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Current efficiency in the chlorate cell process

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Abstract: A mathematical model has been set up for current efficiency in a chlorate cell acting as an ideal electrochemical tubular reactor with a linear increase in hypochlorite concentration from the entrance to the exit. Good agreement was found between the results on current efficiency experimentally obtained under simulated industrial chlorate production conditions and the theoretical values provided by the mathematical model.

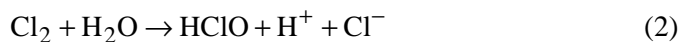
Keywords: chlorate; active chlorine; limiting diffusion current; current efficiency.

INTRODUCTION

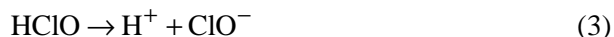
During the electrolytic production of chlorate by the electrolysis of concentrated sodium chloride solution, chlorine is evolved at the anode by the anodic oxidation of chloride ions:



The evolved elemental chlorine diffuses through the anodic diffusion layer towards the bulk solution where it is subject to hydrolysis. The hydrolysis reaction is fast and, therefore, at pH values of the solution above 6.0, almost all the dissolved chlorine hydrolyses near the anode:^{1–13}



In the solution, equilibrium of the hypochlorous acid dissociation reaction is established:



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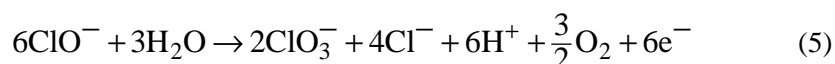
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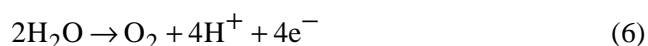
In the bulk solution, the resulting hypochlorous acid and hypochlorite (active chlorine) ions are converted to chlorate:



Active chlorine diffuses into the anode, where it is oxidised to chlorate in an undesirable reaction:¹⁻¹³



Maximum anodic current efficiency, η_a , is obtained if only reactions (1)–(4) occur. Reaction (5) in the diffusion-controlled electrochemical production of chlorate causes anodic current losses. Chlorine diffusion and hydrolysis, and active chlorine diffusion are determinants of the concentration profile of active chlorine in the anode diffusion layer. This profile determines the flux of active chlorine on the anode surface and, hence, the anodic current losses, which are additionally caused by water oxidation:¹⁻¹³

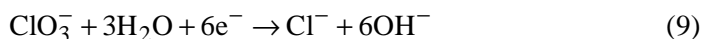
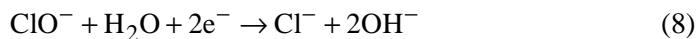


During chlorate production by the electrolysis of concentrated sodium chloride solutions, current losses due to the anodic oxidation of water are negligible.^{1,11-14} The relatively high temperature of the solution, $t > 80$ °C, ensures a high rate of chemical conversion of active chlorine into chlorate (reaction (4)) and, hence, a relatively low steady-state concentration of active chlorine. In the chlorate production process, the pH of the solution, $6.1 < \text{pH} < 6.5$, ensures an optimal ratio of hypochlorous acid to hypochlorite ion concentrations for the maximum rate of the chemical conversion of active chlorine into chlorate.¹⁻¹³

Hydrogen evolution is the primary reaction at the cathode:



Apart from reaction (7), the reduction of active chlorine and chlorates may also occur at the cathode:



Cathodic current losses are completely prevented by the addition of 2 to 5 g dm^{-3} $\text{Na}_2\text{Cr}_2\text{O}_7$ to the solution.^{1,2,6,7,16-22} Sodium dichromate plays multiple roles: a) it develops a thin layer of chromium oxide and hydroxide on the cathode surface, thus completely preventing the cathodic reduction of active chlorine and chlorite, b) it inhibits the corrosion of the steel cathode,²³ c) its buffering effect ensures an optimal pH for the chemical conversion of active chlorine into chlorate and d) it has a catalytic effect on the chemical conversion.^{4,8}

