and sample size). Then, in the first

approximation, concentration of dissolved hydrogen under defect can be supposed to be constant ($\bar{c}$), equilibrium with respect to the gas phase according to Sievert's law: $\bar{c} \propto \sqrt{p}$). Dissolved atomic hydrogen diffused to the outlet surface, recombinated into molecules, and desorbed. Mass-spectrometer registered the permeation flux. The boundary-value problem neglecting surface processes was analytically studied only for the case of an infinite plate ($L \to +\infty$). The main weakness of such definition of the problem is that the dynamics of surface processes which has attracted a lot of attention recently, is ignored in the model [10].

2. Diffusion model

As a basic model of hydrogen transfer inside the membrane we consider the boundary-value problem of hydrogen permeability with diffusion as the only limiting factor [10]:

$$\frac{1}{D}\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\cdot\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2}, \quad r \in (0, L),\ z \in (0, H),\ t \in (0, t_*), \tag{1}$$

$$c(0, r, z) = 0,\ r \in [0, L],\ z \in [0, H], \quad c(t, r, 0) = c_0,\ r \in [0, r_0], \tag{2}$$

$$\partial_z c(t, r, 0) = 0,\ r \in (r_0, L], \quad c(t, r, H) = 0,\ r \in [0, L],\ t \geqslant 0, \tag{3}$$

$$\partial_r c(t, L, z) = 0,\ \partial_r c(t, +0, z) = 0, \quad z \in [0, H],\ t \geqslant 0. \tag{4}$$

Here $c(t, r, z)$ is concentration of dissolved atomic hydrogen. The experiment is carried out at constant temperature $T = \overline{T}$. The material is nearly homogeneous, so c_0 and D are constants. For definiteness let $c_0 = \bar{c}$; values of $\bar{c}(T, p)$ can be found in reference books. The defect is small, we assume it round and situated in the center: this is not a fundamental constraint for numerical simulation. At time t_* the permeation flux $J(t)$ reaches the stationary value. The determination is asymptotic: $J(t) \approx \text{const}$, $t \geq t_*$. The boundary condition (2) corresponds to rapid (compared to t_*) establishment of local equilibrium on the inlet side.

The aim is to develop the algorithm of simulation of the flux of hydrogen from the outlet surface. For the model (1)–(4): $J(t) = -D\int_0^L \partial_z c(t, r, H)\, 2\pi r\, dr$. Iterative numerical algorithm is based on implicit difference schemes and the Thomas algorithm. Control of hydrogen balance is used for checking the calculation. We used the Richardson extrapolation to improve accuracy of the calculations. The method of grid condensation was used for $r_0 \ll L$.

Dimensionless form of the boundary-value problem. To present the results we pass to dimensionless variables, using values intrinsic for this problem: $u = c/c_0$, $\rho = r/L$, $\zeta = z/H$, $\tau = (D/L^2)t$. The value of L^2/D is treated as the characteristic time of concentration stabilization due to diffusion. In the areas with length-scale parameters comparable to L (on vertical direction, i.e., z-direction) diffusion is faster for $H \sim L$, due to vacuum from the outlet side. Denoting $\rho_0 = r_0/L < 1$, $R = L/H$, we get the boundary value problem:

$$\frac{\partial u}{\partial \tau} = \frac{1}{\rho}\frac{\partial}{\partial \rho}\Big(\rho\frac{\partial u}{\partial \rho}\Big) + R^2\frac{\partial^2 u}{\partial \zeta^2},\ \rho \in (0, 1),\ \zeta \in (0, 1), \quad u(\tau, \rho, 0) = 1,\ \rho \in [0, \rho_0],$$

$$\partial_\zeta u(\tau, \rho, 0) = 0,\ \rho \in (\rho_0, 1],\ \rho_0 < 1, \quad u(\tau, \rho, 1) = 0,\ \rho \in [0, 1],\ \tau \geqslant 0,$$

$$\partial_\rho u(\tau, 1, \zeta) = 0, \quad \partial_\rho u(\tau, +0, \zeta) = 0, \quad u(0, \rho, \zeta) = 0,\ \rho \in [0, 1],\ \zeta \in [0, 1].$$

Varying parameters are $R > 0$ and $\rho_0 \in (0, 1)$. We obtained an anisotropic diffusion equation: $D_\rho = 1$, $D_\zeta = R^2$. The smaller H (i.e., the thinner the membrane), the faster the diffusion in the ζ-direction. Coefficient D_ζ represents the ratio of the geometric characteristics. During the "time" τ the significant "length" in the ρ direction is $\sqrt{\tau}$, and in the ζ direction it is $R\sqrt{\tau}$. Steady-state (i.e., $\partial_\tau u \approx 0$) is determined by the value $\tau_* = (D/L^2)t_*$.

