

INFLUENCE OF THE DIRECTION OF FLOWS ON THE BASIC TECHNICAL CHARACTERISTICS OF MEMBRANE APPARATUSES WITH CAPILLARIES PERMEABLE TO HYDROGEN

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A system of differential equations and boundary conditions which describes the distribution of the pressure and the flow rate of hydrogen inside a hydrogen-permeable capillary with a closed end is obtained. The algorithm of solution is given. It is shown that the direction of flows (concurrent flow-counterflow) in the high-pressure cavity exerts no substantial influence on the technical characteristics of the membrane apparatus. The influence of the design parameters of the capillaries on the basic characteristics of operation of the apparatus is investigated.

The cost of elements made of palladium alloys constitutes one basic component of the price of high-temperature membrane apparatuses intended to extract hydrogen of special purity from gaseous mixtures. Therefore, optimization of the design and technological parameters of their operation is a necessary stage of the design work.

The influence of the direction of flows (concurrent flow-counterflow) in a high-pressure cavity manifests itself only in the presence of the hydraulic resistance in a low-pressure cavity. Below, we analyze the influence of the direction of flows in apparatuses equipped with tubular membrane elements. The analogous problem for plane membrane elements has been considered in [1].

It is well known that the larger the pressure difference a membrane can withstand, the larger the hydrogen flow that can be allowed to pass through its unit area. Tubular membrane elements can withstand larger differences of pressures than plane elements. The magnitude of the permissible pressure difference is bounded by the wall thickness and the tube diameter. The smaller the diameter, the larger the pressure difference that can be withstood by a tube and the larger the number of tubes that can be located in a unit volume of the apparatus. On the other hand, the smaller diameter corresponds to the increased hydraulic resistance within the tube and consequently the decreased hydrogen flow in it. In [2], it has been shown that the diameter and the thickness of the wall can proportionally be changed in the process of manufacture of capillaries. As follows from the Lamé formulas, the stability of them to external loads is preserved. This circumstance can be taken into account in optimizing the geometric parameters of capillaries.

To select the optimum relations between geometric and technological parameters it is desirable to have mathematical expressions relating them. The analysis of the works indicated in [3] and in other references shows that, for various reasons, it is quite difficult to use the results of the earlier investigations for engineering calculations. The passage of only pure hydrogen through membranes made of palladium alloys enables one to substantially simplify the description of the processes occurring in capillaries and to develop mathematical models suitable for calculations.

The model proposed is based on the fact that the final stage of passage of hydrogen through the membrane is desorption from the interior wall of the capillary. Therefore, the longitudinal velocity of the flow on the interior capillary surface can be considered to be equal to zero. Evaluation of the Reynolds number ($Re \ll 1000$) shows that flow in the tubes with a closed end in question is exclusively laminar in character. The equality of the longitudinal velocity to zero enables us to use the Poiseuille-Hagen formula (whose derivation has been reproduced in [4]) to calculate the pressure difference in an area element:

$$dp = \lambda \frac{1}{d} \frac{\rho u^2}{2} dz. \quad (1)$$

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It is assumed in the model that the relationship between the hydrogen flow through the membrane and the pressure difference on it is described by the well-known Siverts–Richardson formula that has the form (in the notation introduced)

$$dQ = \frac{\gamma}{\delta} (p_v^r - p^r) dF. \quad (2)$$

The exponent r allows for the presence of the dissociation of the gas in its adsorption and dissolution (if the gas does not dissociate at all, $r = 1$; for a dissociating biatomic gas $r = 1/2$). According to the data of Baichtok et al. [5–7], the values of r differ strongly and are in the limits $[1/2 \leq r \leq 1]$.

It can be shown that for $r = 1$ and the absence of the hydraulic resistance in the high-pressure cavity the basic parameters of high-temperature membrane apparatuses in the regime of total displacement are related by

$$F_0 = \frac{Q_0 \delta (1 - X_0)}{p_{v0} \gamma (1 - b_1)^2} \left[\frac{(X_0 - X_r) (1 - b_1)}{(1 - X_r) (1 - X_0)} + \ln \left(\frac{(X_0 - b_1) (1 - X_r)}{(X_r - b_1) (1 - X_0)} \right) \right], \quad (3)$$

while in the regime of total mixing they are related by the relation

$$F_0 = \frac{Q_0 \delta (X_0 - X_r)}{\gamma (X_r - b_1) (1 - X_r) p_{v0}}, \quad (4)$$

where $b_1 = p_2/p_{v0}$.

