

Mutual Effect of Current Density, pH, Temperature, and Hydrodynamic Factors on Current Efficiency in the Chlorate Cell Process

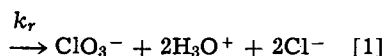
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ABSTRACT

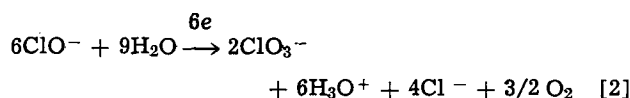
The simultaneous mutual effect of pH, temperature, current density, and hydrodynamic factors on current efficiency in the chlorate cell process has been investigated and considered. Certain practical considerations of the process optimization are also given. Some contributions to the scale-up of chlorate cells have also been introduced. It has been pointed out that by adjusting all other parameters at their optimal values (temperature, pH, and the linear velocity of flow), the current density is then the main factor providing high current yields.

The basic electrode process in electrochemical chlorate production is anodic chloride ion oxidation, accompanied by immediate hydrolysis of the resulting elemental chlorine, that yields as a further intermediate product hypochlorous species or available chlorine.¹ Two simultaneous parallel ways remain for active chlorine to reach the final state of chlorate formation. The first and the useful one (t_1) would be its direct chemical conversion



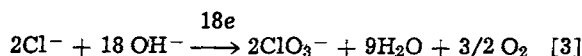
well known as the Foerster reaction of chemical chlorate formation (1).

The second and unavoidable path represents another Foerster reaction of further anodic hypochlorite oxidation to the final state



also known as the reaction of electrochemical chlorate formation (1), which represents an unnecessary loss of current (t_2).

For the sake of Faradaic balance treatment, it is much more convenient to present the reaction of electrochemical chlorate formation in a form of total anodic oxidation process from chloride ion to the final species



In the chlorate cell process one practically neglects anodic chlorine evolution and defines as efficient (t_1) the electrode path in which the electrochemical oxidation goes to the hypochlorous species only, with chlorate as further final product of the pure chemical conversion. Considering the total anodic chloride oxidation to the final state (reaction [3]) as unavoidable anodic current losses (t_2), it can easily be shown that the over-all current efficiency (t) of the whole electrolytic process is the same as that of the first stage chloride anion oxidation (t_1), or in another words, that $t_1 + t_2 = 1$.

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Key words: active chlorine, hypochlorous species, steady-state current yields, back-mix-flow reactor, plug-flow reactor, instantaneous current efficiency.

¹ "Available chlorine" comprises the sum of concentrations of hypochlorous acid, hypochlorite ion, and dissolved elemental chlorine. However, at the pH of usual electrolytic chlorate production the latter can be neglected, so that the more convenient term active chlorine will be used henceforth for hypochlorous entities only.

Both reactions (Eq. [1] and [3]) are dependent on each other and hence both depend on pH, temperature, current density, electrolyte volume ratios, and their active chlorine contents, as well as on the hydrodynamic conditions inside the cells.

A chlorate production system mainly consists of the cells and the holding volume usually in a closed loop. The cell has often been considered primarily as a generator of active chlorine, and the holding volume as a reactor for its further conversion to the final product. (2).

Faradaic stoichiometry and material balance consideration have been leading to the derivation of an equation which relates the over-all current efficiency (t_1) of chlorate production to the operational parameters of the process including all partial volume contributions of active chlorine conversion (see Appendix I) throughout the system (2)

$$t_1 = \frac{2}{3} + \frac{2f_c^2 \cdot k_{r,c} \cdot V_c \cdot F}{I} \cdot \frac{K^* \cdot c \cdot (a_{\text{H}_3\text{O}^+})_c^2 \cdot C_{sc}^3}{[K^* \cdot c + (a_{\text{H}_3\text{O}^+})_c]^3} + \frac{2}{3} F \left(\frac{q}{I} \right) \cdot (C_{sc} - C_{sh}) - \frac{2}{3} (t_3 + t_4) \quad [4]$$

or otherwise (2)

$$t_1 = \frac{2}{3} + \frac{2f_c^2 \cdot k_{r,c} \cdot V_c \cdot F}{I} \cdot \frac{K^* \cdot c \cdot (a_{\text{H}_3\text{O}^+})_c^2 \cdot C_{sc}^3}{[K^* \cdot c + (a_{\text{H}_3\text{O}^+})_c]^3} + \frac{2f_h^2 \cdot k_{r,h} \cdot V_h \cdot F}{I} \cdot \frac{K^* \cdot h \cdot (a_{\text{H}_3\text{O}^+})_h^2 \cdot C_{sh}^3}{[K^* \cdot h + (a_{\text{H}_3\text{O}^+})_h]^3} - \frac{2}{3} (t_3 + t_4) \quad [5]$$

where I denotes the total current or the cell load; k_r is the rate constant for the reaction [1]; q , the flow rate; V , the electrolyte volume; F , the Faraday constant; f , the activity coefficient of hypochlorous acid; K^* , the rearranged dissociation constant of hypochlorous acid (see below); $a_{\text{H}_3\text{O}^+}$, the hydronium ion activity; C_s , the active chlorine concentration; and t_3 and t_4 , possible current losses for chlorine evaporation and cathodic hypochlorite reduction, respectively. The last two terms could be neglected in common practice of the chlorate production, that means $t_1 + t_2 + t_3 + t_4 \approx t_1 + t_2 = 1$. Subscripts c and h shall refer, throughout, to the quantities corresponding to the cells and to the holding volume, respectively. In the above equations f^2 approximately represents the Brönsted's kinetic coefficient (3, 4) for the reaction of chemical chlorate formation (Eq. [1]).

The first term in Eq. [4] and [5] defines current yields under conditions such that all electrolytically produced active chlorine simultaneously undergoes the further electrochemical oxidation to chlorate according to Eq. [3]. The next two terms represent contributions to the over-all current efficiency of the chemical conversion of hypochlorous species taking place inside the cells and the holding volume, respectively.

The pH Effect of the Whole Chlorate System

One could immediately draw some general conclusions considering Eq. [4] and [5] by quite a simple analysis. Firstly, in very acid solutions, when hypochlorous species decompose and tend to negligible concentration, chlorine evolution approaches its maximal current yields ($t_3 \rightarrow 1$), chlorate current efficiency takes small values, and the whole cell operates as a chlorine producing unit. On the contrary, in alkaline solutions ($a_{H_3O^+} \rightarrow 0$), hypochlorous acid approaches zero concentration, and all active chlorine builds up its concentration and exists in the form of hypochlorite ions. This reduces chemical conversion of available chlorine to negligible rates, so that the final effect represents chlorate production taking place from total anodic oxidation only (Eq. [3]). Therefore, one has to seek an intermediate pH range providing the optimal operating conditions and yielding the maximal current efficiencies. In the two limiting cases, just discussed, neither the temperatures and the current density, nor any other operating variable and parameter could bring about any improvement of the chlorate cell efficiency. Hence, a certain mutual effect of variable optimization must exist somewhere in between these two limiting cases.

