STUDY OF PUMPING EFFECT IN FLOW-THROUGH ELECTROLYSERS

Ivo Roušar, Michal Provazník and Pavel Stuhl
Prague Institute of Chemical Technology,
Department of Inorganic Technology, 166 28 Prague 6

Received July 1st, 1981

In electrolysers with recirculation, where a gas is evolved, the pumping of electrolyte from a lower to a higher level can be effected by natural convection due to the difference between the densities of the inlet electrolyte and the gaseous emulsion at the outlet. An accurate balance equation for calculation of the rate of flow of the pumped liquid is derived. An equation for the calculation of the mean volume fraction of bubbles in the space between the electrodes is proposed and verified experimentally on a pilot electrolyser. Two examples of industrial applications are presented.

In technical practice, circulation of electrolyte between a reservoir (or reactor) and the electrolyser proper is effected by means of a pump placed in the connecting tube. If a gas is evolved in the electrolyser, in the case of a suitable arrangement it is possible to achieve that the gas emulsion (with a lower density) streams into the reservoir, while the solution from the reservoir (without the gas bubbles) passes into the electrolyser. This principle, is *e.g.*, utilized in water electrolysis[1] and in electrochemical production of chlorates[2]. It is energetically acceptable if no high rates of flow are required, and it operates reliably since there are no moving parts and no maintenance problems. For high rates of flow or large pumping height, pumping by the gas lift is energetically too expensive.

THEORETICAL

The calculation of the pumping rate is based on a pressure balance in the corresponding hydraulic circuit[3] (Fig. 1). Bubbles are formed in the inter electrode space, so that the mean relative content of the gas phase in a part of the circuit of height L_E is equal to $\bar{\alpha}$. In a part of the tubing above the electrolyser of a height L_H the mean content of the gas phase is equal to α_T, which is higher than $\bar{\alpha}$. The electrolyte in the separator and in the connecting pipe of height L_T is without bubbles. Circulation of the electrolyte is caused by a difference between the densities of the electrolyte at the inlet and in a part of the electrolyser. The power consumed per unit volume of the flowing electrolyte (W/(m^3/s) or J/m^3) is changed irreversibly to heat (by friction); any heat evolved in the system is conducted to the surroundings so that the system can be considered approximately isothermal.

Let us choose two levels, 1 – 1 and 2 – 2 (Fig. 1), at which the balance of the kinetic and potential energies will be made. Then,

$$\Delta E_{pot} = g\varrho'_E L_T - g\varrho'_E L_E(1 - \bar{\alpha}) - g\varrho'_E L_H(1 - \alpha_T)\,, \tag{1a}$$

$$\Delta E_{kin} = \tfrac{1}{2}\varrho'_E(\dot{V}_E/F_{11})^2 - \tfrac{1}{2}\varrho'_E(1 - \alpha_T)(\dot{V}_E/F_{22})^2\,, \tag{1b}$$

$$\Delta E_{diss} = \Delta p_M + \Delta p_p + \Delta p_z\,. \tag{1c}$$

The second term in Eq. (*1a*) involves the mean content of bubbles, $\bar{\alpha}$, and the third one the content of bubbles in the top portion of the electrolyser, α_T. The cross-sectional areas of flow at the levels 1 – 1 and 2 – 2 are denoted as F_{11} and F_{22}. It should be noted that for closed systems the planes 1 – 1 and 2 – 2 should fuse to a single one, so that term ΔE_{kin} would be equal to zero.

The terms in Eq. (*1c*) correspond to losses due to friction in the section containing a mixture of the gas and electrolyte (Δp_M) or electrolyte only (Δp_p), and energy dissipated in placed where the shape of the tube changes (Δp_z).

The above equations can be combined to give

$$g\varrho'_E L_T - g\varrho'_E L_E(1 - \bar{\alpha}) - g\varrho'_E L_H(1 - \alpha_T) = \Delta p_M + \Delta p_p + \Delta p_z + \\ + \frac{1}{2}\left(\varrho'_E\,\frac{v_E^2}{1 - \bar{\alpha}} - \varrho'_E v_p^2\right). \tag{1d}$$

Here, g denotes acceleration of gravity, ϱ'_E electrolyte density, L_T height of the tubing filled with pure electrolyte, L_E height of the electrolyser filled with the gas emulsion

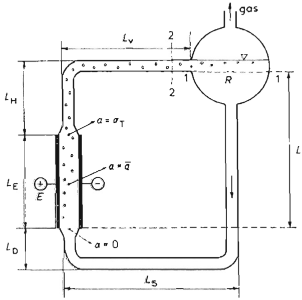

FIG. 1

Scheme of electrolyser with reservoir with electrolyte circulation caused by the formation of gas bubbles. L_E electrode height; L_H vertical part of outlet tubing; L_D vertical part of inlet tubing; L_v, L_s length of connecting tubing at the outlet and inlet; L_T height of inlet tubing (reactor) filled with electrolyte; E electrolyser; R separator; direction of flow is denoted by arrows with a mean bubble volume fraction $\bar{\alpha}$, L_H length of the tubing above the electrolyser filled with gas emulsion with a bubble volume fraction α_T. The pressure loss due to frition between the electrodes is denoted as Δp_M, in the inlet tubing Δp_p, and the pressure loss due to shape change of the tubing (or change in the direction of flow) Δp_z. The velocity of flow of the electrolyte between the electrodes is denoted v_E and in the inlet tubing as v_p.

