

PARAMETRIC IDENTIFICATION OF HYDROGEN PERMEABILITY MODEL BY DELAY TIMES AND CONJUGATE EQUATIONS

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Introduction

One of the effective research methods of hydrogen interaction with construction materials is the method of permeability [1]. At one side of a membrane the constant pressure of H₂ is maintained at the fixed temperature, and about other one gas is pumped out by vacuum system. The membrane does not contain hydrogen at initial time instant. On outlet side a desorption flux J is determined. The dependence $J = J(t)$ contains the information about physical and chemical transfer processes and is used for identification of kinetic parameters. The model in the form of Dirichlet boundary-value problem for diffusion equation is used in most of papers. In that case the equilibrium concentration is set on the inlet side, and zero concentration – on the outlet side. Under certain experimental conditions it is allow to determine the diffusion coefficient by delay time with enough high precision. But thus, we do not take into account nonlinear dynamical sorption-desorption processes. If these processes are essential then «tabulated data» of diffusion coefficient is only initial approximation. The algorithms of processing of permeability experimental curves, which would guarantee uniqueness of definition of kinetic parameters set of diffusion and sorption-desorption, are necessary. Cut-and-try approach is effective if there is enough information content about material, which allow from a set of coefficients (at which experimental and modelling curves practically coincide) to choose a «correct» set of data. Non-uniqueness of such choice is one of the reasons of parameter estimations differences by experimental data. The subsequent computer modelling (with the purpose of reduction of research expenses, especially for extremal conditions of a material operation) can lead to essentially various qualitative conclusions.

The work is devoted to uniqueness problem and information content of experiment.

Mathematical model

We consider the model of hydrogen transfer taking into account diffusion, reversible capture by traps, dissolution and desorption [2]:

$$\frac{\partial c}{\partial t}(t, x) = D \frac{\partial^2 c}{\partial x^2}(t, x) - a_1 c(t, x) + a_2 z(t, x),$$

$$\frac{\partial z}{\partial t}(t, x) = a_1 c(t, x) - a_2 z(t, x), \quad t \in (0, t^*),$$

$$c(0, x) = \varphi(x), \quad z(0, x) = \psi(x), \quad x \in [0, \ell],$$

$$\frac{dq_0}{dt} = \mu s p_0(t) - b q_0^2(t) + D \frac{\partial c}{\partial x}(t, 0), \quad c_0 = g q_0,$$

$$\frac{dq_\ell}{dt} = \mu s p_\ell(t) - b q_\ell^2(t) - D \frac{\partial c}{\partial x}(t, \ell), \quad c_\ell = g q_\ell.$$

Here $c(t, x)$ is for concentration of dissolved hydrogen, $c_0 = c(t, 0)$, $c_\ell = c(t, \ell)$; $z(t, x)$ is for concentration of H captured by traps; D – diffusion coefficient; $q_{0,\ell}(t)$ – surface concentration; g – quick dissolution coefficient; μ – kinetic constant; s – adhesion coefficient of hydrogen in gas phase to a surface; b – desorption coefficient; a_i – parameters of capture and release by traps; $p_{0,\ell}(t)$ – pressures of H₂ from the inlet and outlet sides of a membrane. Pressure p_0 is considered small enough that concentrations c , z were sufficiently small: model parameters depend only on temperature. For the same reason the traps capacity is not also considered: for example, $a_1 c [1 - z/z_{\max}] \approx a_1 c$ at $z \ll z_{\max}$. We assume that the evacuating system is powerful enough and therefore very small amount of desorbed hydrogen returns back to the outlet side: $\mu s p_\ell \approx 0$. Desorption outlet flux density $J(t) = b q_\ell^2(t)$ is determined using p_ℓ . Below we suppose that pressure of molecular hydrogen from the inlet side is constant, i.e. $p_0(t) = \bar{p}_0$. Model coefficients depend on temperature in an Arrhenius way, for instance, $D = D(T) = D_0 \exp\{-E_D / RT(t)\}$.

Parametric identification

1. *The analysis of stationary permeability.* It is impossible to determine the model parameters uniqueness by values of a stationary level \bar{J} of a penetration flux at various inlet pressures. Only certain combinations of parameters are determined.