Industrial systems for the electrolytic production of chlorates consist of cells and a holding tank, usually in a closed loop. Active chlorine is generated in the cells, and the chemical conversion of the active chlorine into chlorate occurs in the holding tank. During the production, a steady-state concentration of active chlorine is achieved in each volume element of the system ($\partial c_2 / \partial \tau = 0$). The anodic current efficiency ranges from $2/3$ to 1 ($2/3 \leq \eta_a \leq 1$).¹⁻⁶ The current efficiency can be lower than $2/3$ only if the active chlorine concentration is higher than the steady-state concentration (non-steady-state conditions). In modern industrial chlorate plants, the current efficiency is only dependent on the ratio of the amount of chlorate resulting from the chemical conversion (reaction (4)) to the amount of chlorate produced by the electrochemical oxidation of active chlorine (reaction (5)). The contributions of the two reactions depend on the pH, temperature and volume of the solution, total current, current density, hydrodynamic electrolyte flow regime and electrochemical cell design.

The objective of this study was to set up a new mathematical model for current efficiency in the chlorate cell and experimentally verify the model in a laboratory chlorate plant.

EXPERIMENTAL

The experiment was conducted using laboratory apparatus composed of an electrochemical cell, a gas/liquid separator, a holding tank, a thermostat, a pump, a flow check valve and a flow metre (Fig. 1).

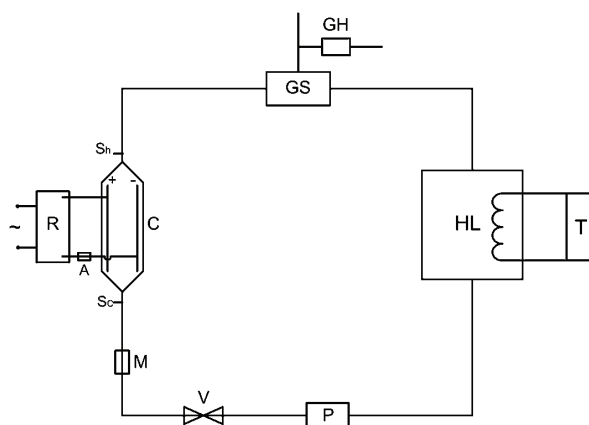


Fig. 1. Laboratory chlorate producing apparatus: C – electrochemical cell; GS – gas/liquid separator; GH – gas analyser; HL – holding tank; T – thermostat; P – pump; V – flow check valve; M – flow metre; R – rectifier; A – ammeter and SC; Sh – sampling valves.

The cell case, gas separator and the holding tank were made of Plexiglas and connected by polypropylene tubing. The holding tank contained 12.0 dm^3 of the solution. The total volume of the solution in the apparatus was 13.5 dm^3 . The anode was a titanium plate activated by a catalytic 40 mol % RuO_2 , 60 mol % TiO_2 (DSA) coating. A titanium plate-

-shaped cathode 200 cm² in surface area was placed parallel to the anode at a distance of 0.3 cm. Both electrodes were 0.3 cm in thickness. Three different electrochemical cells equipped with electrodes identical in surface area, but differing in height, L , and width, b , were used in the experiment: a) $L = 25$ cm, $b = 8$ cm; b) $L = 50$ cm, $b = 4$ cm and c) $L = 100$ cm, $b = 2$ cm. The electrolyte flow in the apparatus was controlled by both the pump P and valve V. The flow was adjusted in such a way as to ensure the same electrolyte velocity of 50 cm s⁻¹ in the inter-electrode gap in all cells.

The solution temperature was 80±0.5 °C, and was adjusted by regulating the flow of water through a cooling coil. The pH of the solution was adjusted to within ±0.05 pH units by the addition of NaOH alkali or HCl acid to the solution using an automatic titrator.

The solution was composed of 300 g dm⁻³ NaCl and 3 g dm⁻³ Na₂Cr₂O₇. It was prepared using reagent-grade chemicals and triple-distilled water. The active chlorine concentration was determined by titration with sodium arsenite, and the current efficiency for chlorate formation was measured using the composition of the output gas mixture.^{1,5,6} The composition of the mixture was determined by the gas chromatography. Measurements were conducted after reaching a steady state. The experimental values presented are the mean of ten measured values.