The basic physical parameters for the gas emulsion with a bubble volume fraction α are given as

$$\varrho'_M = \varrho'_E(1 - \alpha), \quad \mu_M = \mu_E(1 - \alpha)^{-2.5}, \tag{2a,b}$$

$$v_M = v_E/(1 - \alpha). \tag{2c}$$

The expression for the dynamic viscosity μ_M is discussed in ref.[4]. The corresponding Reynolds number is given as

$$\boldsymbol{Re}_M = \frac{v_E D_E \varrho'_E}{\mu_E}(1 - \alpha)^{2.5} = \boldsymbol{Re}(1 - \alpha)^{2.5}, \tag{2d}$$

where D_E is the equivalent channel diameter

$$D_E = 2wd/(w + d). \tag{3}$$

Here, w denotes width and d interelectrode distance. In practice, $w \gg d$.

The pressure losses in the interelectrode space can be calculated as

$$\Delta p_M = \lambda_M(L_E/2D_E)\,\varrho'_E(\dot{V}_E/wd)^2\,(1 - \bar{\alpha})^{-1}, \tag{4a}$$

where

$$\lambda_M = 96/\boldsymbol{Re}_M \quad \text{for} \quad \boldsymbol{Re}_M < 2\,300, \tag{4b}$$

$$\lambda_M = 0{\cdot}314/\boldsymbol{Re}_M^{0.25} \quad \text{for} \quad \boldsymbol{Re}_M > 2\,300. \tag{4c}$$

Analogous equations apply to Δp_p. For Δp_z, the term L_E/D_E is set equal to the value found in tables[5]. For example, for a change in direction at a right angle, this term lies between 30 and 70.

The volume fraction of bubbles, $\alpha(x)$, at a height x can be expressed as

$$\alpha(x) \approx \dot{V}_G(x)/(\dot{V}_E + \dot{V}_G(x)) \tag{5a}$$

provided that the bubble velocity due to buoyancy is much smaller than the velocity of the liquid.

The mean volume fraction of bubbles is given as

$$\frac{\bar{\alpha}}{\alpha_T} = \int_0^1 \frac{\alpha(x_r)}{\alpha_T}\, dx_r\,, \tag{5b}$$

where $x_r = x/L_E$ is the reduced height. It was assumed[3] that $\bar{\alpha}/\alpha_T = 0{\cdot}5$ corresponding to constant current density (independent of x or x_r). It will be shown that this simplification is possible if $\alpha_T \to 0$, whereas in the general case of current distribution along the height of the electrolyser $\bar{\alpha}/\alpha_T > 0{\cdot}5$.

Calculation of $\bar{\alpha}/\alpha_T$ for a Bipolar Electrolyser

To calculate the integral in Eq. (*5b*), we need the distribution of current densities. The underlying equation for the voltage balance referring to a current line a bipolar electrolyser reads

$$U = a'_A + b'_A j(x_r) + a'_K + b'_K j(x_r) + j(x_r)\,(S_A \varrho_A + S_K \varrho_K) + \\ + j(x_r)\, d\varrho_E \left(1 + 1{\cdot}5K_3 \int_0^{x_r} \frac{j(x_r)}{\bar{j}}\, dx_r\right). \tag{6}$$

This gives the terminal voltage, U, of the electrolyser. The first four terms on the right-hand side correspond to the anode and cathode potentials:

$$E_A = a'_A + b'_A j(x_r)\,, \quad -E_K = a'_K + b'_K j(x_r)\,. \tag{7a,b}$$

Then comes the voltage drop in the anode and cathode of thickness S_A and S_K and resistivity ϱ_A and ϱ_K. The last term the voltage drop in the space between the electrodes, where the resistivity of the gas emulsion is given by the Maxwell equation[7,3]. Hence,

$$\varrho_M = \varrho_E \left(1 + 1{\cdot}5K_3 \int_0^{x_r} \frac{j(x_r)}{\bar{j}}\, dx_r\right). \tag{8}$$

We assumed in deriving this equation that the velocity of bubbles in the electrolyte is practically equal to its velocity. This is true if the bubbles are sufficiently small so that their rising velocity can be neglected against that of the electrolyte. Further,

$$K_3 = \alpha_T/(1 - \alpha_T) = \dot{V}_{GT}/\dot{V}_E\,. \tag{9}$$

Equation (*8*) is strictly valid only if $\alpha_T < 0{\cdot}2$, whereas for higher values of α_T the resistivity of the emulsion is better expressed by the Bruggeman equation[6]

$$\varrho_M = \varrho_E \left(1 + K_3 \int_0^{x_r} \frac{j(x_r)}{\bar{j}}\, dx_r\right)^{1.5} . \tag{10}$$

Since we want to obtain an analytical solution, we shall use Eq. (*8*) for any values of α_T, taking into account that for higher values of α_T the calculated resistivity and the ratio of $\bar{\alpha}/\alpha_T$ will be smaller than with the use of Eq. (*10*).