The pH Effect of the Holding Volume

Partial differentiation with respect to ($a_{H_3O^+}$) of both terms relating over-all current efficiency in Eq. [5] to the contributions of hypochlorous species conversion inside the two volumes, V_c and V_h , reveals the optimal pH region providing maximal current yields to be

$$pH_M = pK^* - \log 2 \quad [6]$$

The rearranged dissociation constant (5), as well as its corresponding thermodynamic value, represents a quantity dependent on temperature.

It has previously been shown elsewhere (5) that the relevant equilibrium constant for calculating the actual hypochlorous species contents at the ionic strengths of the chlorate cell brine and for evaluating the over-all current efficiency according to Eq. [5], is

$$K^* = \frac{a_{H_3O^+} \cdot C_{ClO^-}}{C_{HClO}} = K_a \frac{f \cdot a_{H_2O}}{f_{ClO^-}} \approx 10 \cdot K_a \quad [7]$$

where K_a stands for its thermodynamic value, and other signs have the usual meaning.

Caramazza (6) revealed the functional temperature dependence of the thermodynamic dissociation constant of the hypochlorous acid to obey the equation

$$pK_a = \frac{800}{T} + 4.892 \quad [8]$$

However, Morris (7) has recently presented somewhat more reliable data expressed by the following relation

$$pK_a = \frac{3000.00}{T} - 10.0686 + 0.0253 \cdot T \quad [9]$$

which was asserted to be valid up to 45°C (7).

Thus, combining Eq. [8] and [9] with [6] and [7], one obtains the temperature dependence of the optimal pH range (pH_M) for the chlorate cell process. Some experimental and calculated values are shown in Fig. 1. One easily observes that the higher the temperature, the lower is the optimal pH value which provides maximal current yields in the electrolytic chlorate production [cf. (5)]. This matter has been discussed in more detail elsewhere (5).

The pH Effect of the Chlorate Cell

The pH effect of the chlorate cell itself on the over-all current yield was investigated as a function of the holding volume temperature at constant current density (Fig. 2). It has again been experimentally confirmed that the optimal pH range given above provides maximal current efficiencies. However, one could accept as much more important the optimal pH value to be maintained inside the holding volume, whose content and retention time are of incomparably higher values. Due to the chemical conversion of available chlorine, as well as the reaction proceeding (Eq. [1]) the electrolyte tends to be more acid. Hence, one needs a somewhat higher pH value of the brine leaving the cell and entering the holding volume, in order to maintain optimal acidity inside the latter. Of course, this also depends on the buffer content (hydrochloric acid) in the brine. At the same time one tends to reduce and maintain an optimal dichromate concentration for many important reasons. First, of all, the latter is partially lost during the crystallization of the final product. Also, although dichromate enables the cathodic hypochlorite reduction to be effectively suppressed, and

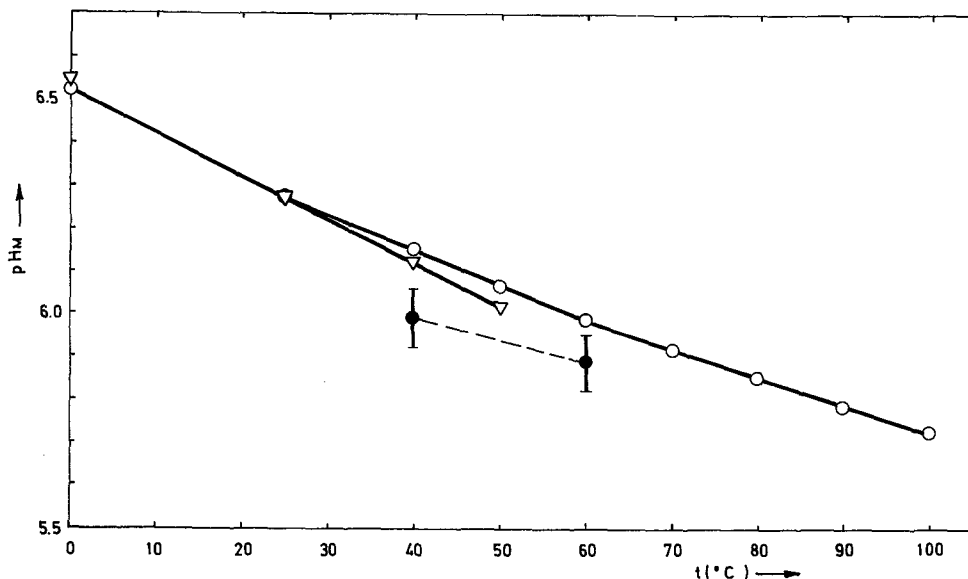


Fig. 1. Theoretical (\circ , ∇) and experimental (\bullet) temperature dependence of the optimal pH value (pH_M) providing maximal active chlorine conversion rates into chlorate inside the holding volume [\circ and ∇ according to Caramazza (6) and Morris (7), respectively].

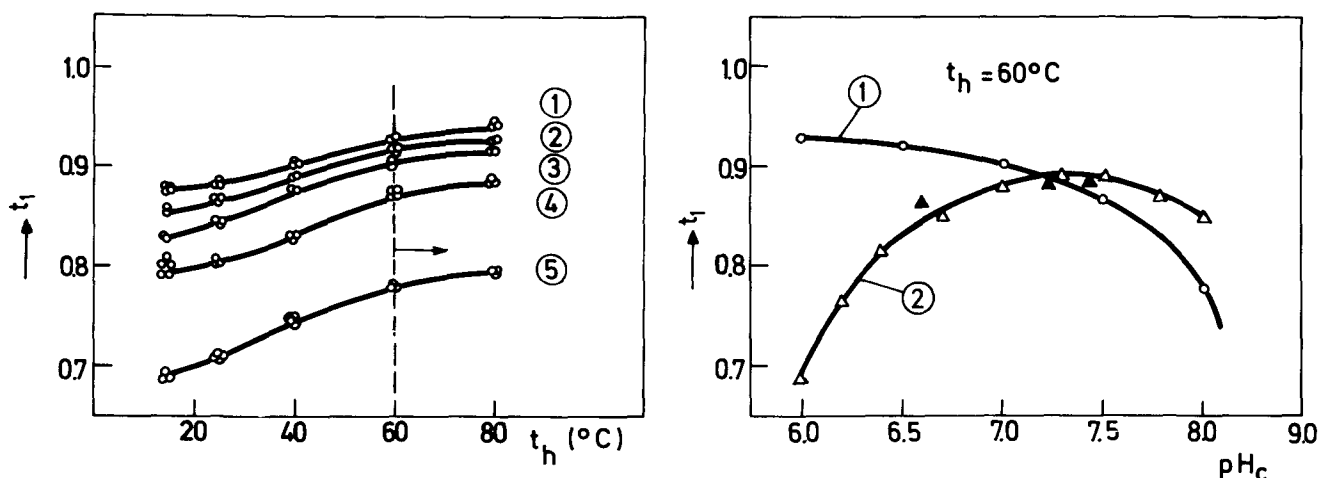


Fig. 2. Mutual effect of the cell pH (pH_c) and the holding vessel temperature (t_h) on the current efficiency (η) in the electrolytic chlorate process. \circ , experimental data (pH_c : 1—6.0; 2—6.5; 3—7.0; 4—7.5, and 5—8.0); other operating parameters being maintained constant, I , i , q , V_c , V_h , and t_c ; Δ and \blacktriangle , theoretical and experimental values, respectively, according to Claus (12) [cf. (33)].

enables useful buffering of the brine, chromate ions simultaneously exhibit an undue effect on the anodic cell process (8). On the other hand, however, chromate ions represent an efficient inhibitor of corrosion for precious metals deposited on titanium anodes and hence, one may need to increase their brine content (9) for this reason.