Let us introduce a dimensionless, average (on the base of the π square) outward flux

$$U(\tau) = -\frac{1}{\pi}\int_0^1 R^2 \partial_\zeta u|_{\zeta=1}\, 2\pi\rho\, d\rho.$$

The function $U(\tau)$ increases monotonically approaching asymptotically a steady-state value $U_* = U(\tau_*)$. If a protective coating is absent (formally consider $\rho_0 = 1$), we have a maximum of $U_* = R^2$: $\partial_\rho u = 0$, $\partial_\zeta u|_{\tau_*} = -1$. Original averaged flux can be expressed as follows:

$$I(t) \equiv \frac{J(t)}{\pi L^2} = \frac{Dc_0}{H} V(\tau) \ (\tau = DL^{-2}t), \quad V(\tau) = R^{-2}U(\tau) = -\frac{1}{\pi} \int_0^1 \frac{\partial u}{\partial \zeta}\Big|_{\zeta=1} 2\pi\rho \, d\rho.$$

The value of Dc_0/H is density of the permeation steady-state flux for the membrane without a protective coating ($\rho_0 = 1$). The number $V(DL^{-2}t) \in (0, 1)$ is a fraction of $I(t)$ in the highest possible density of the output flux Dc_0/H. Letting $\rho_0 = 1$ we have a maximum $V_* = 1$.

The range for the diffusion coefficient is fixed as $D: 10^{-7} - 10^{-5}$ cm^2/c. We will consider cylindrical membrane dimension as comparable with a coin (the barrier of a pipeline).

Output parameters of the computing experiment are the values τ_*, τ_0, U_* (V_*), where τ_0 is the delay time calculated by the formula $\tau_0 = \tau_* - S(\tau_*)/\dot{S}(\tau_*) = \tau_* - S(\tau_*)/U(\tau_*)$, $S(\tau) \equiv \int_0^\tau U(\tau) \, d\tau$ $\left(\dot{S} \equiv dS/d\tau\right)$. In the original variables we obtain $t_0 = t_* - \int_0^{t_*} J(t)dt/J(t_*)$. Geometrically this is the point of intersection of the axis t with asymptotes of the function $Q(t) = \int_0^t J(\tau)d\tau$ (the number of hydrogen atoms permeating through the membrane). The accuracy of calculation of $\tau_0(t_0)$ increases with increasing $\tau_*(t_*)$ taking into account the asymptotic behavior of the stabilized mode permeation flux. The time of stabilization of the permeation flux, the value of the steady-state flux, and the delay time are experimentally measured. These values serve as the input information for the inverse problem of evaluation of the kinetic parameters of hydrogen permeability using measurements; see, e.g. [12] ($\rho_0 = 1$)). Additionally, calculation checking was carried out for $\rho_0 = 1$, this case corresponds to a membrane without a protective coating. Calculations confirmed that hydrogen concentration is $u(\tau, \rho, \zeta) = 1 - \zeta$ ($\tau \geq \tau_*$) and the delay time through the plate of thickness ℓ is equal to $\ell^2/[6D]$, it is $1/[6R^2]$ using our notation. Besides we checked asymptotic behavior of $U_* \to R^2$ for $\rho_0 \to 1$.

Dimensionless characteristics τ_* and τ_0 weakly depend on radius of the defect. We restrict the discussion to the case of $\rho_0 < 0.2$, because this is the adopted limit of a protective coating. Functions $\tau_*(\rho_0)$ and $\tau_0(\rho_0)$ have extrema at $R < 1.5$ (derivative sign changes, in Fig. 1, 2). This is caused by growing influence of the boundary conditions (insulated lateral surface). Functions $\tau_*(\rho_0)$, $\tau_0(\rho_0)$ are monotone for $R \geq 1.5$. The curve for $R = 1.5$ is indicated by a dotted line. "Interfluve value" $R = 1.5$ is rather nominal. It separates relatively small and large values of R at the qualitative level. At the qualitative level we obtain the following results focusing on an "ideal" experimental error under 10% and not distinguishing output model fluxes under 1%. The influence of the boundary conditions with $r = L$ on stationary permeation flux is insignificant for $R = L/H > 3$, $\rho_0 < 0.2$; such membrane can be considered as a plate ($L \to +\infty$). This corresponds to the results by [10]: analytical methods of research are useable for $R > 3$. Practically, it is possible to estimate when permeation flux is proportional to the number of defects (or their density). The developed software allows to analyze spatial distribution of hydrogen in the membrane at any points of time (Fig. 3, 4).