We introduce dimensionless criteria and simplexes

$$j_r = j(x_r)/\bar{j}\,, \quad K_1 = (U - a'_A - a'_K)/\bar{j}\, d\varrho_E\,, \tag{11, 12}$$

$$K_{2B} = (b'_A + b'_K)/d\varrho_E + (S_A\varrho_A + S_K\varrho_K)/d\varrho_E\,. \tag{13}$$

Then, Eq. (*6*) can be rearranged into the form

$$K_1 = K_{2B} j_r + j_r \left(1 + 1{\cdot}5 K_3 \int_0^{x_r} j_r\, dx_r\right). \tag{14}$$

The value of K_1 (or U) is not known, but it can be calculated by using the equation for the current density balance

$$\int_0^1 j_r\, dx_r = 1\,. \tag{15}$$

Equation (*14*) can be transformed by substituting

$$\int_0^{x_r} j_r\, dx_r = \mathrm{H} \tag{16}$$

into the form

$$K_1 = K_{2B} H' + (1 + 1{\cdot}5 K_3 H)\,. \tag{17}$$

The boundary conditions are $H(0) = 0$, $H(1) = 1$. Since the value of K_1 is not known, two boundary conditions are needed; the latter follows from Eq. (*15*). The solution leads to

$$K_1 = 1 + K_{2B} + 0{\cdot}75 K_3\,, \tag{18}$$

$$H(x_r) = [(3K_1K_3x_r + (1 + K_{2B})^2)^{1/2} - 1 - K_{2B}]/1{\cdot}5K_3\,, \tag{19}$$

$$H'(x_r) = j_r = K_1(3K_1K_3x_r + (1 + K_{2B})^2)^{-1/2}\,. \tag{20}$$

The following equation is important for further calculations:

$$H(x_r) = \int_0^{x_r} j_r \, dx_r = \dot{V}_G(x_r)/\dot{V}_{GT} . \qquad (21)$$

Equation (*5b*) can be rearranged to the form (by using (*5a*) and (*21*))

$$\bar{\alpha} = \int_0^1 \frac{\dot{V}_G(x_r)\, dx_r}{\dot{V}_E + \dot{V}_G(x_r)} = \int_0^1 \frac{H \, dx_r}{\dot{V}_E/\dot{V}_{GT} + H} . \qquad (22a)$$

From the definition of K_3, we then obtain

$$\frac{\bar{\alpha}}{\alpha_T} = (1 + K_3) \int_0^1 \frac{H \, dx_r}{1 + K_3 H} . \qquad (22b)$$

By substituting Eq. (*19*) for H in (*22b*) and integrating we obtain the resulting equation for the volume fraction of bubbles

$$\bar{\alpha}/\alpha_T = (1 + 1/K_3) \{1 - [(3K_1K_3 + (1 + K_{2B})^2)^{1/2} - 1 - K_{2B}]/K_1K_3 + + (K_{2B} - 0{\cdot}5) \ln [((3K_1K_3 + (1 + K_{2B})^2)^{1/2} - K_{2B} + 0{\cdot}5)/1{\cdot}5]\} . \qquad (23)$$

This equation shows that the ratio of $\bar{\alpha}/\alpha_T$ increases with the value of K_2 and for $K_3 \to 0$ approaches 0·5.

In calculating the value of K_3, we must know the value of $\dot{V}_{GT}$ corresponding to the total current I_T flowing through the system. For example, for diaphragmless water electrolysis in alkaline medium we have

$$\dot{V}_{GT} = \frac{I_T}{F} \left(\tfrac{1}{4}\eta_{O_2} + \tfrac{1}{2}\eta_{H_2}\right) \frac{RT_T}{P} , \qquad (24)$$

where $\eta_{O_2} \leqq 1$, $\eta_{H_2} \leqq 1$, F denotes Faraday's constant, and RT/P is the molar volume of the (ideal) gas at a pressure P and temperature T_T at the upper edge of the electrolyser electrodes.

Power Loss Due to Pumping

We shall consider the system shown in Fig. 2; the pumping power, N_B, and the pressure loss to be compensated, Δp, are given as

$$N_B = \dot{V}_E \, \Delta p , \quad \Delta p = \varrho'_E g \, \Delta L , \qquad (25), (26)$$

where $\dot{V}_E$ denotes the volume rate of flow of the pumped liquid and ΔL the difference in the electrolyte levels before and behind the electrolyser.

The bubble volume fraction at the upper edge of the electrodes, α_T, is a factor determining the mean voltage drop between the electrodes, as follows from Eqs (*12*), (*13*), and (*18*):

$$U_M = j\,\mathrm{d}\varrho_E[1 + 0{\cdot}75\alpha_T/(1 - \alpha_T)]\,. \tag{27a}$$

If a pump were used to increase the level height by ΔL at the same rate of flow $\dot{V}_E$, the volume of bubbles in the electrolyser operating without a level height difference would be smaller, hence also the mean voltage drop between the electrodes, U_M would be lower than that in the absence of a pump, U_M. Namely,

$$U_{MP} = j\,\mathrm{d}\varrho_E[1 + 0{\cdot}75\alpha_{TP}/(1 - \alpha_{TP})]\,. \tag{27b}$$