In [8–10], it has been shown that if $r = 1/2$, the corresponding formulas have the form

$$F_0 = \frac{Q_0 \delta (1 - X_0)}{\gamma \sqrt{p_{v0}}} [J(X_0) - J(X_r)], \quad (5)$$

where

$$J(X) = m_0 \left[\frac{\sqrt{X} + b}{1 - X} + m_1 \ln(1 - \sqrt{X}) + m_2 \ln(1 + \sqrt{X}) + m_3 \ln(\sqrt{X} - b) \right],$$

$$m_0 = \frac{1}{1 - b^2}, \quad m_1 = -\frac{1 + b}{2(1 - b)}, \quad m_2 = \frac{1 - b}{2(1 + b)}, \quad m_3 = \frac{2b}{1 - b^2}, \quad b = \sqrt{\frac{p_2}{p_{v0}}}, \quad (6)$$

$$F_0 = \frac{Q_0 \delta (X_0 - X_r)}{\gamma (\sqrt{X_r} - b) (1 - X_r) \sqrt{p_{v0}}}.$$

These expressions are a basis for comparison in evaluating the influence of the direction of flows on the basic characteristics of high-temperature membrane apparatuses with allowance for the hydraulic resistance of capillaries.

In this work, we consider three versions of the direction of flows in high-temperature membrane apparatuses: concurrent flow, counterflow, and cross flow. The last version corresponds to the regime of total mixing.

The element of a high-temperature membrane apparatus is shown in Fig. 1. The flow of the initial mixture Q_0 with concentration of hydrogen X_0 enters the high-temperature cavity. Part of the flow, upon extraction of the hydrogen, leaves the cavity with the retant flow Q_r and concentration of hydrogen X_r . The other part — pure hydrogen — passes through the lateral capillary wall and leaves the element with the permeate flow Q_p .

Assuming that hydrogen is an ideal gas for

$$\lambda = \frac{64}{\text{Re}}, \quad \text{Re} = \frac{4g}{\pi d \eta}, \quad g = \rho u f, \quad g = \rho_{\text{no}} Q, \quad \rho = \rho_{\text{no}} \frac{p}{T} \frac{T_{\text{no}}}{p_{\text{no}}}, \quad f = \frac{\pi d^2}{4}, \quad dF = (\pi d) dz, \quad p_v = p_{v0} X$$

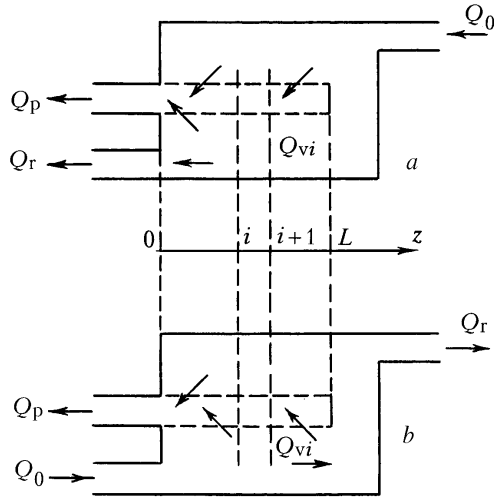


Fig. 1. Schematic diagram of the element of a membrane apparatus: a) concurrent flow; b) counterflow.