3. Modification of the model taking into account the dynamics on the surface
The boundary conditions (2), (3) are replaced by ratio of the flux balance

$$\mu sp - bc^2(t, r, 0) = -D \frac{\partial c}{\partial z}\Big|_{z=0}, \ r \in [0, r_0], \quad bc^2(t, r, H) = -D\frac{\partial c}{\partial z}\Big|_{z=H}, \ r \in [0, L], \quad (5)$$

$J(t) = \int_0^L bc^2(t, r, H) \, 2\pi r \, dr$. Here b is the coefficient of bulk desorption (effective recombination [3]). Additionally, the inlet and outlet surfaces may have different properties, this is easily taken into account in the model: $b = b_1$ at $z = 0$ and $b = b_2$ at $z = H$. Formation and decomposition of hydrid phases are more difficult to be taken account (see [11]); we suppose
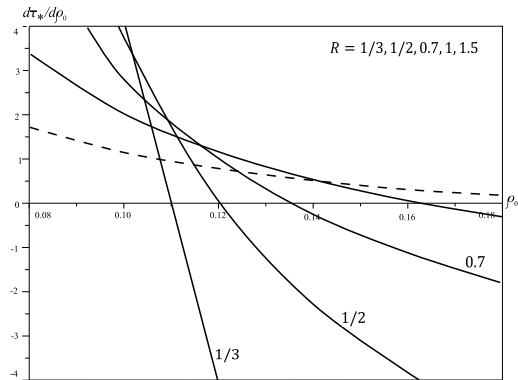
Figure 1. Rate of τ_*, $R \leq 1.5$ change.
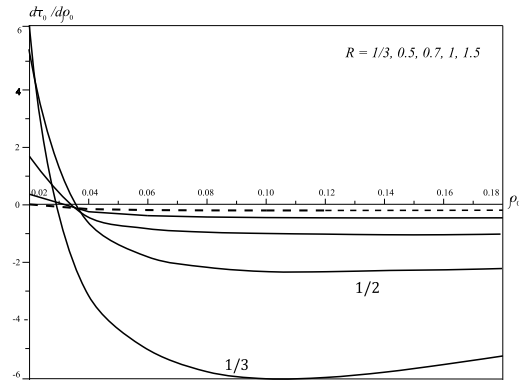
Figure 2. Rate of τ_0, $R \leq 1.5$ change.
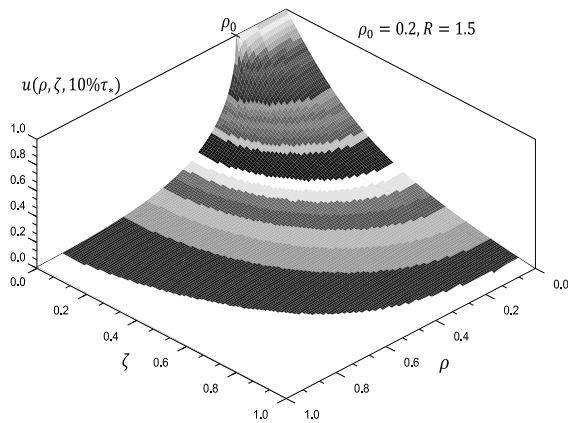
Figure 3. Concentration profile, $\tau = 0.1\tau_*$.
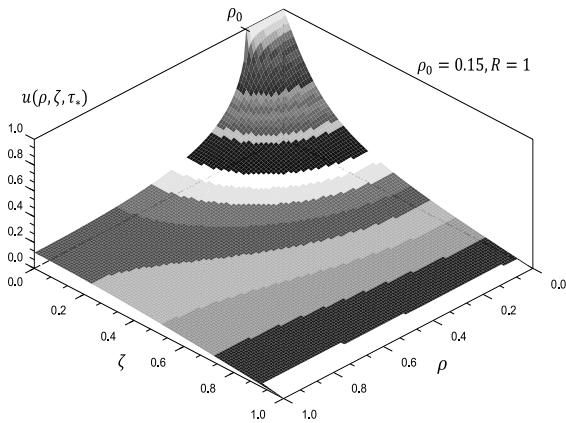
Figure 4. Steady-state concentration level.

they are not important. Vacuum is created at the outlet of the membrane, so resorption is ignored. Output desorption flux is counted in atoms ($[J] = 1/c$). In the equilibrium state the condition $\partial_z c = 0$ is replaced by $\mu s p = b\bar{c}^2$, sort of the Sievert's law $\bar{c} \propto \sqrt{p}$.