The power of a pump necessary to lift the liquid by a height difference $\Delta L = L_T - L_E$ can be calculated as

$$N_B = \dot{V}_E\,\Delta p/\eta_c = \dot{V}_E\varrho'_E g(L_T - L_E)/\eta_c \tag{28a}$$

and the difference in the input power of the electrolyser with electrochemical pumping against that with a pump is given as

$$N_E = (U_M - U_{MP})\,I_T\,. \tag{28b}$$

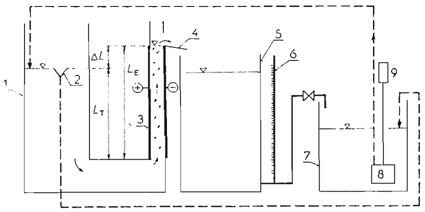

FIG. 2

Experimental set-up. *1* Reservoir with 200 l of 8·77% NaOH; *2* overflow to maintain the level; *3* one cell of bipolar electrolyser, 13 × 70 cm; *4* overflow to reservoir *5* for measurement of the rate of flow; *6* water gauge for reservoir *5*; *7* reservoir with soda lye; *8* pump with controllable speed of revolution of electric motor *9*. L_T level height in reservoir; L_E electrode height; ΔL pumping height

It should be noted that in the case where $\Delta L = 0$, the liquid circulates in a single electrolyser and is pumped by the pump, whereas in the case of electrochemical pumping the liquid passes directly into another reservoir or electrolyser.

EXPERIMENTAL AND RESULTS

Equation (*23*) was verified on a pilot scale diaphragmless electrolyser for water decomposition according to the overall reaction $H_2O = H_2 + \frac{1}{2} O_2$. In the first approximation, we can neglect the parasitic reactions and set $\eta_{O_2} = \eta_{H_2} = 1$. The electrolyte was 8·77% NaOH solution, the electrode width, w, was equal to 130 mm, height $L_E = 703$ mm, interelectrode distance $d = 6$ mm. The electrolyser was connected with a reservoir of 200 l holding capacity, whose outlet led to the lower part of the electrolyser. Current collectors were fastened in ten points on the rear faces of the electrodes, so that the electrolyser could be considered as one cell of a bipolar electrolyser (Fig. 1). The electrolyte level in the reservoir could be maintained from +70 to −320 mm with respect to the overflow located at the upper edge of the electrodes. The outflowing liquid passes into another reservoir, which was provided with a water gauge to measure the rate of flow of the electrolyte.

First, the local resistances and pressure losses in the space between the electrodes were measured at a chosen rate of flow. The following expression for Δp_z was found

$$\Delta p_z = 25{\cdot}7\lambda \varrho'_E v_E^2 \,. \tag{29}$$

Afterwards, the liquid level in the reservoir was set at a chosen height, L_T, and the value of $\bar{\alpha}$ was calculated from the equation

$$g\varrho'_E L_T - g\varrho'_E L_E(1 - \bar{\alpha}) = \left(\lambda_M \frac{L_E}{D_E} + 51{\cdot}4\lambda + 1\right) \frac{1}{2}\, \varrho'_E \frac{v_E^2}{1 - \bar{\alpha}} \,. \tag{30}$$

Here, the kinetic energy of the liquid at the inlet is neglected.

Since the system was not isothermal, namely the temperature at the upper edge of the electrodes was always higher than at the inlet ($T_T > T_0$), the mean dynamic viscosity was calculated as

$$\mu_E = \mu_0 \left[1 + \frac{1}{2\mu_0} \left(\frac{d\mu}{dT}\right)_{T_0} (T_T - T_0)\right] \tag{31}$$

and the gas colume at the upper edge of the electrodes as

$$\dot{V}_{GT} = \dot{V}_{GT,0} \left(1 + \frac{T_T - T_0}{293}\right). \tag{32}$$

In treating the data in Table I, the temperature difference between the outflowing

TABLE I

Survey of input and calculated data

No	$L_E - L_T$ mm exp.	$\bar{j}$ A/cm^2 exp.	$\dot{V}_E \cdot 10^4$ m^3/s exp.	$\dot{V}_{GT} \cdot 10^4$ m^3/s Eq. (32)	α_T Eq. (5a)	U V exp.	U V theor.	K_3 Eq. (9)	$\bar{\alpha}/\alpha_T$ Eq. (30) exp.	$\bar{\alpha}/\alpha_T$ Eq. (23) theor.	Error[a] %
1	40	0·055	0·533	0·093	0·149	2·40	2·33	0·175	0·471	0·541	−12·9
2	40	0·109	1·000	0·187	0·157	2·56	2·51	0·187	0·503	0·543	−7·5
3	40	0·172	1·342	0·294	0·179	2·80	2·72	0·219	0·481	0·550	−12·5
4	40	0·219	1·568	0·374	0·192	2·98	2·88	0·238	0·475	0·554	−14·2
5	40	0·268	1·843	0·459	0·199	3·15	3·04	0·249	0·492	0·556	−11·4
6	40	0·312	2·083	0·534	0·204	3·25	3·19	0·256	0·511	0·557	−8·3
7	40	0·438	2·352	0·750	0·242	3·80	3·65	0·319	0·465	0·570	−18·3
8	40	0·247	2·797	0·967	0·257	4·30	4·10	0·345	0·504	0·575	−12·2
9	40	0·684	2·941	1·176	0·285	4·80	4·57	0·399	0·475	0·584	−18·7
10	40	0·793	3·149	1·366	0·302	5·30	4·99	0·433	0·479	0·590	−18·7
11	80	0·049	0·235	0·084	0·263	2·30	2·33	0·358	0·464	0·577	−19·4
12	80	0·104	0·551	0·178	0·244	2·55	2·51	0·323	0·528	0·570	−7·3
13	80	0·153	0·675	0·262	0·279	2·75	2·70	0·388	0·471	0·582	−19·1
14	80	0·208	0·990	0·356	0·264	2·95	2·88	0·359	0·525	0·577	−8·9
15	80	0·268	1·183	0·459	0·279	3·20	3·10	0·388	0·514	0·582	−11·7
16	80	0·323	1·355	0·553	0·289	3·35	3·30	0·408	0·511	0·586	−12·7
17	80	0·432	1·600	0·742	0·317	3·90	3·72	0·464	0·488	0·595	−10·8
18	80	0·547	2·040	0·940	0·315	4·30	4·14	0·460	0·532	0·595	−10·5
19	80	0·662	2·209	1·140	0·340	4·85	4·61	0·516	0·509	0·604	−15·7
20	80	0·787	2·666	1·359	0·337	5·40	5·07	0·509	0·574	0·603	−8·