RESULTS AND DISCUSSION

The diffusion and hydrolysis of the chlorine generated at the anode and the diffusion of active chlorine can be described by the Danckwerts surface renewal model.^{24,25} This model assumes that during turbulent mixing, the elements of the solution contact the anode surface and spend some time on it. During the electrolysis, some elements of the solution leave the anode surface and go into the bulk solution to be replaced by new fresh elements. The probability for an element of the solution to be replaced on a portion of the anode with another fresh element is not dependent on the length of its contact with the anode. Under steady-state conditions, the portion of the element surface that was in contact with the anode surface in the time interval from τ to $\tau+d\tau$ is $S^{-S\tau}d\tau$, where S denotes the portion of the anode surface on which the old element of the solution was replaced by the new one per unit time. If in an element of the solution brought into contact with the anode surface $c_1(x, \tau)$ – the concentration of chlorine is at a distance x from the anode surface after a time τ that elapsed from the initial contact with the anode, the average chlorine concentration for all elements of the solution on the anode surface at a distance x from the anode is equal to:

$$\bar{c}_1 = S \int_0^{\infty} c_1(x, \tau) e^{-S\tau} d\tau \quad (10)$$

Equation (10) is the Laplace–Carlson transform of the function $c_1(x, \tau)$.

Assuming that chlorine hydrolysis is a first-order reaction, the diffusion and hydrolysis of chlorine in one element of the solution on the anode surface can be presented using the following equation for non-steady-state diffusion:

$$\frac{\partial c_1}{\partial \tau} = D_1 \frac{\partial^2 c_1}{\partial x^2} - k_1 c_1 \quad (11)$$

and Eq. (12) for the diffusion of active chlorine:

$$\frac{\partial c_2}{\partial \tau} = D_2 \frac{\partial^2 c_2}{\partial x^2} + k_1 c_1 \quad (12)$$

The initial and boundary conditions needed to solve the differential equations for chlorine are:

$$\text{for } \tau = 0, c_1 = 0 \quad (13)$$

$$\text{for } x = 0, -D_1 \frac{d\bar{c}_1}{dx} = \frac{j\eta_a}{2F} \quad (14)$$

$$\text{for } x = \infty, c_1 \rightarrow 0 \quad (15)$$

and for active chlorine:

$$c_2 = 0, \text{ for } \tau = 0 \text{ and } x > 0 \quad (16)$$

$$c_2 = 0, \text{ for } \tau > 0 \text{ and } x = 0 \quad (17)$$

$$c_2 = c_0, \text{ for } \tau > 0 \text{ and } x \rightarrow 0 \quad (18)$$

Applying Laplace–Carlson transforms to Eqs. (11) and (12), as well to the initial and boundary conditions (Eqs. (13)–(18)) gives for chlorine:

$$D_1 \frac{d^2 \bar{c}_1}{dx^2} - (k_1 + S) \bar{c}_1 = 0 \quad (19)$$

$$\text{for } x = \delta_a, \bar{c}_1 = 0 \quad (20)$$

and
$$\text{for } x = 0, -D_1 \frac{d\bar{c}_1}{dx} = \frac{j\eta_a}{2F} \quad (21)$$

and for active chlorine:

$$\frac{d^2 \bar{c}_2}{dx^2} - \frac{S}{D_2} \bar{c}_2 = -\frac{c_0}{D_2} S - \frac{k_1 \bar{c}_1}{D_2} \quad (22)$$

$$\text{for } x \rightarrow \infty, \bar{c}_2 = c_0 \quad (23)$$

and
$$\text{for } x \rightarrow 0, \bar{c}_2 = 0 \quad (24)$$

As in case with concentration \bar{c}_1 , concentration \bar{c}_2 is defined using Eq. (10).