Numerical simulation makes it possible to estimate how fast the defect concentration under protective coating is stabilized and how concentration $c(t_*, r, 0)$ differs from the equilibrium level $\bar{c}$. In addition, information about sensitivity of $J(t)$ with respect to variations of the diffusion coefficient and surface processes ("derivatives" on D, b, s) is of special interest.

Let us pass to dimensionless variables: $u = c/c_0$, $\rho = r/L$, $\zeta = z/H$, $\tau = tD/L^2$, $R = L/H$, $\rho_0 = r_0/L$. Concentration c_0, $c_0 < \bar{c}$ for $\rho_0 = 1$ can be taken as a normalizing concentration. However, we accept $c_0 = \bar{c}$ ($u \leq 1$), having the extensive "equilibrium" reference information about metals and alloys available. For the purpose of the model we have $\bar{c} = \sqrt{\mu s p/b}$. Conditions (5) can be written in the form

$$\hat{p} - \hat{b}u^2(\tau, \rho, 0) = -\partial_\zeta u\big|_{\zeta=0}, \ \rho \in [0, \rho_0], \quad \hat{b}u^2(\tau, \rho, 1) = -\partial_\zeta u\big|_{\zeta=1}, \ \rho \in [0, 1], \qquad (6)$$

$\hat{b} \equiv bc_0 H/D$, $\hat{p} \equiv \hat{\mu} s p$, $\hat{\mu} \equiv \mu H/D c_0$, $c_0 = \bar{c}$. The pressure p of molecular hydrogen on the input surface is constant. The coefficient $\hat{b}$ is equal to the ratio of the local desorption density $b\bar{c}^2$ when concentration is close to the equilibrium concentration $\bar{c}$ to the density $D\bar{c}/H$ of the

permeation flux in the diffusion regime, when $c|_H = 0$, $\rho_0 = 1$, $t \geqslant t_*$. Besides, the outlet flux μsp is normalized by value $D\bar{c}/H$. For equilibrium state we have $\mu sp = b\bar{c}^2$, hence $\hat{b} = \hat{p}$. We denote this parametric variable by W. In the present model we obtain $W = HbS\sqrt{p}/D$ $\left(H\sqrt{p}F/D = L\sqrt{p}F/RD\right)$, where $F \equiv \sqrt{b\mu s}$, $S \equiv \sqrt{\mu s/b}$ is dissolution ($\bar{c} = S\sqrt{p}$).

W is called a transporting parameter when protective coating is absent ($\rho_0 = 1$) [3]: if $W \gg 1$ diffusion limits permeation; this is the diffusion limited regime, DLR. The asymptotic condition $W \ll 1$ corresponds to the SLR (surface limited regime). The transitory area is estimated within $W \in (10^{-2}, 10^4)$. For the problem under consideration when hydrogen permeates through a defect of the protective coating ($\rho_0 < 1$) we have three independent parameters R, ρ_0, W. The value of R^2 serves as a "diffusion coefficient" on the ζ direction, and W parametrizes the left parts of the boundary conditions (6): $W[1 - u^2(\tau, \rho, 0)]$, $Wu^2(\tau, \rho, 1)$.

Model with surface desorption. Boundary conditions (2), (3) are replaced by the following:

$$\partial_t q_0 = \mu sp - bq_0^2(t, r) + D\partial_z c\big|_0, \ r \in [0, r_0], \quad \partial_t q_H = -bq_H^2(t, r) - D\partial_z c\big|_{z=H}, \ r \in [0, L], \quad (7)$$

$c(t, r, 0) = gq_0(t, r)$, $c(t, r, H) = gq_H(t, r)$, $q_0 = q_H = 0$ $(t = 0)$, $J(t) = \int_0^L b\, q_H^2(t, r) \, 2\pi r \, dr$. Here q_0, q_H is the surface concentration on the inlet and outlet surfaces, $[q] = 1/\text{cm}^2$; g is the coefficient of concordance between the hydrogen atoms concentration in the near-surface bulk and on the surface (a coefficient of fast dissolution, $[g] = 1/\text{cm}$); b is the coefficient of surface desorption, $[b] = \text{cm}^2/\text{c}$ ($b = b_{\text{surf}} = g^2 b_{\text{vol}}$). Dynamic boundary conditions (7) allow to take into account and estimate storage effect of hydrogen atoms on the surface. These conditions are agreed (in the classical context) with zero initial data $c(0, r, z) = 0$ (as $t \to +0$). But keep in mind that, generally speaking, $\partial_t q_0(0, r) = \mu sp \gg 1$.

