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OPTIMIZATION OF THE GEOMETRIC DIMENSIONS OF VERTICAL ELECTROLYZERS WITH GAS-GENERATING ELECTRODES

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16. Abstract

A study is made to determine whether, under the conditions of electrolyte circulation induced by evolved gases, it is possible to increase the vertical scale without a great increase in cell voltage. The mathematical modeling used is discussed, and a comparison is made with experimental results and conclusions. It is found it is possible to increase the vertical scale without producing a cell voltage increase.

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Optimization of the Geometric Dimensions of Vertical Electrolyzers with Gas-Generating Electrodes *

by Wolfgang Thiele, KDT and Martin Schleiff

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Electrochemical reactors are used for the production of peroxodisulfuric acid and peroxodisulfates, in which the catholyte is circulated [1] within the cell by the buoyancy of the hydrogen generated. For the optimization of the geometric dimensions of such electrolyzers [2] the knowledge of the influence of the evolved gas bubbles on the cell voltage is of utmost importance. For a vertical electrode arrangement the gas loading in the electrolyte increases with increasing electrode height, with increasing current density and with decreasing slot width of the electrode volume. For constant inlet velocity of the pure liquid phase and for a specified buoyancy rate of the gas bubbles, Hertwig and coworkers [3] found an optimum width of the electrode volume where the voltage drop was a minimum. By the

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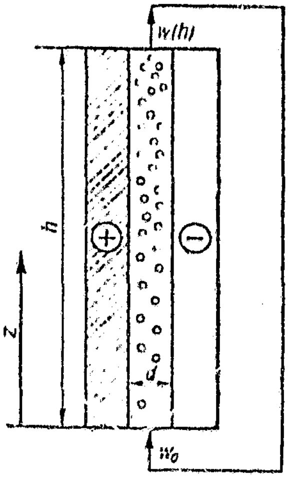
evaluation of an approximating mathematical model and by comparison with experimental results we planned to investigate whether under the conditions of electrolyte circulation induced by the evolved gases we could succeed in increasing the vertical scale without a significant increase in cell voltage.



$$p_A = p_B$$

$$g h \varepsilon = \frac{a w_0 \eta}{d^2} (1 + \bar{\varepsilon})$$

$$\varepsilon(h) = \frac{1}{W_1 + 1}, \quad \bar{\varepsilon} = \frac{1}{W_1}$$

$$w(h) = \frac{c_0 h_I}{d} \cdot \frac{1}{2} (W_1 + 1)$$

$$w_0 = \frac{c_0 h_I}{d} \cdot \frac{1}{2} (W_1 - 1)$$

$$\Delta U = \frac{\bar{i} d}{\eta} \cdot \frac{(W_1 + 0{,}5)}{(W_1 - 1)}$$

$$W_1 = \sqrt{1 + \frac{2}{a} \cdot \frac{g \varrho d^3}{c_0 \eta h_I}}$$

Figure 1 Model and model equations

Mathematical modeling

The reactor shown schematically in figure 1 is imagined as a one-dimensional system with the average current density $\bar{i}$ and the average gas phase share $\bar{\varepsilon}$. The flow of the electrolyte in the electrode volume is a two-phase split flow. After separation of the gases the liquid returns via a return-flow channel into the electrode volume. The steady-state circulation of the electrolyte is controlled by the force equilibrium between the buoyant force of the gas bubbles and the friction pressure loss. In the derivation of the approximation model we made the following assumptions:

- The momentum of the gas bubbles is transferred completely to the liquid

- The steady-state two-phase flow is developed completely over the entire cell height
- A uniform model is assumed with negligibly small gas slippage, $\varepsilon = \varepsilon_{\ell}$, applies
- The mass proportion of the gas phase is small compared to the liquid phase
- The friction in the electrolysis flow channel is the sole governing factor for the pressure loss in the circulation system.
- For the friction pressure loss

$$\frac{\Delta p}{\Delta z} = a \frac{w_0 \eta}{d^2} (1 - \bar{\varepsilon})$$

  represents a useful approximation.
- For the average gas phase proportion the following applies

$$\bar{\varepsilon} = \frac{\varepsilon(h)}{2 - \varepsilon(h)}$$

- For **x=d/b** the value for the constant a is

$$a = \frac{12}{1 - 0{,}63025\, x + 1{,}255 \frac{x}{e^{\pi/x} + 1}}.$$

- The electric conductivity in the two-phase range is:

$$\varkappa_{GF} = \varkappa_F \frac{1 - \bar{\varepsilon}}{1 + 0{,}5\, \bar{\varepsilon}}$$

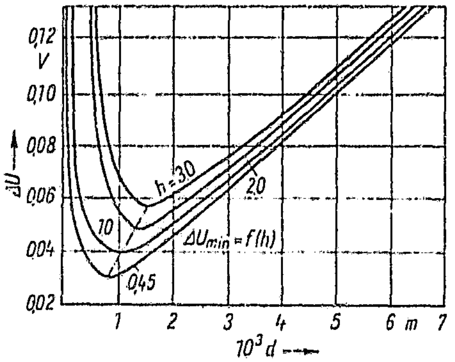


Figure 2 Voltage drop as a function of slot width for different cell heights

$x = 0$
$c_0 = 1{,}27 \cdot 10^{-7}\ m^3 \cdot A^{-1} \cdot s^{-1}$
$\eta = 3 \cdot 10^{-3}\ kg \cdot s^{-1} \cdot m^{-1}$