Solving Eqs. (19) and (22) results in the following expressions for the concentration profiles of chlorine (Eq. (25)) and active chlorine (Eq. (26)) in the anodic diffusion layer of the chlorate cell:

$$\bar{c}_1 = \frac{j\eta_a}{2F} \frac{1}{K(1+M)^{0.5}} \exp\left(-\frac{K}{D_1}(1+M)^{0.5} x\right) \quad (25)$$

$$\bar{c}_2 = \frac{j\eta_a M}{2FK(1+M)^{0.5} \left[(1+M) \left(\frac{D_2}{D_1} - 1 \right) \right]} \times \left\{ \exp \left[- \left(\frac{K^2}{D_1 D_2} \right)^{0.5} x \right] - \exp \left[- (1+M)^{0.5} \frac{K}{D_1} x \right] + c_0 \left\{ 1 - \exp \left[- \left(\frac{K^2}{D_1 D_2} \right)^{0.5} x \right] \right\} \right\} \quad (26)$$

where:

$$M = \left(\frac{k_1}{D_1} \right)^{0.5} \delta_a \quad (27)$$

and

$$K = (SD_1)^{0.5} = \frac{D_1}{\delta_a} \quad (28)$$

as according to [25]:

$$S = \frac{D_1}{\delta_a^2} \quad (29)$$

The flux of active chlorine at the anode surface defines the portion $(1-\eta_a)$ of the anodic current density that is consumed for the oxidation of active chlorine to chlorate (reaction (5)):

$$\frac{1-\eta_a}{F} = D_2 \left. \frac{d\bar{c}_2}{dx} \right|_{x=0} \quad (30)$$

Combining Eqs. (26) and (30) and solving for η_a gives a relatively simple expression for the anodic current efficiency:

$$\eta_a = \frac{1 - D_2 c_0 F (j\delta_a)^{-1}}{1.5 - 0.5 \left(1 + \frac{k_1}{D_1} \delta_a^2 \right)^{-0.5}} \quad (31)$$

Equation (31) is valid for an ideal stirred electrochemical reactor, in which the active chlorine concentration is invariable within each element of the volume. The active chlorine concentration at the entrance to the cell, $c_{2,c}$ is identical to that at the exit from the cell, $c_{2,h}$.

Equation (31) was used to determine the theoretical dependence of the current efficiency on the steady-state concentration of active chlorine (Fig.2). The same dependence was also experimentally determined (Fig. 2). A cell equipped with a 25 cm high anode was used in the experiment. The desired steady-state

concentration of active chlorine was adjusted through changes in the solution pH. The difference between active chlorine concentration at the entrance to the cell and that at the exit was less than 2.6 % for $c_{2,c} = 0.1 \text{ mol dm}^{-3}$. The current efficiency presented in Fig. 1 was determined by the mean of the inlet and outlet concentrations. A difference of less than 0.1 % was found between the current efficiency calculated from the inlet concentration and that from the outlet concentration. This suggests that the electrochemical cell equipped with a 25 cm high anode acted practically as an ideal stirred reactor.

The diagram in Fig. 2 shows the agreement between the experimental values for current efficiency and the theoretical values calculated using Eq. (31), which confirms the validity of the mathematical model.

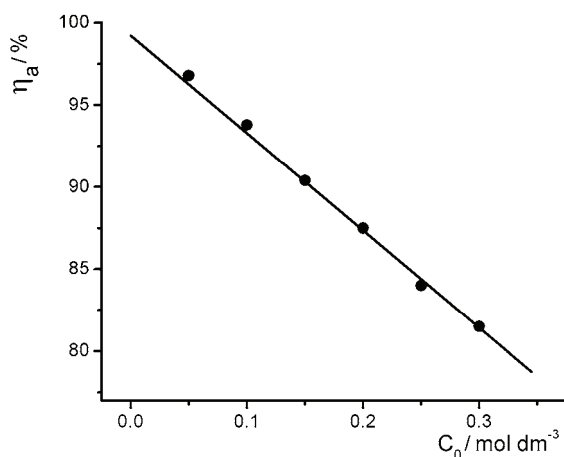


Fig. 2. Anodic current efficiency, η_a , as a function of active chlorine concentration c_0 (300 g dm^{-3} NaCl, 3 g dm^{-3} $\text{Na}_2\text{Cr}_2\text{O}_7$, $t = 80 \text{ }^\circ\text{C}$, $j = 300 \text{ mA cm}^{-2}$, $v = 50 \text{ cm s}^{-1}$, $L = 25 \text{ cm}$): (—) theoretical values derived from Eq. (31) and ● – experimental values.