21	160	0·098	0·194	0·169	0·564	2·58	2·58	0·871	0·509	0·653	−22·0
22	160	0·155	0·316	0·268	0·458	2·82	2·82	0·848	0·525	0·650	−19·3
23	160	0·213	0·482	0·367	0·432	3·10	3·03	0·761	0·568	0·639	−11·1
24	160	0·268	0·633	0·461	0·421	3·30	3·24	0·728	0·594	0·635	−6·4
25	160	0·312	0·732	0·536	0·422	3·40	3·42	0·732	0·600	0·636	−5·5
26	160	0·432	0·985	0·745	0·431	4·10	3·92	0·756	0·609	0·639	−4·6
27	160	0·552	1·115	0·955	0·453	4·60	4·47	0·829	0·593	0·648	−8·5
28	160	0·667	1·320	1·157	0·467	5·15	5·00	0·876	0·589	0·654	−9·9
29	160	0·777	1·418	1·352	0·488	5·75	5·56	0·953	0·571	0·663	−13·8
30	240	0·169	0·168	0·293	0·636	3·00	3·11	1·747	0·554	0·735	−24·5
31	240	0·219	0·291	0·378	0·564	3·20	3·23	1·295	0·635	0·698	−9·0
32	240	0·263	0·334	0·454	0·468	3·48	3·46	1·318	0·635	0·700	−9·3
33	240	0·318	0·443	0·539	0·549	3·70	3·65	1·217	0·666	0·691	−3·5
34	240	0·434	0·602	0·755	0·556	4·35	4·27	1·254	0·672	0·695	−3·1
35	240	0·552	0·719	0·964	0·573	4·90	4·91	1·340	0·665	0·702	−5·3
36	240	0·662	0·772	1·163	0·601	5·55	5·62	1·506	0·637	0·717	−11·0
37	240	0·765	0·943	1·346	0·588	6·00	6·07	1·427	0·670	0·710	−5·6
38	320	0·328	0·184	0·581	0·759	3·95	4·71	3·156	0·623	0·808	−22·8
39	320	0·438	0·314	0·774	0·711	4·60	5·10	2·461	0·681	0·778	−12·3
40	320	0·547	0·389	0·973	0·714	5·20	5·86	2·498	0·688	0·779	−11·7
41	320	0·640	0·458	1·146	0·714	5·80	6·49	2·498	0·697	0·779	−10·5
42	320	0·766	0·600	1·376	0·696	6·60	7·10	2·291	0·740	0·769	−3·6

[a] Mean error in the determination of $\bar{\alpha}/\alpha_T$ is equal to −12%.

and inlet electrolyte was calculated as

$$\Delta T = \left(U - \frac{\Delta H^0_{298}}{2F}\right) \frac{I_T}{\dot{V}_E \varrho'_E c_{pE}}\,. \tag{33}$$

The following physical constants were used:

$\Delta H^0_{298} = 241{\cdot}8\,.\,10^3$ J for water decomposition[8]; $c_{pE} = 3\,789$ J/kg K (ref.[9]); $\mu_E = 0{\cdot}00173$ Ns/m^2 (ref.[10]); $\varrho'_E = 1\,095$ kg/m^3 (ref.[11]); $\varrho_E = 0{\cdot}03435\ \Omega$ m (ref.[12]).

DISCUSSION

Based on experimental data and Eq. (*18*), the values of $K_{2E} = 0{\cdot}408$ and $a'_E + a'_K = 2{\cdot}16$ V were calculated by the least squares method. The ratio of $\bar{\alpha}/\alpha_T$ was then calculated from Eq. (*23*); and the same quantity was calculated from the experimental data with the aid of Eq. (*30*).