The Over-All Temperature Effect of the Chlorate System

The temperature effect of the chlorate producing system is confined by a certain number of kinetic parameters encompassed by the relationships for current efficiency given above, i.e., k_r , K^* and, as will be seen below, over the rate constant for chlorine hydrolysis. In addition the simultaneous effect of increasing temperature on cell voltage decrease is well known, thus providing for power consumption to be efficiently decreased as well. One tends, therefore, to increase the temperature throughout the whole system. However, the temperature exhibits a negative effect on anode consumption. Thus, economical considerations define a rather limited level of temperature inside the chlorate cells.

One of the most important temperature effects for the process would be to increase the rate of the chemical conversion of active chlorine (Eq. [1]), which otherwise represents a slow reaction. Hence, an economical compromise is found for cells with graphite anodes in temperature range of about 40°C . Nevertheless, to increase chemical chlorate formation inside the whole system, it has been suggested that the retention volume of the reactor should be elevated to a relatively higher temperature level (2).

Due to platinum metal coating corrosion, one also chooses, as well suited from an economical point of view, a rather compromised temperature range of about 60°C for chlorate cells with titanium (DSA) anodes (9). This higher temperature increases current yield and reduces the over-all power consumption.

There exists another important reason for limiting the temperature of the chlorate producing system. It appears because of the thermal decomposition of the hypochlorous species resulting in oxygen evolution and reverting active chlorine to its initial state of chloride ions (10, 11). Therefore, an exact derivation of the relationships given before the over-all current efficiency (Eq. [4] and [5]) requires that the thermal decomposition rate of active chlorine should also be included in the whole material balance treatment of the system [cf. (12)].

All the above considered reasons have resulted in a temperature range for actual chlorate systems of about 60°C .

This region has also been confirmed experimentally and assessed as the optimal and efficient one (Fig. 2 and 3). Namely, mainly due to the relatively low active chlorine concentration inside the optimal pH region for chlorate production, a rather asymptotic leveling effect of temperature on the current efficiency appears above 60°C . This is much more pronounced at lower current densities as could be noted in Fig. 4. Therefore, it could be concluded that the heating effect of the holding volume (2) is efficient enough indeed, and of practical importance only for chlorate cells running at low current densities (unipolar cells with graphite anodes).

The over-all current efficiency (η) dependence on the holding vessel temperature is evidently not a straightforward one. One should consider that, in addition to kinetic parameters $k_{r,h}$ and K^*_{h} , the effect of active chlorine content (C_{sh}) in Eq. [4] and [5] is also temperature dependent in a quite complex manner. This could be comprehended as follows. Both relationships (Eq. [4] and [5]) reflect primarily the Faradaic stoichiometry which states that, the larger the current efficiency, the higher should be the accumulation of the active chlorine inside the cell ($C_{sc} - C_{sh}$) or the lower the hypochlorous species content leaving the holding volume ($C_{sh} \rightarrow 0$). However, a quite converse require-

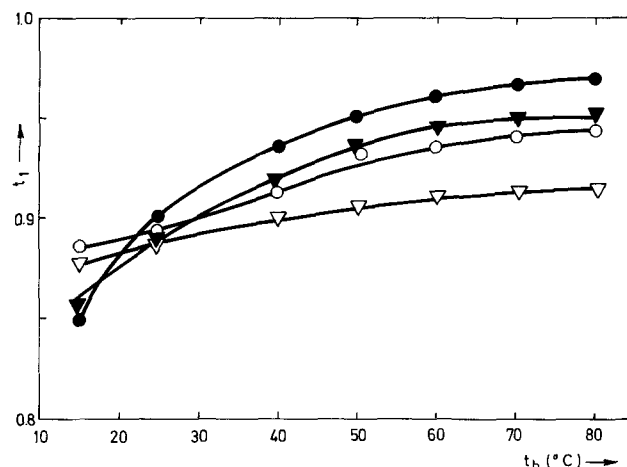


Fig. 3. Mutual effect of the temperature (t_h) and the pH inside the holding volume (pH_h) on the current efficiency (η) in the chlorate cell process: \bullet and \blacktriangledown experimental data at pH_h 6.0 and 6.5, respectively; other operating parameters being maintained constant: I , i , q , V_c , V_h , and t_c . \circ and ∇ denote calculated values according to Eq. [10] for experimental values of the C_{sc} at the pH_h 6.0 and 6.5, respectively.

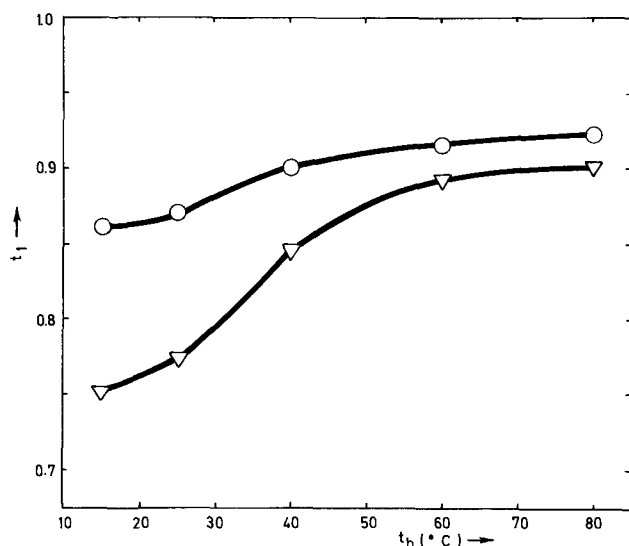


Fig. 4. Mutual effect of the current density (i) and the holding vessel temperature (t_h) on the current efficiency (t_1) at a constant pH of the cell (pH_c—6.0). ○ and ▽ denote experimental data at current densities 6.67 and 1.8 A/sq. dm., respectively. Other operating parameters of the system being maintained constant are q , V_c , V_h , and t_c .

ment arises from hydrodynamic considerations (see below), because the increase of the C_{sc} leads consequently to proportional current losses due to increased direct anodic oxidation.

Therefore, although the concentration difference ($C_{sc} - C_{sh}$) is needed as large as possible, one should at the same time also try to maintain the C_{sc} as low as possible. This fact is in itself a practical reason causing the existence of an optimal holding vessel to cell volume ratio (V_c and V_h), previously often considered in terms of current concentration. This is also the reason why active chlorine concentration (C_{sh}) entering the cell is never negligible compared to the one leaving it or why the former does not tend to zero or negligible values at all, as required by Eq. [4], to approach the maximal current efficiencies. Therefore, the increase in the rate of active chlorine conversion into chlorate with temperature must exhibit an asymptotic tendency to a certain maximal value, in spite of the fact that the rate constant is increasing, because the concentration factor in the rate expression (Eq. [5]) decreases with the third power (Fig. 3). Hence, both values of active chlorine content, entering and leaving the cell, under practical operating conditions of chlorate production are usually of the same order.