and introducing the dimensionless parameters

$$\alpha = \frac{Q_p}{Q_0}, \quad w = \frac{p}{p_2}, \quad v = \frac{Q_v}{Q_0}, \quad \omega = \frac{z}{L}, \quad s = \frac{Q}{Q_0}, \quad b = \left(\frac{p_2}{p_{v0}} \right)^r,$$

we transform Eqs. (1) and (2) and the boundary conditions in all the versions to the form

$$\frac{dw}{d\omega} = m_v \frac{s}{w}, \quad (7)$$

$$\frac{ds}{d\omega} = -m_s (X^r - bw^r), \quad (8)$$

$$\omega = 0, \quad s = \alpha, \quad w = 1, \quad (9)$$

$$\omega = 1, \quad s = 0, \quad (10)$$

where

$$m_v = \frac{128}{\pi} \frac{p_{no}}{T_{no}} \eta T \frac{L}{d^4} \frac{Q_0}{p_2}, \quad (11)$$

$$m_s = \frac{\pi d L \gamma p_{v0}^r}{\delta Q_0}. \quad (12)$$

From the equations of balance of the substance and hydrogen in the i th cross section it follows that: for the concurrent flow $v + s = 1$,

$$X = \frac{X_0 - s}{1 - s}; \quad (13)$$

for the counterflow $v - s = 1 - \alpha$,

$$X = \frac{X_0 - \alpha + s}{1 - \alpha + s}; \quad (14)$$

for the cross flow (total mixing in the high-temperature chamber)

$$X = X_r = \frac{X_0 - \alpha}{1 - \alpha}. \quad (15)$$

The resultant system of differential equations and boundary conditions describes the distribution of the pressure and of the hydrogen flow inside the capillary and the distribution of the hydrogen concentrations along the high-temperature chamber. Solution can be carried out by the Runge–Kutta method of numerical integration or the Euler method. For this purpose the capillary length is arbitrarily subdivided into n equal intervals and the system of differential equations and boundary conditions is transformed to the difference form

$$s_{i+1} = s_i + \Delta s_i, \quad (16)$$

$$w_{i+1} = w_i + \Delta w_i, \quad (17)$$

$$i = 0, \quad s_i = \alpha, \quad w_i = 1, \quad (18)$$

$$i = n, \quad s_i = 0. \quad (19)$$

Algorithm of Solution. For the prescribed quantities $d, L, \delta, \gamma, p_{v0}, p_2, p_{no}, T, T_{no}, Q_0, X_0$, and η we determine m_v and m_s according to formulas (11) and (12); we find the minimum possible value of the concentration of hydrogen $X_{r \min} = p_2/p_{v0}$ and the maximum possible value of the separation of flows $\alpha_{\max} = (X_0 - X_{r \min})/(1 - X_{r \min})$ [8, 9]; we prescribe α in the limits $0 < \alpha < \alpha_{\max}$; we determine the quantities Δs_i and Δw_i for $i = 1, 2, \dots$, and $n - 1$ according to the formulas of the adopted method of solution: in the Euler method, these are $\Delta s_i = -m_s(X_i^r - bw_i^f)\Delta\omega$ and $\Delta w_i = m_v \frac{s_i}{w_i}\Delta\omega$, where $X_i = (X_0 - s_i)/(1 - s_i)$ for the concurrent flow, $X_i = (X_0 - \alpha + s_i)/(1 - \alpha + s_i)$ for the counterflow, and $X_i = X_r = (X_0 - \alpha)/(1 - \alpha)$ for the cross flow; we compute s_{i+1} and w_{i+1} according to formulas (16) and (17). If $|s_n| > \varepsilon$ (ε is the prescribed accuracy of calculation), we take another value of α and repeat the calculation; if $|s_n| \leq \varepsilon$ we find all the quantities sought in the process of calculation.

In the case of the appropriate selection of the number of intervals ($n \geq 100$), the results of the numerical and analytical [11] calculations of the cross-flow regime coincide with the required accuracy.

The influence of the direction of flows on the technicoeconomic characteristics of high-temperature membrane apparatuses is most pronounced if the flow rates of the permeate are the same. Therefore, we have illustrated the capabilities of the model proposed by calculating the quantities Q_0, α, X_r , and $\delta F\%$ for $Q_p = \text{const}$.

The values of the permeabilities of the membranes have been determined from the results of processing of 10 points of the experimental dependence $Q_p(Q_0)$ given in [1]. It has finally been established that a value of $r = 1$ in formula (3) corresponds to $\gamma = 0.279 \cdot 10^{-12} \text{ m}^2/(\text{sec} \cdot \text{Pa}^{1/2})$ and $\sigma = 6.2\%$, while $r = 1/2$ in (5) corresponds to $\gamma = 0.302 \cdot 10^{-9} \text{ m}^2/(\text{sec} \cdot \text{Pa}^{1/2})$ and $\sigma = 2.7\%$.