Industrial chlorate cells have considerably larger anodes. Therefore, the active chlorine concentration in these cells increases from the entrance through to the exit. Vogt²⁶ set up a mathematical model for the anodic current efficiency in the chlorate cell process, assuming that the hypochlorite bulk concentration in the cell exhibited a linear axial increase.

Later, Vogt²⁷ established the true axial concentration profile taking into account the interaction between the current density and gas volume fraction, the resulting variation in the flow velocity and the mass transfer of hypochlorite. The true profile was close to the linear profile, and it could be concluded that the linear profile assumption is a satisfactory model assumption.

The increase in the amount of gas bubbles of cathode-evolved hydrogen from the entrance to the exit decreases the local current density in the same direction.

In industrial cells under steady-state conditions, the local densities change by up to 5 %. In the current density range between 150 and 500 mA cm^{-2} , changes

in current density of 5 % have practically no effect on the current efficiency, as illustrated by Eq. (31).

The above considerations show that the axial concentration profile in a chlorate cell can be presented using the following equation:

$$c_{2,l} = \frac{c_{2,h} - c_{2,c}}{L}l + c_{2,c} \quad (32)$$

Combining Eqs. (31) and (32) gives an expression for the current efficiency in the chlorate cell acting as the ideal tubular reactor, where the active chlorine concentration linearly increases from the entrance to the exit:

$$\eta_a = \frac{1 - 0.5D_2F(j\delta_a)^{-1}(c_{2,c} + c_{2,h})}{1.5 - 0.5\left(1 + \frac{k_1}{D_1}\delta_a^2\right)^{-0.5}} \quad (33)$$

Equation (33) was used to determine the theoretical dependences of the current efficiency of chlorate cells on the output concentration of active chlorine. Both the theoretical and experimental values for current efficiencies are presented in Fig. 3.

To ensure identical solution velocity between the electrodes and identical active chlorine production per unit time, four cells differing in anode size (cells a–d) were used in the experiments.

The diagrams in Fig. 3 indicate good agreement between the experimentally obtained values for the anodic current efficiency and the theoretical values calculated using Eq. (33), thus confirming the assumption that the chlorate cell serves as an ideal tubular reactor with a linear axial concentration profile of active chlorine.

Combining the expression for the solution flow rate in the cell:

$$q = vbg = \frac{vAg}{L} \quad (34)$$

and the expression for the amount of active chlorine evolved per unit time:

$$n = \frac{I\tau}{2F} \quad (35)$$

gives the expression for the output concentration of active chlorine:

$$c_{2,h} = c_{2,c} + \frac{n}{q} = c_{2,c} + \frac{j\tau L}{2Fvq} \quad (36)$$

Replacing $c_{2,h}$ in Eq. (33) with the expression for $c_{2,h}$ defined by Eq. (36) results in the expression defining the anodic current efficiency as a function of anode height and solution velocity:

$$\eta_a = \frac{1 - D_2 F (j \delta_a)^{-1} \left[c_{2,c} + j \tau L (4 F v g)^{-1} \right]}{1.5 - 0.5 \left(1 + \frac{k_1}{D_1} \delta_a^2 \right)^{-0.5}} \quad (37)$$

Equation (37) was used to determine the theoretical dependences of current efficiency on anode height for different input concentrations of active chlorine. These theoretical dependences and the experimentally determined current efficiencies are presented in Fig. 4.