Considering Eq. [4], it could be easily found that the higher the flow rate (q), the smaller the difference of the two active chlorine contents ($C_{sc} \rightarrow C_{sh}$) and the whole term reflecting the holding volume contribution to the over-all current efficiency of the system asymptotically tends to its limiting value.

Quite a simple analysis would lead to the conclusion that, just due to the small active chlorine contents throughout the system, the plug-flow type of reactor (V_h), for the same volume, provides higher degrees of conversion to chlorate and higher current yields, than does the back-mix flow one (26).

The Contributions of Hydrodynamic Factors to Over-All Current Yield

There has been an old general acceptance in the chlorate cell process that the motion of the electrolyte inside the cell should be reduced in order to provide concentration polarization for the anodic oxidation of the active chlorine. However, Ibl and Landolt (13) were the ones to show an interesting and complex

nature of its anodic diffusion layer. Namely, due to the subsequent chlorine hydrolysis, which prevalently takes place within the diffusion layer, hypochlorous species diffuse in both directions from and toward the generating electrode, thus creating a certain concentration maximum inside the diffusion layer (13).

Hence, in order to really provide the concentration polarization, the diffusion layer should be cut down from the solution side by increasing the linear velocity of brine flow increasing thereby the fraction of hypochlorous species, which then avoids a further anodic oxidation.

The concentration profile, the resulting active chlorine flux and the concentration gradient at the anode surface, were also analytically given by Ibl and Landolt (13). Equating the Ibl-Landolt equation for the flux with the fraction of the current used for further active chlorine anodic oxidation, Despic et al. (14) were able to derive a quantitative expression relating the over-all current efficiency to the hydrodynamic, operational, and kinetic parameters of the process

$$t_1 = \frac{1 - \frac{D_2 \cdot F}{i \cdot \delta} \cdot f_{sc} \cdot C_{sc}}{\frac{3}{2} - \frac{1 - \exp(-\delta \sqrt{k_1/D_1})}{2\delta \cdot \sqrt{k_1/D_1}}} \quad [10]$$

where δ is the anodic diffusion layer thickness; k_1 , the rate constant for the reaction of chlorine hydrolysis; i , the current density; D_1 and D_2 are the diffusion coefficients of the elemental chlorine and the active chlorine, respectively; while f_{sc} represents the formal activity coefficient of both hypochlorous species taken together as active chlorine. This relationship differs from the original flux equation [cf. (13)] by the correction introduced to extend its application to concentrated solutions. In other words, instead of the concentration, one relates the flux and thereby the current efficiency to the activity of active chlorine (14). Namely, one could easily find it much more convenient to use the chemical potential as the driving force of diffusion in concentrated solutions and, hence, to relate fluxes of the considered species to their individual activities in the first approximation. In general this is a better approximation anyway compared to the application of their concentrations in the Fick's equation (18). Some ions, however (and particularly the hydronium ion is usually the most important among them in aqueous solutions) undergo considerable, but regular activity changes in concentrated solutions of some neutral salts (19). The same conclusion is found to be valid for the hypochlorite ion, and in concentrated solutions of neutral salts also for both hypochlorous species taken formally together in the form of active chlorine (18).

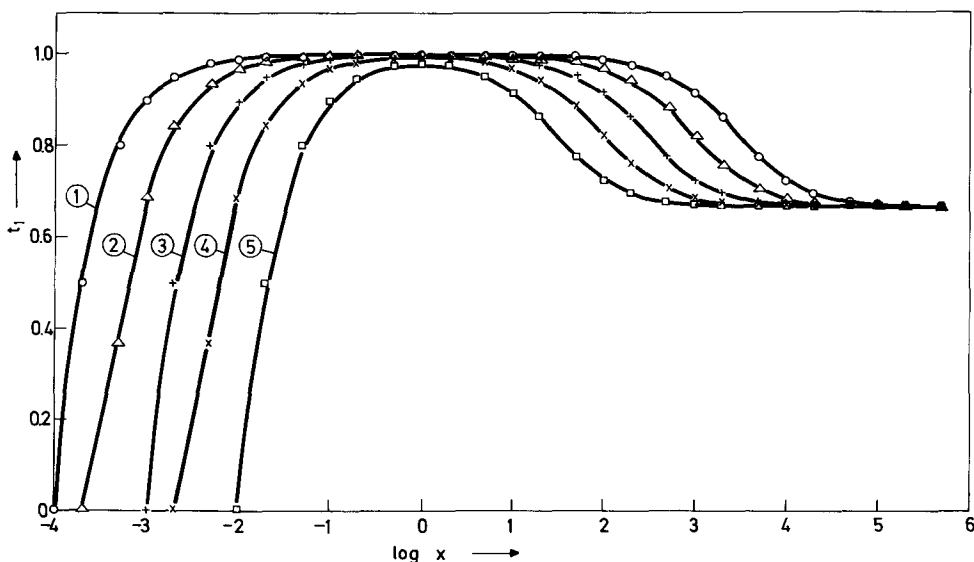
Certain individual activities have recently appeared as experimentally attainable values in the first approximation at least (19, 20). It will be shown at another instance that these activities obey the diffusion relationships much better than their corresponding concentrations (18).

One should not overlook the fact that the concentration of active chlorine, C_{sc} , does not represent an independent value, but a variable of a very complex nature. Therefore, Eq. [10] is valid for its steady-state values only (2, 14).

Of course, Eq. [10] could be combined with relations [4] and [5], as well as with the one expressing material balance of the holding vessel, in order to eliminate or to introduce the steady-state C_{sc} and C_{sh} values in resulting relationship [cf. (14) and (21)].

According to Eq. [10], the over-all current efficiency exhibits a region of maximal values as function of the anode diffusion layer thickness (Fig. 5). This range is defined by the following transcendental function

Fig. 5. The current efficiency (t_1) of the chlorate cell as a function of the anode diffusion layer thickness (δ) for various C_{sc}/i ratios taken as parameter at 25°C (see Appendix II). Calculated values according to Eq. [10].



$$i - D_2 F \cdot f_{sc} \cdot C_{sc} \sqrt{\frac{k_1}{D_1}} + i \sqrt{\frac{k_1}{D_1}} \cdot \delta_M$$

$$= \left(i - 3 D_2 F f_{sc} \cdot C_{sc} \cdot \sqrt{\frac{k_1}{D_1}} \right) \cdot \exp \left(\delta_M \sqrt{\frac{k_1}{D_1}} \right) \quad [11]$$

or approximately by the relation

$$\delta_M \approx 2 \sqrt{\frac{D_2 \cdot F \cdot f_{sc} \cdot C_{sc}}{i}} \cdot \sqrt{\frac{D_1}{k_1}} \quad [12]$$

It would be worthwhile to point out that the current yields always reach their maximal values for $\delta_M > 0$. Such a conclusion results from the consideration of Eq. [11]. Namely, its left-hand side represents a straight line, while its right-hand side defines an exponential function of the diffusion layer thickness. Both lines, however, always cross each other for $\delta_M > 0$. Moreover, under practical operating conditions this represents an easily attainable required condition.