$\bar{i} = 1200\ A \cdot m^{-2}$
$\varkappa = 65\ \Omega^{-1} \cdot m^{-1}$
$\varrho = 1{,}3 \cdot 10^3\ kg \cdot m^{-3}$

The model equations thus obtained are listed in figure 1. As shown in figure 2, the thus calculated voltage drop goes through a minimum, which for increasing cell height is displaced only little toward greater slot widths. For the optimum the calculation gives

$$d_{\mathrm{opt}} = 1{,}7088 \sqrt[3]{\frac{2\, c_0\, h\, \bar{i}\, \eta}{a\, g\, \varrho}},$$

$$\Delta U_{\mathrm{min}} = 3{,}473\ \frac{\bar{i}}{z F} \sqrt[3]{\frac{2\, c_0\, h\, \bar{i}\, \eta}{a\, g\, \varrho}}$$

It becomes clear that under these conditions the voltage drop increases only as the cube root of the cell height. Independently of the material values one obtains at the optimum a constant average gas-phase portion of $\bar{\varepsilon}_{\mathrm{opt}} = 0{,}3820$.

Variablen 1			gemessen 2		berechnet 3		$(w_0)_{\mathrm{gem}}$
h	d	$\bar{i}$	w_0	ΔU	w_0	ΔU	$(w_0)_{\mathrm{ber}}$
0,45	0,005	800	0,005	0,140	0,144	0,004	0,035
0,45	0,005	1200	0,018	0,145	0,175	0,008	0,102
0,45	0,003	800	0,026	0,053	0,125	0,040	0,208
0,45	0,003	1200	0,041	0,070	0,151	0,002	0,272
1,35	0,005	800	0,060	0,083	0,244	0,007	0,246
1,35	0,005	1200	0,089	0,124	0,295	0,102	0,302
1,35	0,003	800	0,094	0,050	0,208	0,043	0,452
1,35	0,003	1200	0,117	0,080	0,249	0,067	0,470

Table 1. Comparison of calculated and experimental values

1- variables 2- measured 3- calculated

Comparison with experimental results and conclusions

Based on a mathematical-statistical test plan we changed, in a model electrolyzer with electrolyte circulation [4], the cell height, slot width and current density on two levels each and measured the developing inlet velocities. Some of the test values obtained are listed in table 1 next to the data calculated with the model (with: b = 0.007 m).

The quotient of the measured and calculated inlet velocity as a measure of the fit of the model is small at low flow velocities, but increases significantly with cell height, current density and decreasing slot width. Obviously the assumptions made in the derivation of the model are then satisfied much better. Thus the calculated values take on the significance of limiting values which can be approached by suitable choices of the geometric dimensions and the electrolysis conditions. The results point out that an increase in vertical scale with circulation of the electrolyte does not necessarily have to bring about an increase of the cell voltage. For a most favorable hydrodynamic shaping of the circulation system and simultaneous approach of the optimum, it is even possible to attain a lowering of the cell voltage. A comparison of the results obtained when the cell height was increased to the three-fold value (table 1) makes this clear.

It was already possible to successfully check these findings in cells in technical colleges with a construction height of 2 m. Since they are limited in no way to the present application case, they also make possible, for other electrode processes proceeding with gas evolvement, an increase of the current capacity to be accommodated per unit area and thus an improvement in the effectiveness.

Summary

In electrochemical reactors with gas-evolving electrodes, narrow limits are set to vertical scale increases for the purpose of increasing the volume-time yield, since the gas quantity generated increases proportionally with the cell height. With the aid of an approximation model and experimental results from model cells for the production of peroxodisulfuric acid, we have shown that by utilization of the buoyant effect of the gas bubbles for the circulation of the electrolyte with optimal sizing of the electrolysis volume it becomes possible to increase the vertical scale without necessarily encountering a thus connected cell voltage increase.

Nomenclature

symbol	explanation	unit
a	coefficient depending on d/b	-
b	slot width of the electrode volume	m
c_o	developed gas volume per unit area and charge	$m^3.A^{-1}.s^{-1}$
d	slot thickness of the electrode volume	m
h	height of the electrode volume	m
i	current density	$A.m^{-2}$
P	force	N
p	pressure	Pa
U	cell voltage	V
w	velocity	$m.s^{-1}$
w_o	inlet velocity	$m.s^{-1}$
z	height coordinate	m
ε	gas-phase portion in volume element	-
η	viscosity	$kg.m^{-1}.s^{-1}$
x	specific conductivity of the electrolyte	$\Omega^{-1}.m^{-1}$
ϱ	density	$kg.m^{-3}$

Indices

A	buoyancy
F	liquid phase
G	gas phase
R	friction
opt	optimal
min	minimal

References

[1] Thiele, W. and Matschiner, H.: Chem. Techn. 29 (1977) 148.
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