Hence, it is necessary to analyze transients. But in this case it is also not enough «standard» curves of saturation (permeability). Moreover, it is impossible to distinguish the accepted model from simplified one with Dirichlet boundary conditions (certainly, values of parameters will be different). Therefore we suppose to increase information content of permeability method as follows. When outlet flux becomes stabilize it is necessary to raise the pressure steeply and wait for a new level of stationary desorption flux. The reason is not only distinction of inlet pressures: at the beginning the initial concentration in membrane equal to zero, but after pressure jump the initial concentration is stationary which corresponds to previous pressure.

2. *A conjugate equations method.* The main idea consists in the following [3]. We consider for definiteness the basic diffusion equation $c_t = Dc_{xx}$. One can make identical transformations with integration by parts:

$$0 = \int_0^t \int_0^l \psi(t, x)(c_t - Dc_{xx}) dx dt = \dots = \int_0^t \int_0^l c(t, x)(\psi_t + D\psi_{xx}) dx dt + f.$$

Item f contains the variables connected with boundary conditions. Namely, the measurements are made on the bound. If now we choose the solution of the conjugate equation $\psi_t = -D\psi_{xx}$, then obtain the equation $f = 0$, connecting measurements with estimated parameters. Note that for the conjugate equation initial and boundary conditions are cancelled (the main difficulties are connected with these conditions during solution of boundary-value problems). There are infinitely many functions ψ , that allows to form a system of equations for parameters estimation.

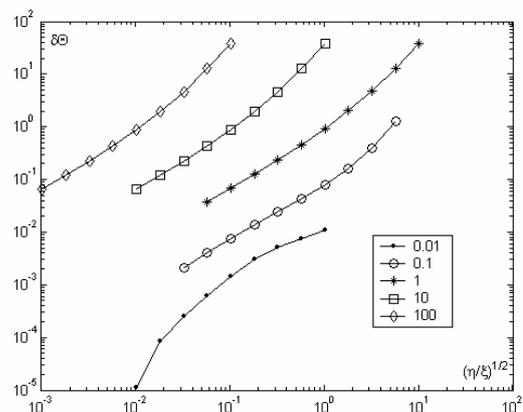
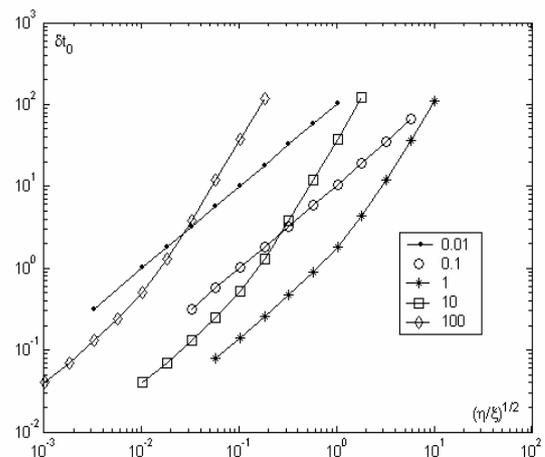
3. *Delay time.* For the considered model the expression for time-delay of outlet flux (cross point of asymptote to hydrogen permeability curve and time axis) is received. That together with a conjugate equations method allows to construct the iterative computing algorithm. It allows to uniquely determine the kinetic parameters of hydrogen permeability.

Computing experiments

Testing of algorithm is made in a wide range of model parameters. In particular, we find a saddle point effect with respect to dissolution coefficient g . A commensurability scale for bulk and surface processes is needed to introduced: diffusion time $\xi = \ell^2 / 2D$, surface time $\eta = 2 / \sqrt{bP}$ and so-called «splash-time» $\Theta = \int_0^{t^*} [-Dc_x - \bar{J}] d\tau / \bar{J}$

($x=0$). Let t_0 be the delay time, $\tilde{t}_0 = t_0 - t_0^I$, $t_0^I = \ell^2 / 6D$, $\tilde{\Theta} = \Theta - 2t_0^I$. Upper index I corresponds the situation when the considered boundary-value problem degenerates to Dirichlet problem. For \tilde{t}_0 and $\delta t_0 = \tilde{t}_0 / \xi$ we observe «inflection» with respect to $\nu \equiv \sqrt{g\ell}$ (the values of parameter ν is in the legend). But for $\tilde{\Theta}$ and $\delta\Theta = \tilde{\Theta} / \xi$ there is a uniform dependence.

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References

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