Since all experimental values of $\bar{\alpha}/\alpha_T$ lie below the calculated ones (Fig. 3), it is probable that a factor comes into play which we did not consider and which causes a decrease of the volume rate of flow of the bubbles, $\dot{V}_{GT}$. There are three possibilities *a*) Back reactions on the electrodes, hence $\eta_{H_2} < 1$ and $\eta_{O_2} < 1$. *b*) The bubbles have a certain rising velocity, v_R, resulting in a decrease of the value of α_T and hence K_3, which is equivalent to lowering of the value of $\dot{V}_{GT}$. Then, the value of α_T is given as[3]

$$\alpha_T = \dot{V}_{GT}/[\dot{V}_{GT} + \dot{V}_E + w\,\mathrm{d}v_R(1 - \alpha_T)^{4\cdot5}]\,. \tag{34}$$

c) The effect of nonuniform flow of bubbles in the interelectrode channel. It can be assumed that the content of bubbles in the emulsion at the electrode is higher than

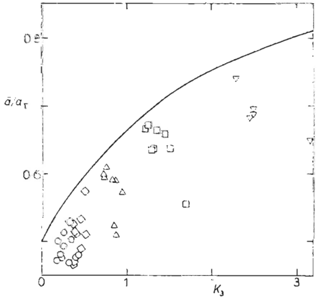

FIG. 3

Dependence of $\bar{\alpha}/\alpha_T$ on K_3 for $K_{2B} = 0{\cdot}478$. Solid line corresponds to Eq. (*23*). Experimental values were calculated from Eq. (*30*) with ΔL: ○ 40 mm; ◊ 80 mm; △ 160 mm; □ 240 mm; ▽ 320 mm in the middle of the channel, and that the bubbles in this region are larger and move more rapidly, contributing only little to the pumping of the electrolyte.

In the calculations, the use of Eq. (*23*) can be recommended to estimate the upper limit of the pumping effect. The lower limit of $\bar{\alpha}/\alpha_T$ lies according to our experiments by about 20% below the values calculated from Eq. (*23*). It should be noted that this equation was verified for $K_3 \in \langle 0{\cdot}1, 3\rangle$ and therefore it cannot be used for $K_3 > 3$.

APPENDIX

Example 1

The first example refers to the production of chlorates using a sequence of electrolysers forming a cascade with a reservoir at the end. The electrolysers pump the electrolyte upwards and it flows from the reservoir by gravity into the first member of the cascade, as shown in Fig. 4. In calculating the rate of flow $\dot{V}_E$ and the pumping height ΔL, we assume that an electrode of a height $L_E = 0{\cdot}7m$ and width $w = 0{\cdot}7$ m is placed in each electrolyser; the distance between the electrodes $d = 4$ mm, current density 0·3 A/cm^2. The pumping height ΔL can be calculated by solving the following two equations:

$$\varrho'_E g(L_E - \Delta L) - \varrho'_E g(L_E + L_{VH})(1 - \bar{\alpha}) =$$

$$= \left[\left(\lambda_M \frac{L_E}{D_E} + 51{\cdot}4\lambda\right) + 1\right] \tfrac{1}{2}\varrho'_E \left(\frac{\dot{V}_E}{wd}\right)^2 \frac{1}{1 - \bar{\alpha}}, \qquad (35)$$

$$3'\varrho g(\Delta L - L_p) = \lambda_T \left(\frac{L_T}{D_T} + 200\right) \tfrac{1}{2}\varrho'_E \left(\frac{4\dot{V}_E}{\pi D_T^2}\right)^2. \qquad (36)$$

The first equation gives the balance between the pressure losses in the electrolyser and in the inlet of the electrolyte into the interelectrode space and the driving force (density difference). The quantity $L_{VH} = 0{\cdot}003$ m represents a correction for the convex shape of the solution level.

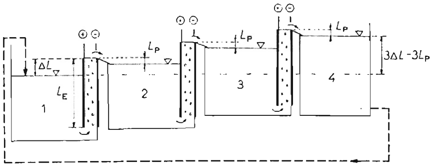

FIG. 4

Pumping of electrolyte by a cascade of electrolysers into a reservoir. *1*, *2*, *3* electrolysers; *4* reservoir. L_E electrode height; ΔL pumping height for one electrolyser; L_p height loss during overflow from one into another electrolyser

We assume that for $K_3 \approx 0$ it is possible to set $\bar{\alpha} = 0{\cdot}5\alpha_T$, where

$$\alpha_T = \dot{V}_{GT}/(\dot{V}_E + \dot{V}_{GT})\,. \tag{37a}$$

Equation (*36*) gives the balance for the pressure loss in the tubing of a length L_T and diameter D_T. The coefficient $200 = 5{\cdot}40$ is due to considering five elbows bent at an angle of 90°. For various values of L_T and D_T, we find the values of ΔL and the mean voltage drop between the electrodes, U_M.