It is also worthwhile to note that the current efficiency, according to Eq. [10] could reach values lower than 2/3 only for unsteady-state active chlorine contents. In such a case, t_1 does not represent the steady-state yield, but the instantaneous one, which changes successively with time and with the active chlorine consumption. It asymptotically approaches both C_{sc} and t_1 , the final steady values. Moreover, the chlorate cell anode represents in itself a self-adjusting system. That means, the larger the diffusion layer thickness the lower is the instantaneous current efficiency (see Eq. [10]), but it also means the more intensive is oxygen evolution. On the other hand, gas evolution represents an efficient short-circuiting of the diffusion layer [cf. (15, 16, and 31)] and hence, the latter begins to decrease in accordance with oxygen evolution rate, resulting in a gradual increase of the current efficiency with time.

As one could easily note, current losses ($1 - t_1$) now do not represent a direct, but a very complex function of the active chlorine concentration [cf. (3)]. This results from quite an unusual diffusion layer structure and the very complex active chlorine profile, the latter being quite different from the Nernst linear distribution.

Equation [10] has been experimentally found well suited in the chlorate cell process (14) (Fig. 3). In conclusion, it could also be emphasized that the hydrodynamic operating parameters and conditions of the cell represent essential factors (Fig. 5) for the process inside the latter because of the occurrence of quite unusual and specific events taking place inside the anode diffusion layer.

The Effect of Current Density

The main characteristic of the two parallel anodic reactions taking place simultaneously in the chlorate cells represents the fact that, in common industrial practice at least, chloride oxidation abounds in the ions present (usually the steady-state concentration is about 2 moles/liter), while the reaction of hypochlorous species, being rather concentration polarized, is suppressed (C_{sc} is usually of the order $3 - 5 \cdot 10^{-2}$ moles/liter). Therefore, the most efficient and intrinsic parameter of the chlorate cell process providing higher current efficiencies is the current density itself (cf. below Fig. 9). However, in order to effectively use these common conclusions regarding concentration polarization and to adjust the anodic process, a suitable anode material is needed.

Figure 6 shows the current efficiency dependence on the current density. Experimental data are compared with data predicted by Eq. [10] as well as with other values appearing from another theory (12) for environmental (25°C) temperatures and common active chlorine concentrations.

For more than eighty years graphite has been the unique anode material in electrolytic chlorate production. Mainly due to its relatively poor polarization characteristics for the anode reaction of chlorine evolution, and also because of its relatively high resistance, one has had to reduce the current density to between 2.5 and 5.0 A/dm² for the industrial cell process.

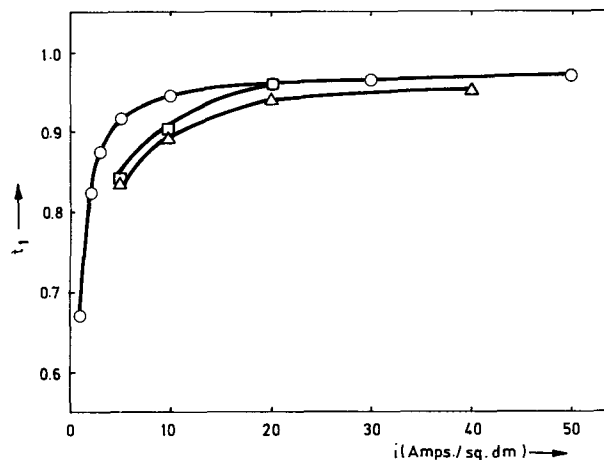


Fig. 6. The current efficiency (t_1) of the chlorate cell as a function of the current density (i). \circ , theoretical values according to Eq. [10] for the common active chlorine concentration ($C_{sc} = 4.0 \cdot 10^{-2}$ mol/liter); δ , $8.2 \cdot 10^{-4}$ cm; f_{sc} , 0.1; and t_c , 25°C; \square , experimental data; and \triangle , values according to Claus (12).

At the same time, one had to reduce the cell temperature to maintain the graphite wear to economical conditions of consumption. The graphite wear, however, also represents, besides other factors, an anodic property depending on its potential and thereby on the current density (22). Therefore, both the concentration polarization for the active chlorine oxidation at the anode and its chemical conversion to the final state, have been inconveniently restricted. The resulting current efficiencies, for chlorate cells with unipolar graphite electrodes, at least, are thereby in practice usually rather limited to values of about 0.8 (see Fig. 6). In accordance with relationships [4] and [5], in order to increase the current efficiency, even in the case of cells using graphite anodes, some suggestions have been given (2) consisting of an independent increase of the holding volume temperature, while maintaining the reasonably low temperature of the cell. This provides further intensification of chemical conversion inside the former and, thereby its further contribution to the over-all current yields (30).

Recently, however, metallic electrodes of dimensionally stable behavior and with greatly advanced polarization characteristics (DSA-electrodes) (23) finally appeared.

The higher the current density, the more economical is the consumption of precious metals. However, the IR-drop severely increases linearly with the current density and, moreover, very soon the limiting current is reached for the anode oxidation of chloride ions. Therefore, besides the quite advanced polarization properties of DSA-electrodes which results in a higher asymptotic effect of the current density on the current efficiency (Fig. 6), a range of about 30 A/dm² has been chosen as a compromise and accepted as the most convenient. Of course, this requires an optimal pH region of the brine to be maintained, too, because out of it, not only the current density, but also all other process parameters are practically of no effect. The cell operates either as a chlorine producer in the acid region, or produces chlorate as the final product of total electrochemical oxidation in the alkaline region thus yielding the lower steady-state value of the current efficiency ($t_1 \rightarrow 2/3$).

Some Scale-Up Considerations of the Chlorate Cells

Equation [10] relates the current efficiency to the average value of the actual steady-state active chlorine concentration (C_{sc}) for chlorate cells operating as back-mix-flow reactors. A different situation arises in the more frequent case of plug-flow cells. In the latter case one must first integrate a material balance equation (2, 17, 24) for an element of the cell volume along the anode (Fig. 7)

$$\frac{dC_{sc}}{dl} = \frac{i}{2Fq} (3t_{1(l)} - 2) \quad [13]$$

where $t_{1(l)}$ denotes the local current yield depending on the anode length (l). The $t_{1(l)}$ from Eq. [10] may be substituted in relationship [13], on the assumption that the former relates the local current efficiency for any element of the anode length to its particular active chlorine concentration ($C_{s(l)}$). Integrating from entering hypochlorous species content of the cell (C_{sh} , $l =$

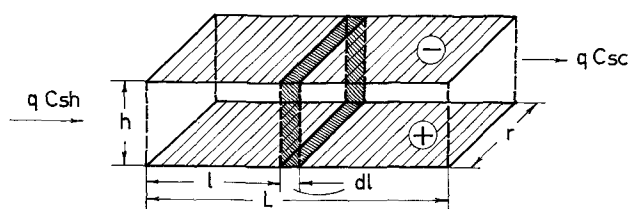


Fig. 7. Elemental cross section of the chlorate cell plug-flow running.