We may pass to the dimensionless problem, as it was done above. But the introduction of an additional parameter g does not reduce the number of independent numeric hydrogen permeability characteristics. Hence we illustrate the model using physical units of measurement. The following value specifies transport parameter estimation $W = HD^{-1}b_{\text{vol}}\bar{c} = HD^{-1}b\bar{c}/g^2$.

General geometric values of parameters for presented computing experiments (Fig. 5–6) were $L = 1$ cm, $H = 1/3$ cm, $r_0 = 0.1$ cm. Note that the flux decreases for increasing b, because desorption on the inlet surface predetermines hydrogen permeability to a greater extent (decreases the equilibrium level of concentration $\bar{c}$). Interesting effect is visible on Fig. 6. Steady state establishment time t_* decreases monotonically as the diffusion coefficient D (10^{-7}–10^{-5}) increases. In this case stabilized flux level J_* increases at first and then decreases, because hydrogen atoms come up to the lateral isolated surface faster, get "reflexed" and thus increase concentration, simultaneously decreasing gradient ($|\partial_z c|$) and the diffusion flux.

4. Conclusions

The paper presents the hydrogen permeability models of a cylindrical membrane made of a structural material in the presence of protective coating defect on the inlet surface. Iterative numerical algorithm based on implicit difference schemes and the Thomas algorithm is developed. The basic model assumes local equilibrium between gaseous and dissolved (under defect) hydrogen and diffusion as the only limiting factor. Further hierarchy of models consists in sequential adding adsorption-desorption processes described by nonlinear and dynamic boundary conditions. Limit transition is valid: with reduction of hydrogen atoms accumulation on the surface, and with increase of desorption coefficient and inlet pressure, the model with nonlinear dynamic boundary conditions becomes a basic model.

Some qualitative characteristics of permeability are presented. In particular, weak dependence for stabilization and delay times on radius of the defect is detected. It means that the informative value of time characteristics for inverse problem solution is low. The ratio is revealed wherein flux is insensitive to the isolation conditions (when flow is proportional
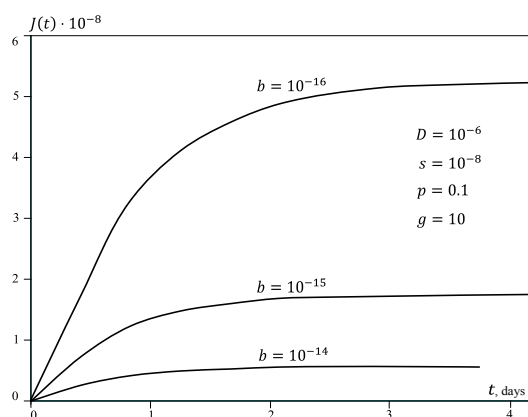
Figure 5. Effect of a desorption coefficient.
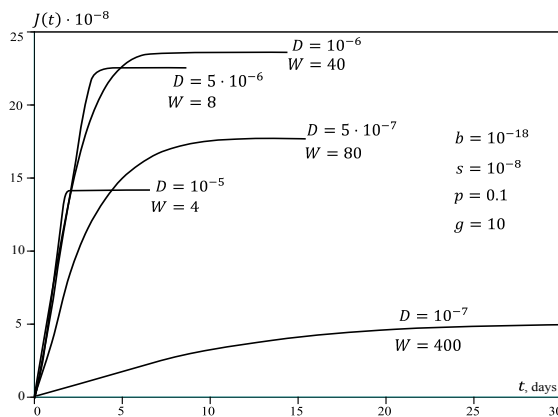
Figure 6. Effect of a didffusion coefficient.

to the number of such defects). It allows to reduce experimental cost. The flux decreases for increasing desorption coefficient, because desorption on the inlet surface predetermines hydrogen permeability to a greater extant (decreases the equilibrium level of concentration) than provides outward flux on the output surface. Steady state establishment time decreases monotonically as the diffusion coefficient increases. In this case, stabilized flux level increases at first and then decreases. Presented nonlinear effects should be taken into account while experimental curves processing to estimate limiting factors of hydrogen permeability.

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