TABLE II

Results of calculation for a system of three electrolysers according to Figs 4 and 5

No	D_T m	L_T m	α_T Fig. 4	α_{TP} Fig. 5	$\dot{V}_E . 10^4$ m^3/s Fig. 4	$\dot{V}_E . 10^4$ m^3/s Fig. 5	N_B W Eq. (*28a*)	N_E W Eq. (*28b*)
1	0·04	3	0·24	0·17	6·77	8·97	5·46	145·2
2	0·08	3	0·20	0·17	7·58	8·97	1·88	48·3
3	0·16	3	0·19	0·17	7·80	8·97	1·75	39·6
4	0·32	3	0·19	0·17	7·81	8·97	1·74	38·9
5	0·04	6	0·25	0·17	5·48	8·97	6·48	166·4
6	0·08	6	0·20	0·17	7·54	8·97	2·01	49·7
7	0·16	6	0·19	0·17	7·80	8·97	h1·75	39·6
8	0·32	6	0·19	0·17	7·81	8·97	1·74	49·8
9	0·04	9	0·26	0·17	5·24	8·97	7·5	185·8
10	0·08	9	0·20	0·17	7·51	8·97	2·05	51·1
11	0·16	9	0·19	0·17	7·80	8·97	1·75	39·7
12	0·32	9	0·19	0·17	7·81	8·97	1·74	38·9

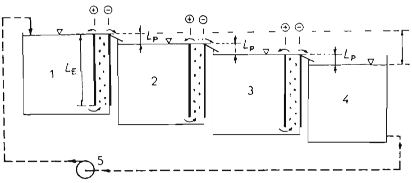

FIG. 5

Electrolyser cascade with electrolyte overflow and pump. *1*, *2*, *3* electrolysers; *4* reservoir; *5* pump. L_p height loss for one stage

If we change the system according to Fig. 5, we must use a pump (we assume a pumping efficiency $\eta_C = 0{\cdot}5$), but the value of U_M decreases to U_{MP}. Regardless of the problems of maintenance of the pump, the variant according to Fig. 5 is in all real cases preferable from the energetic point of view. The calculated data are given in Tabke II.

Example 2

We shall consider a system of 30 bipolar electrolysers (Fig. 6), connected according to Fig. 6 in one circuit with a reactor, where the gaseous phase is separated. We shall consider either a system without a pump or one where the pressure losses are compensated by a pump at an elevat-

TABLE III

Results of calculation for system with pump

No	α_{TP}	$\dot{V}_E \cdot 10^4$ m^3/s	N_B W Eq. (*28a*)	N_E W Eq. (*28b*)
1	0·125	12·7	81	290
2	0·110	14·7	193	541
3	0·097	17·1	361	757
4	0·085	19·8	612	944
5	0·074	22·9	986	1 106
6	0·067	25·2	1 331	1 201

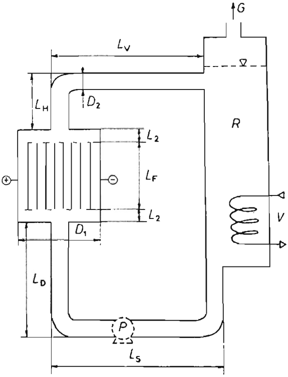

FIG. 6

Chlorate electrolyser circuit with reactor. L_E Electrode height in bipolar electrolyser; L_2 inlet and outlet height for electrolyser with adiameter D_1; L_S, L_V, L_D, L_H lengths of connecting tubing; *R* reactor; *V* cooler; *G* outlet of gases from reservoir; *P* pump ed rate of flow of the electrolyte. The basic data are: current density of 0·3 A/cm^2, electrode width $w = 0{\cdot}7$ m, electrode height $L_E = 0{\cdot}7$ m, $L_2 = 0{\cdot}3$ m, $L_H = 1$ m, $L_D = 0{\cdot}7$ m, $L_V = L_S = 1$ m, and $D_2 = 0{\cdot}2$ m. The following equation applies:

$$g\varrho_E'(L_H + L_2 + L_E) - g\varrho_E' L_E(1 - \bar{\alpha}) - g\varrho_E'(L_H + L_2)(1 - \alpha_T) = \\ = \Delta p_M + \Delta p_z\,, \qquad (37b)$$

where Δp_M denotes the pressure loss in the interelectrode space and Δp_z the total pressure loss in the whole circuit including the elbow. The calculation leads to the values of α_T, $\dot{V}_E$, and U_M for the system without a pump. In our case, $\alpha_T = 0{\cdot}14$, $\dot{V}_E = 11{\cdot}0 \,.\, 10^{-4}$ m^3/s, and $U_M = 0{\cdot}436$ V for a single cell.

If a pump is used at a rate of flow $\dot{V}_E$, the pressure loss Δp compensated by the pump is given by the difference of the right and left sides of Eq. (*37*):

$$\Delta p = \Delta p_M + \Delta p_z - g\varrho_E'(L_H + L_2 + L_E) + g\varrho_E' L_E(1 - \bar{\alpha}) + \\ + g\varrho_E'(L_H + L_2)(1 - \alpha_T)\,. \qquad (38)$$

Also in this example, the pumping efficiency η_C is set equal to 0·5.

As in Example 1, the use of a pump appears theoretically advantageous up to a certain rate of flow (about 23 . 10^{-4} m^3/s in our case). To elucidate why in practice no pump is used in the considered case, we indicate the total inpout power of the system, 1 470 A × 3·0 V × 30 cels = = 132·3 kW. For example, a saving of 396 W (Table III, 3rd line) represents only 0·3% or the total input power. This saving can be obtained, *e.g.*, by a more thorough control of the technological process or by another technical provision.