0), to the leaving one (C_{sc} , $l = L$), one easily comes to the distribution relation for the active chlorine concentration along the anode (17). Now, again, the over-all current efficiency of chlorate cells running in plug-flow is obtained as an average of the local current yields (17), i.e.

$$t_1 = \frac{1}{L} \int_0^L t_{1(l)} dl \quad [14]$$

or, finally

$$t_1 = \frac{2}{3} + \frac{2}{3} \cdot \frac{Fq}{irL} \left[\frac{i(1 - \exp(-\delta\sqrt{k_1/D_1}))}{3D_2Ff_{sc}\sqrt{k_1/D_1}} - C_{sh} \right] \cdot \left\{ 1 - \exp \left\{ -\frac{3}{2} \cdot \frac{irL}{Fq} \cdot \frac{D_2Ff_{sc}}{i\delta} \right\} \right\} \cdot \left\{ \frac{3}{2} - \frac{1 - \exp(-\delta\sqrt{k_1/D_1})}{2\delta\sqrt{k_1/D_1}} \right\} \quad [15]$$

where r denotes the anode width. This relationship, as well as the intermediate ones, have also been experimentally tested in a ribbon type of cell and found to well obey the process (17, 24).

The final equation [15] was examined by analogue computer analysis in order to relate the current yields to the anode diffusion layer thickness and cell dimensions (Fig. 8). It could easily be found that the relationship [15] reflects in essence the previous relation (Eq. [10]), which already has been discussed, and which is also implicitly encompassed by the former. In other words, by increasing the linear brine velocity of flow along the anode, the current yields first also increase, and after some maximum, decrease again. At relatively fast flow rates, the anode length exhibits a more pronounced effect, but in its optimal range, the longitudinal cell dimension has practically no further effect on the yields within very wide limits. However, because of an intrinsic effect of gas bubble collection at the upper part of the cell (25), the anode length should be reduced. At the same time the flow rate along it optimized, thus providing the diffusion layer thickness maintained within the optimal range. The latter requirement is, of course, easily attainable by the cell's own gas-lifting effect, known under the term of the natural brine recirculation (32).

Equation [15] was tested experimentally and found well suited (17) (Fig. 9). As one could expect from the theory (cf. Eq. [10]), the current efficiency exhibits its maximum range as a function of the diffusion layer thickness or of the linear flow velocity along the anode.

It should also be noted that all the presented equations relating the current efficiency to the hydrodynamic parameters (δ) are based on the Ibl and Landolt (13) relation for the active chlorine gradient at the anode. However, the authors neglected the chemical conversion of hypochlorous species within the anode diffusion layer. This is correct only for their operating conditions of high pH values and low temperatures. Hence, a more complete diffusion relation would be [cf. (13) and (24)]

$$D_2 \left(\frac{d^2 a_s}{dx^2} \right) + k_1 \cdot a_{Cl_2(x)} - 3f_c^2 \cdot k_{r,c} \cdot \frac{K^* (a_{H_3O^+})^2(x)}{[K^* + (a_{H_3O^+})_{(x)}]^3} \cdot C_{s(x)} = 0 \quad [16]$$

The latter, however, could not be easily analytically solved. It would not lead to a simple analytic form of