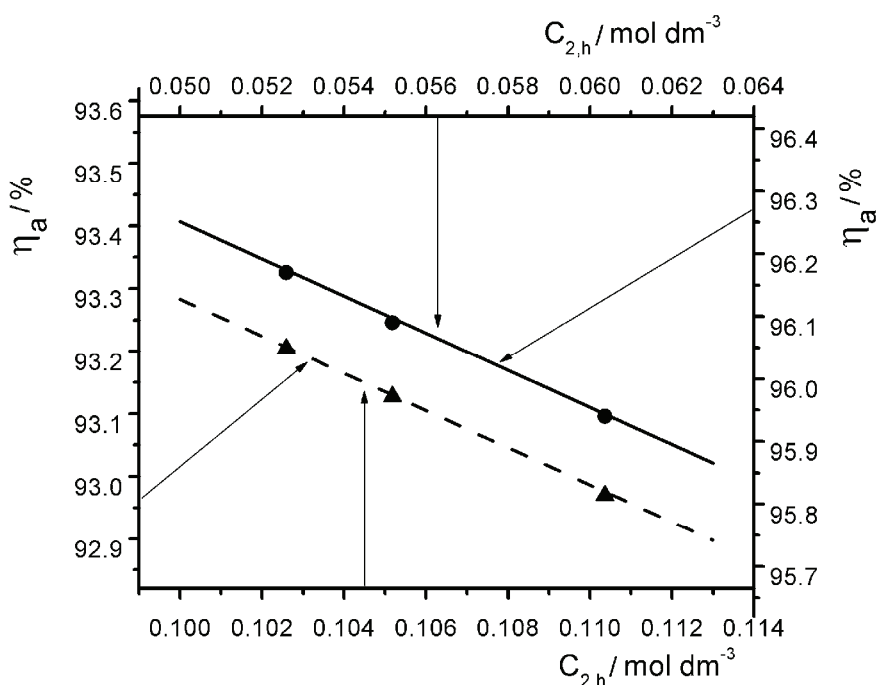


Fig. 3. Anodic current efficiency, η_a , as a function of the output concentration of active chlorine, $c_{2,h}$, for different input concentrations, $c_{2,c}$. Theoretical values derived from Eq. (33) for: $c_{2,c} = 0.05 \text{ mol dm}^{-3} \text{ NaClO}$ (—); $c_{2,c} = 0.10 \text{ mol dm}^{-3} \text{ NaClO}$ (---). Experimental values for: $c_{2,c} = 0.05 \text{ mol dm}^{-3} \text{ NaClO}$ (●); $c_{2,c} = 0.10 \text{ mol dm}^{-3} \text{ NaClO}$ (▲); $(300 \text{ g dm}^{-3} \text{ NaCl}, 3 \text{ g dm}^{-3} \text{ Na}_2\text{Cr}_2\text{O}_7, t = 80 \text{ }^\circ\text{C}, j = 300 \text{ mA cm}^{-2}, v = 50 \text{ cm s}^{-1})$.

The good agreement between the theoretical and experimental values for the current efficiency in the chlorate cell process suggests that the established mathematical models could be employed to determine the parameters for the optimisation of both the electrolyser and chlorate plant design.