Consequently, a value of $r = 1/2$ is in better agreement with experimental data.

Calculation results are given in Table 1 and Fig. 2. From the table it is seen that, despite the increased pressure difference inside the capillary in the regime of concurrent flow, it corresponds to lower flow rates of the initial mixture and a lower area loss. A comparison of the versions shows that the advantages of the concurrent flow are insignificant as compared to the counterflow. The cross flow, despite the intermediate value of the pressure difference, requires a substantially higher flow rate of the initial mixture.

In the cases considered, $\sim 60\%$ of the effective membrane area is lost because of the hydraulic resistance of the capillaries for $d = 0.35 \text{ mm}$ and $L = 2 \text{ m}$. A comparison of the parameters which correspond to diameters of 0.7 mm and 0.35 mm (with proportional change in the wall thickness) shows that in the first case the volume of the ex-

TABLE 1. Influence of the Diameter of the Capillary and the Direction of Flows on the Basic Parameters of a High-Temperature Membrane Apparatus for $r = 1/2$ and 1 ($Q_p = 4 \text{ cm}^3/\text{sec}$, $p_{v0} = 1 \text{ MPa}$, $p_2 = 0.125 \text{ MPa}$, $T = 873 \text{ K}$, $X_0 = 0.75$, and $L = 2 \text{ m}$)

Parameters	$d = 0.7 \text{ mm}$, $\delta = 0.1 \text{ mm}$, $V = 34.9 \text{ cm}^3$			$d = 0.35 \text{ mm}$, $\delta = 0.05 \text{ mm}$, $V = 8.7 \text{ cm}^3$		
	concurrent flow	counterflow	cross flow	concurrent flow	counterflow	cross flow
$r = 1/2$, $\gamma = 0.302 \cdot 10^{-9} \text{ m}^2/(\text{sec} \cdot \text{Pa}^{1/2})$						
Q_0 , cm^3/sec	5.714	5.738	7.489	16.05	16.74	30.56
w_p	1.278	1.168	1.224	2.912	2.844	2.879
$\delta F\%$	9.921	12.11	8.605	62.71	63.09	62.86
α	0.700	0.697	0.534	0.249	0.239	0.131
X_r	0.166	0.175	0.4633	0.667	0.672	0.712
$r = 1$, $\gamma = 0.279 \cdot 10^{-12} \text{ m}^2/(\text{sec} \cdot \text{Pa})$						
Q_0 , cm^3/sec	5.749	5.764	7.571	7.410	7.603	11.99
w_p	1.290	1.157	1.226	3.060	2.693	2.884
$\delta F\%$	7.490	8.974	5.890	53.84	55.77	53.43
α	0.696	0.694	0.528	0.540	0.526	0.334
X_r	0.178	0.183	0.470	0.457	0.473	0.625

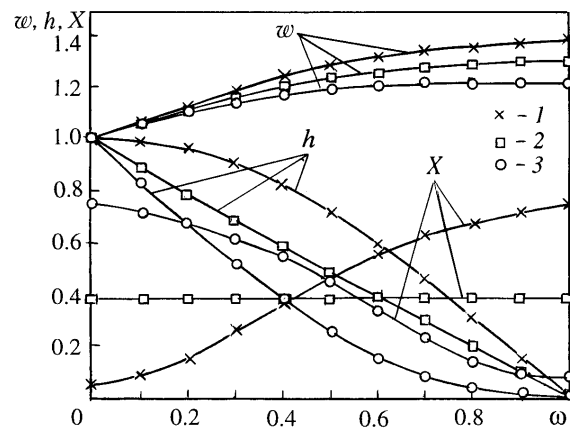


Fig. 2. Distribution of the pressure ($w = p/p_2$), the flow rate ($h = Q/Q_p$), and the concentration (X) along the capillary $r = 1/2$, $X_0 = 0.75$, $\gamma = 0.302 \cdot 10^{-9} \text{ m}^2/(\text{sec} \cdot \text{Pa}^{1/2})$, $d = 0.35 \text{ mm}$, $\delta = 0.05 \text{ mm}$, $p_{v0} = 20 \text{ MPa}$, $p_2 = 1 \text{ MPa}$, and $Q_p = 22 \text{ cm}^3/\text{sec}$: 1) concurrent flow; 2) cross flow; 3) counterflow.