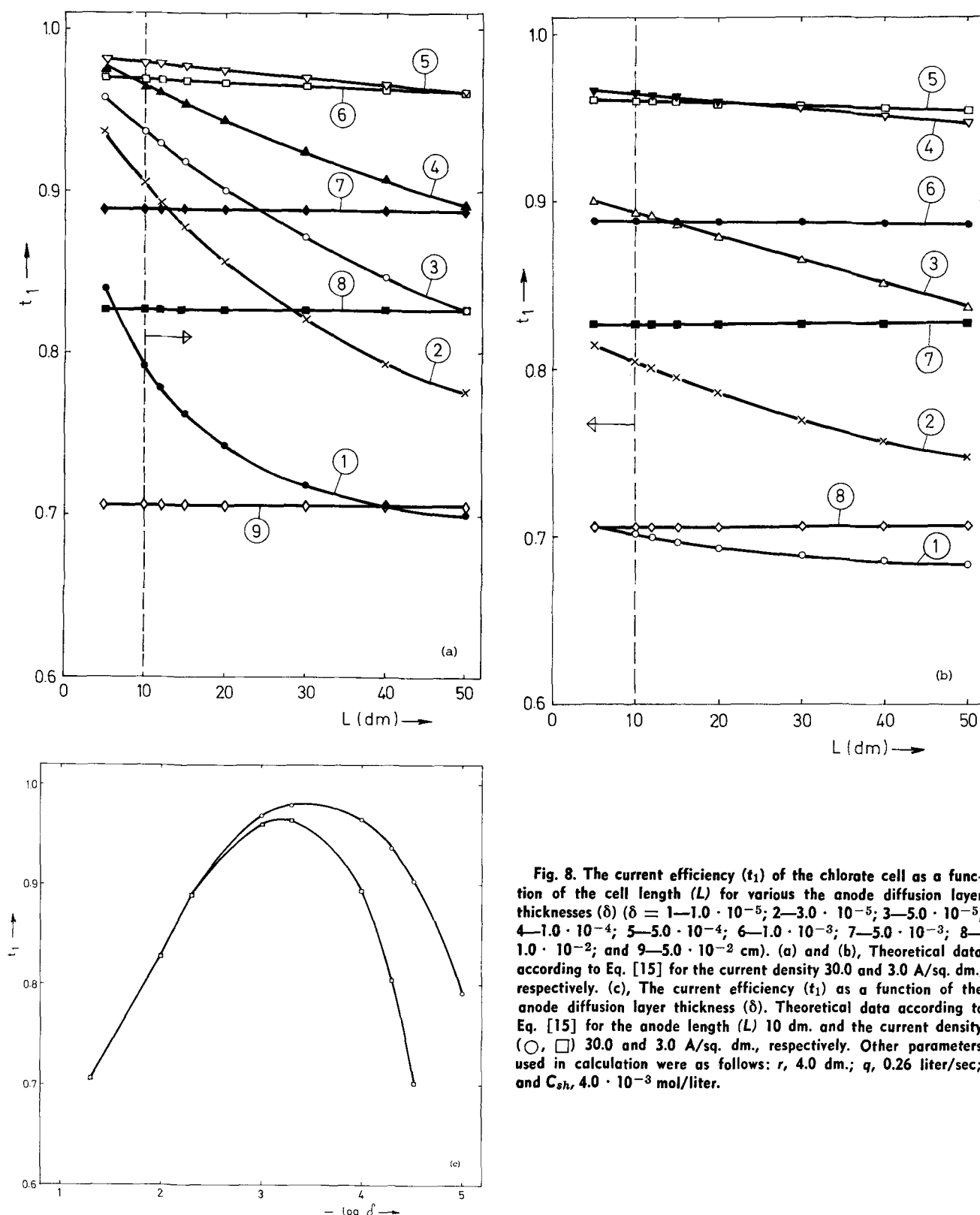


Fig. 8. The current efficiency (t_1) of the chlorate cell as a function of the cell length (L) for various the anode diffusion layer thicknesses (δ) ($\delta = 1-1.0 \cdot 10^{-5}$; $2-3.0 \cdot 10^{-5}$; $3-5.0 \cdot 10^{-5}$; $4-1.0 \cdot 10^{-4}$; $5-5.0 \cdot 10^{-4}$; $6-1.0 \cdot 10^{-3}$; $7-5.0 \cdot 10^{-3}$; $8-1.0 \cdot 10^{-2}$; and $9-5.0 \cdot 10^{-2}$ cm). (a) and (b), Theoretical data according to Eq. [15] for the current density 30.0 and 3.0 A/sq. dm., respectively. (c), The current efficiency (t_1) as a function of the anode diffusion layer thickness (δ). Theoretical data according to Eq. [15] for the anode length (L) 10 dm. and the current density (○, □) 30.0 and 3.0 A/sq. dm., respectively. Other parameters used in calculation were as follows: r , 4.0 dm.; q , 0.26 liter/sec; and C_{sh} , $4.0 \cdot 10^{-3}$ mol/liter.

equation, due to the third power of concentration dependence. Also, the hydrogen ion distribution within the diffusion layer is of rather a complex nature. Thus, it is necessary to solve simultaneously several rather complicated differential equations, encompassing all equilibria, all diffusion fluxes, and also all the electrode reactions at the anode. This advanced and more complex matter will be reported at a latter instance (27).

It should also be noted that, in a view of the fact that active chlorine exhibits the appearance of a maximum concentration within the diffusion layer, which exceeds that in the bulk (13), its further chemical con-

version must not be neglected for higher operating temperatures at least. However, such temperatures just lately characterize up-to-date chlorate cell industrial practice.

The above treatment might be usefully applied as the one leading to the limiting optimal conditions. This implies that, just as the thermodynamic method usually gives the lower limits for the considered processes to be able to proceed at all, the present treatment also provides operational and dimensional limiting conditions for optimal cell current yields. Namely, providing the above-defined optimal cell parameters and main-

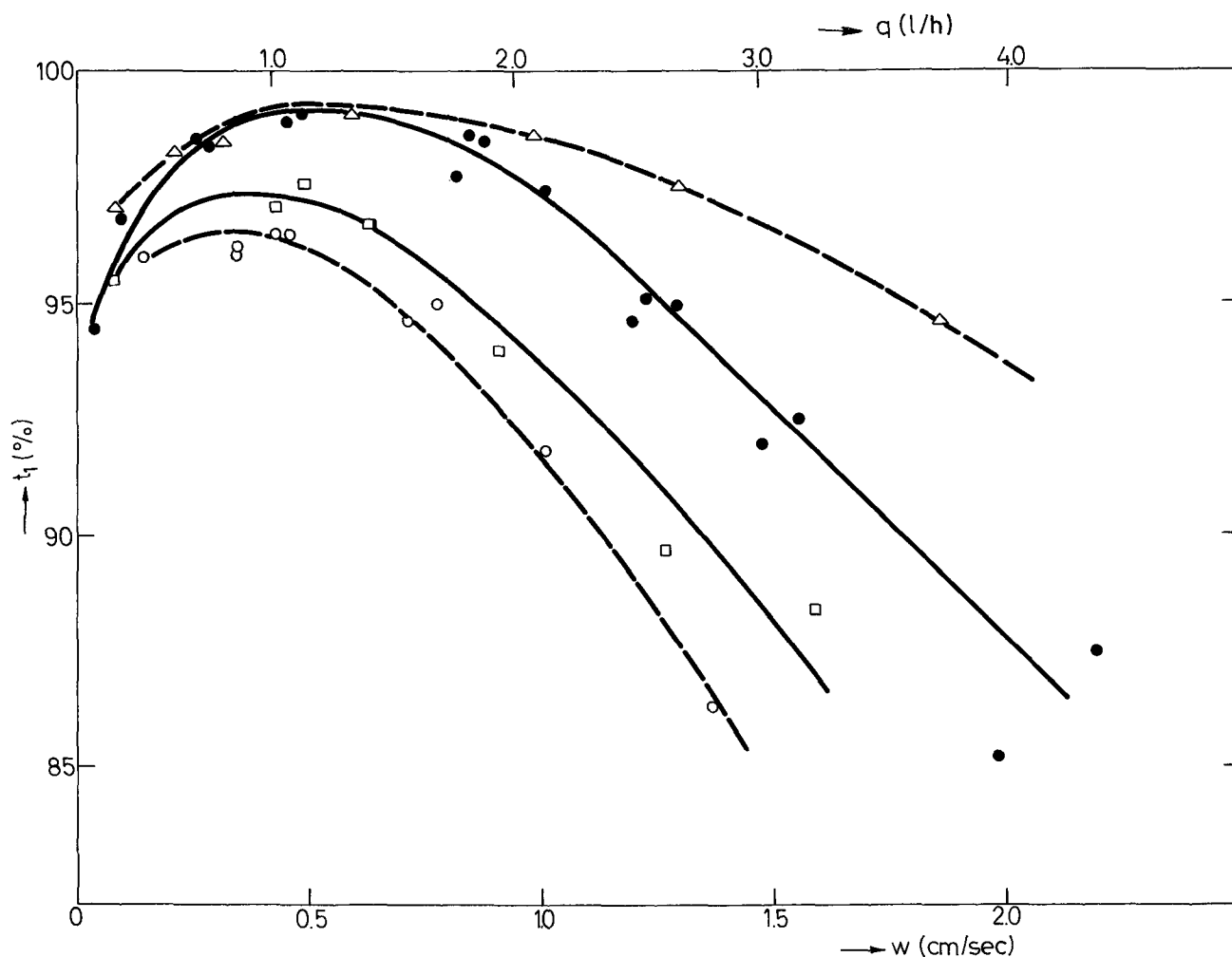


Fig. 9. The effect of the linear velocity of the brine flow on the over-all current efficiency in the chlorate cell plug-flow running. Experimental data for the ribbon type of the cell. ●, □, and ○, values for pH_c —6.5, 7.6, and 8.1, respectively, and at the current density 1.97 A/sq. dm.; △, values for pH_c —6.5 and $i = 3.61$ A/sq. dm.

taining their mutual effect, i.e., the linear velocity of the brine flow, current density, pH, and temperature (just because of the effect of the latter on the decrease of the C_{sc} through its further chemical conversion to chlorate which was neglected in all the equations based on diffusion layer analysis); one could doubtlessly expect better results only, than those predicted by the above equations and consideration (cf. Fig. 5). It should also be noted that both relations which comprise the hydrodynamic factors (Eq. [10] and [15]), exhibit a very pronounced sensitivity on the active chlorine concentration (C_s). Hence, the higher the temperature, the lower should be the active chlorine content, and thereby the higher the current efficiency.