CONCLUSIONS

Equation (*23*) for the calculation of the volume fraction of bubbles was verified experimentally on a pilot scale electrolyser. This theoretical equation gives also the upper limit for the rate of flow of the electrolyte; the lower limit is about 80% of the value calculated from Eq. (*23*). This equation is further important in calculating the circulation rate of the electrolyte or the pumping height for industrial electrolysers for production of hydrogen, oxygen, or chlorates.

LIST OF SYMBOLS

a_A', a_K'	constants of the linearized Tafel equation (7) (V)
b_A', b_K'	constants of the linearized Tafel equation (7) (V m^2/A)
c_{pE}	specific heat of electrolyte (J/kg K)
d	interelectrode distance (m)
D_E	equivalent diameter of interelectrode space (m)
D_T	diameter of tubing (m)
E_A, E_K	potential of anode and cathode (V)
F	Faradays constant (96484 C)
g	acceleration of gravity (9·81 m/s^2)
H	function defined by Eq. (*16*)
I_T	total current flowing through electrolyser (A)
j	local current density (A/m^2)
$\bar{j}$	mean current density (A/m^2)

j_r	reduced local current density
K_1, K_{2B}	criteria defined by Eqqs (*12*) and (*13*)
K_3	criterion defined by Eq. (*9*)
ΔL	pumping height equal to $L_E - L_T$ (m)
L_E	electrode height (m)
L_H	length of tubing above the electrolyser (m)
L_p	height loss between subsequent members of a cascade (m)
L_T	level height in reservoir (m)
L_{VH}	level height increment due to overflow (m)
L_2	height dimension (Fig. 5) (m)
n_{O_2}, n_{H_2}	number of electrons transferred per molecule of O_2 or or H_2
N_B, N_E	pumping performance, Eq. (*28a,b*)
Δp_M, Δp_p, Δp	pressure losses in the interelectrode space, in the inlet tubing, and in elbows (N/m^2)
P	pressure at the upper edge of the electrode (N/m^2)
R	gas constant ($J K^{-1} mol^{-1}$)
Re, Re_M	Reynolds criterion for the electrolyte and for gas emulsion
S_A, S_K	thickness of anode and cathode (m)
T	temperature (H)
T_0, T_T	temperatures at the inlet and outlet (K)
ΔT	temperature difference, $T_T - T_0$ (H)
U	terminal voltage of the electrolyser (V)
U_M, U_{MP}	mean voltage drops in the interelectrode space without and with the use of a pump (V)
v_E, v_M	velocities of electrolyte and of gas emulsion between the electrodes (m/s)
v_p	velocity of electrolyte in the inlet channel (m/s)
v_R	rising velocity o bubbles (m/s)
$\dot{V}_E$	volume rate of flow of electrolyte (m^3/s)
$\dot{V}_G(x)$	volume rate of flow of gas at a height x (m^3/s)
$\dot{V}_{GT}$	volume rate of flow of gas at upper electrode edge (m^3/s)
w	electrode width (m)
x, x_r	distance from lower electrode edge (m), reduced distance x/L_E
$\alpha(x)$, $\bar{\alpha}$	volume fraction of bubbles at a height x between the electrodes and its mean values (Eqs (*5a*) and (*22a*))
α_T, α_{TP}	volume fractions of bubbles at upper electrode edge without and with pumping of the electrolyte
ϱ_A, ϱ_K, ϱ_E, ϱ_M	resistivity of anode, cathode, electrolyte, and gas emulsion (Ωm)
ϱ'_E, ϱ'_M	density of electrolyte and gas emulsion (kg/m^3)
μ_E, μ_M	dynamic viscosity of electrolyte and gas emulsion (kg/m s)
μ_0	dynamic viscosity of electrolyte at inlet temperature
λ	friction coefficient of electrolyte in a tube
λ_M	friction coefficient of gas emulsion between electrodes
η_c	pump efficiency
η_{O_2}, η_{H_2}	current efficiency for oxygen and hydrogen
ΔE_{pot}	potential energy difference of electrolyte (Ws/m^3)
ΔE_{kin}	kinetic energy difference of electrolyte (Ws/m^3)
ΔE_{diss}	dissipated energy of electrolyte (Ws/m^3)

REFERENCES

1. Regner A.: *Technická elektrochemie* I, p. 360. Academia, Prague 1967.
2. Kuhn A. T.: *Industrial Electrochemical* Processes, p. 94. Elsevier, Amsterdam 1971.
3. Roušar I.: J. Electrochem. Soc. *116*, 676 (1969).
4. Zuber N.: Chem. Eng. Sci. *19*, 897 (1964).
5. Míka V.: *Sbírka příkladů z chemického inženýrství*, p. 123. Published by SNTL, Prague 1978.
6. Maxwell J. C.: *A Treatise on Electricity and Magnetism*, Vol. 1, p. 435. Clarendon Press, Oxford 1881.
7. Bruggeman D. A. G.: Ann. Phys. (New York) *24*, 636 (1935).
8. Moore W. J.: *Physical Chemistry*, p. 91. Czech translation, Published by SNTL, Prague 1979.
9. Bertetti J. W., McCabe W. L.: Ind. Eng. Chem. *28*, 375 (1936).
10. *Spravochnik Khimika*, Vol. III, p. 718. Khimiya, Moscow 1964).
11. Ref. 10, p. 544.
12. Ref. 10, p. 666.

Translated by K. Micka.