pensive material of the capillaries for manufacture of apparatuses of equal capacity decreases four times, while the flow rate of the initial mixture increases. The smaller the diameter, the stronger the influence of the parameter r on the results of calculation of the basic characteristics of a high-temperature membrane apparatus.

From Fig. 2 it is clear that the pressure increase (dp/dz) at the open end of the capillary is the largest in the regime of concurrent flow. The pressure attains its maximum at the closed end where $dp/dz = 0$. The increase in the flow rate at the closed end is the largest in the case of a concurrent flow and the smallest in the case of a counterflow. At the open end, the increase in the flow rate is the largest in the case of a counterflow.

The model proposed reflects the basic interrelations between the parameters of the process of production of hydrogen of special purity in high-temperature membrane apparatuses equipped with capillaries of palladium alloys. The model makes it possible to optimize the parameters of the capillaries (d , L , and δ) and of the technological regime (Q_0 , Q_r , Q_p , p_{v0} , p_2 , and T) with allowance for the hydraulic resistance in the low-pressure cavity and the direction of flows in the high-temperature cavity.

NOTATION

d , inside diameter, m; F , interior-surface area, m^2 ; F_0 , interior-surface area corresponding to the absence of hydraulic resistance, m^2 ; f , free area, m^2 ; g , variable mass flow rate of hydrogen, kg/sec; L , length, m; p_1 , p , and p_2 , pressure of hydrogen in the capillary at the closed end, variable pressure, and pressure at the open end, Pa; p_{no} , pressure of hydrogen under normal conditions, Pa; p_v and p_{v0} , partial pressure of hydrogen variable along the exterior surface and pressure in the high-pressure cavity, Pa; T , temperature in the high-temperature membrane apparatus, K; T_{no} , temperature under normal conditions, K; Q and Q_p , variable rate of flow of hydrogen and rate of flow coming out of the high-pressure cavity, m^3 /sec; Q_0 , Q_v , Q_{vi} and Q_r , rate of incoming, variable, running in the i th cross section, and coming out flow of mixture, m^3 /sec (all the parameters refer to one capillary; the volumetric flow rates are reduced to normal conditions: $p_{no} = 10^5$ Pa and $T_{no} = 273$ K); u , average-over-the free area variable velocity of the hydrogen flow along the capillary, m/sec; V , volume of palladium alloy for the high-temperature membrane apparatus of output $1\text{ m}^3/\text{h}$, cm^3 ; $w_p = p_1/p_2$, maximum pressure difference inside the capillary; X_0 , X , and X_r , concentration of hydrogen in the incoming flow of the mixture, the running flow, and the flow coming out of the high-pressure cavity; z , coordinate axis with the origin at the open end of the capillary; α , volume of the permeate produced from 1 m^3 of the initial mixture, m^3/m^3 ; γ and γ_k , permeability of the membrane and permeability corresponding to the k th point, $\text{m}^2/(\text{sec}\cdot\text{Pa}^r)$; δ , membrane thickness, m; $\delta F\% = (1 - F_0/F)100$, loss of the effective area of the membranes because of the hydraulic resistance inside the capillary, %; η , dynamic viscosity of hydrogen, Pa·sec; λ , coefficient of resistance; ρ and ρ_{no} , variable density of hydrogen in the capillary and under normal conditions, kg/m^3 ; $\sigma =$

$$\frac{1}{\gamma} \sqrt{\sum_k^{10} \frac{(\gamma_k - \gamma)^2}{9}}$$

, standard deviation. Subscripts and superscripts: r , exponent; 0, inlet; i , number of the interval; n , number of intervals; no, normal conditions; p, permeate; r, retant; v, variable, v0, constant.

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