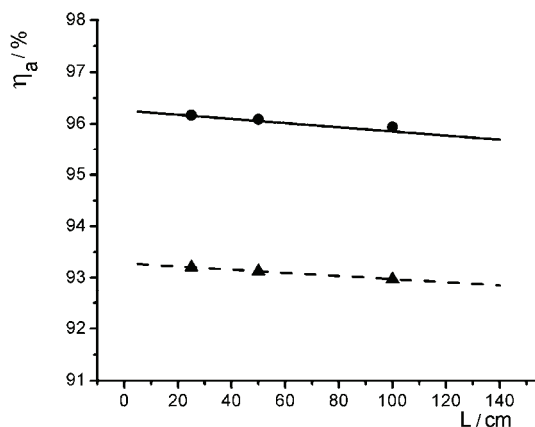


Fig. 4. Anodic current efficiency, η_a , as a function of anode height, L , for different input concentrations of active chlorine, $c_{2,c}$. Theoretical values values derived from Eq. (37) for: $c_{2,c} = 0.05 \text{ mol dm}^{-3} \text{ NaClO}$ (—); $c_{2,c} = 0.10 \text{ mol dm}^{-3} \text{ NaClO}$ (---). Experimental values for: $c_{2,c} = 0.05 \text{ mol dm}^{-3} \text{ NaClO}$ (●); $c_{2,c} = 0.10 \text{ mol dm}^{-3} \text{ NaClO}$ (▲); ($300 \text{ g dm}^{-3} \text{ NaCl}$, $3 \text{ g dm}^{-3} \text{ Na}_2\text{Cr}_2\text{O}_7$, $t = 80^\circ\text{C}$, $j = 300 \text{ mA cm}^{-2}$, $v = 50 \text{ cm s}^{-1}$).

CONCLUSIONS

New mathematical models have been developed to describe current efficiency in the chlorate cell process, both for cells serving as ideal stirred reactors and for those acting as ideal tubular reactors. It was experimentally determined that chlorate cells equipped with short anodes and exhibiting sufficient electrolyte velocity in the inter-electrode gap act as ideal stirred electrochemical reactors. Chlorate cells with a greater anode height behave as tubular reactors with an axial linear concentration profile of active chlorine. Good agreement was obtained between the current efficiency values determined by the established mathematical models and the experimental values.

NOMENCLATURE

- c_1 – chlorine concentration, mol dm^{-3} ;
- \bar{c}_1 – mean chlorine concentration, mol dm^{-3} ;
- c_2 – active chlorine concentration, mol dm^{-3} ;
- \bar{c}_2 – mean active chlorine concentration, mol dm^{-3} ;
- c_0 – active chlorine concentration in the bulk of the solution, mol dm^{-3} ;
- $c_{2,c}$ – active chlorine concentration at the entrance to the cell, mol dm^{-3} ;
- $c_{2,h}$ – active chlorine concentration at the exit from the cell, mol dm^{-3} ;
- $c_{2,l}$ – active chlorine concentration at the height l from the entrance to the cell mol dm^{-3}
- D_1 – diffusion coefficient of chlorine, $D_1 = 1.86 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$;
- D_2 – diffusion coefficient of active chlorine, $D_2 = 1.86 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$;
- δ_a – thickness of anode diffusion layer, $\delta_a = 1.0 \cdot 10^{-2} \text{ cm}$;
- F – Faraday constant, 96487 C mol^{-1} ;
- n – amount of active chlorine;
- k_1 – the rate constant for chlorine hydrolysis, $k_1 = 6.0 \cdot 10^{-3} \text{ s}^{-1}$;

S – part of the anode surface where old elements of the solution are replaced by new ones per unit of time,

τ – time, s;

t – temperature, °C;

j_a – anodic current density, mA cm⁻²;

I – total current in the cell, mA;

L – anode height, cm;

l – coordinate in the flow direction, cm;

b – anode width, cm;

g – interelectrode distance, $g = 0.3$ cm;

A – anode surface area, $A = 200$ cm²;

v – electrolyte flow velocity in the interelectrode gap;

q – volumetric flow rate of electrolyte in the interelectrode gap, cm³ s⁻¹;

η_a – anodic current efficiency.

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ИЗВОД

ИСКОРИШЋЕЊЕ СТРУЈЕ ХЛОРАТНОГ ЕЛЕКТРОЛИЗЕРА

МИРОСЛАВ Д. СПАСОЈЕВИЋ¹, ЛЕНКА Ј. РИБИЋ-ЗЕЛЕНОВИЋ¹ И БРАНИСЛАВ Ж. НИКОЛИЋ²

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Постављен је математички модел за искоришћење струје хлоратног електролизера са равномерним транслаторним током раствора дуж анодне површине. Модел важи за електролизере у којима концентрација хипохлорита линерано расте од улаза до излаза. Установљено је добро слагање експериментално одређених вредности и вредности израчунатих на бази математичког модела.

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