The above consideration represents a certain scale-up and optimization guide for the chlorate cell process based on the Faradaic efficiency. Another side of the medal is represented by its voltage and power optimization. The latter has recently been developed and thoroughly carried out by Rousar *et al.* (25), particularly in examination of the cell dimensions and the gas bubble cell effects. Both methods, the mentioned one (25) and the one presented here, of course, lead to the mutual optimal point at which two independent schemes cross each other and thus define the most suitable operating conditions for the whole electrolytic process.

Experimental Guide

The experimental data presented in this paper were prevalently obtained by means of the same apparatus as that described elsewhere (2). The setup consisted of

an electrolytic cell 0.6 liter in volume and a holding vessel of 2.2 liters connected in a loop so as to provide a constant recirculation of brine at a given flow rate ($q = 8.2 \times 10^{-4}$ liters/sec). The pH in the cell was maintained constant to within ± 0.1 pH unit by means of a pH-stat. The electrolyte was stirred both in the cell and in the holding volume so that they operated as back-mix-flow reactors. The stirring in the cell was intensified by the cathodic evolution of hydrogen and homogenized by an appropriate positioning of both the platinum gauze anode and the wire cathode.

The cell load was maintained at 4.5A, and with the electrode surface area $A = 67.5 \text{ cm}^2$, this implied an anodic current density of 6.67 A/dm².

The cell temperature was maintained at 25°C, while that of the holding volume varied between 15° and 80°C.

In the described setup and under the given hydrodynamic conditions, the diffusion layer thickness was experimentally estimated to be $8.2 \times 10^{-4} \text{ cm}$ by measuring the steady-state limiting diffusion current of the ferrous-cyanide oxidation from a usual and appropriate electrolyte composition [cf. (13)].

Other details of the apparatus and of the determination of the current efficiency may be found elsewhere (2).

The value of the rate constant of chlorine hydrolysis ($k_1 = 0.17 \text{ sec}^{-1}$) was obtained by extrapolation of Spalding's data (28) for the actually existing ionic strength of the chlorate cell brine [cf. (14) and (18)].

The diffusion constants of elemental ($D_1 = 6.7 \times 10^{-6} \text{ cm}^2/\text{sec}$) and active chlorine ($D_2 = 1.2 \times 10^{-5}$

cm²/sec) represents Chao's data (29) corrected for viscosity of solution at the given ionic strength of chlorate production [cf. (14)].

The activity coefficient of hypochlorous acid was taken from data of Imagawa (4) to be about 2.0. The corresponding value for hypochlorite ion, and for active chlorine as well, was estimated to be about 0.1 [cf. (14) and (18)]. Activity of water was approximately taken to be 0.8 (3). The rate constants for the active chlorine chemical conversion to chlorate as function of temperature were taken from data of De Valera (3).

The electrolyte consisted of 300 g/liter of NaCl and about 4.0 g/liter of sodium dichromate. The electrolysis was carried out to 30 g/liter of sodium chlorate, whereupon the electrolyte was renewed.

The apparatus with a ribbon type of cell and the plug-flow circulation was also described elsewhere (17, 24). The entire setup was very similar to the one described elsewhere (2) and partly here, the only difference being that all the dimensions of the apparatus were enlarged. The anode was DSA-electrode supplied by Oronzio de Nora, Milano, Italy ($L = 70$ dm, $r = 4.5$ cm). The current densities were $i = 3.61$ and 1.97 A/sq.dm., and temperature (t_c) was at 14°C .

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1974 JOURNAL.

APPENDIX I

It should be noted that, in deriving Faradaic stoichiometry and mass balance equations, one has been considering (2) both hypochlorous species as potentially equal entities able to take part in both Foerster's reactions of the chemical conversion and the anode oxidation. Hence, both species are together summationally expressed in a certain mutual and more suitable unique form of the active chlorine (C_s). Therefore, for Eq. [1], it could be written

$$-\frac{d[\text{ClO}^-]}{dt} = -\frac{1}{2} \cdot \frac{d[\text{HClO}]}{dt} = \frac{d[\text{ClO}_3^-]}{dt} \quad [\text{A-1}]$$

or, otherwise

$$-\frac{dC_s}{dt} = -\frac{d([\text{HClO}] + [\text{ClO}^-])}{dt} = -3 \frac{d[\text{ClO}^-]}{dt} \quad [\text{A-2}]$$

Further, introducing Foerster's kinetic law for the chemical conversion in concentrated solutions or, in other words, recognizing Brönsted's kinetic theory (1, 4), it could be written

$$-\frac{dC_s}{dt} = 3 \cdot f^2 \cdot k_r [\text{HClO}]^2 \cdot [\text{ClO}^-] \quad [\text{A-3}]$$

As it is already descriptively said, one implies that the active chlorine represents the sum of both hypochlorous species, or otherwise

$$C_s = [\text{HClO}] + [\text{ClO}^-] \quad [\text{A-4}]$$

Two last relations could finally be combined with Eq. [7] that leads to the more suitable form of the kinetic law for the chemical chlorate formation (2, 5)

$$-\frac{dC_s}{dt} = 3 \cdot f^2 \cdot k_r \cdot \frac{K^* \cdot (\alpha_{\text{H}_3\text{O}^+})^2}{[K^* + (\alpha_{\text{H}_3\text{O}^+})^3]} \cdot C_s^3 \quad [\text{A-5}]$$

Namely, considering that both species reversibly interchange their states between each other over an extremely fast reaction of proton exchange [cf. (13)], the active chlorine might be imagined as an instantaneous mutual hybride form similar to an active complex in the transition state. Such a conclusion seems probable for the transition pH range at least, where both hypochlorous species exist in comparable contents.

APPENDIX II

Explanation of Fig. 5

Equation [10] could be presented in a somewhat more convenient form for further computer analysis. Hence, one firstly introduces another parameter (A) being

$$A = D_2 \cdot F \cdot f_{sc} \cdot \frac{C_{sc}}{i \cdot \delta_M} \quad [\text{B-1}]$$

or in combination with Eq. [12] the latter leads to the relation

$$A = \frac{1}{2} \sqrt{\frac{D_2 \cdot F \cdot f_{sc} \cdot C_{sc}}{i}} \sqrt{\frac{k_1}{D_1}} \quad [\text{B-2}]$$

Finally, one more parameter (X) can be introduced

$$X = \frac{\delta}{\delta_M} \quad [\text{B-3}]$$

Replacing Eq. [B-2] and [B-3] into Eq. [10], one obtains its other form

$$t_1 = \frac{1 - A/X}{\frac{3}{2} - \frac{1}{2} \frac{1 - \exp(-4AX)}{4AX}} \quad [\text{B-4}]$$

Thus, the parameter X in Fig. 5 represents in essence the variable δ in a somewhat different and more suitable form. Hence, the various curves in Fig. 5 represent the basic relationship (Eq. [10]), expressed in a more convenient form (Eq. [B-4]), for different ratios C_{sc}/i used as parameter. This is reflected here over different A values ($1 \cdot 10^{-4}$, $2 \cdot 3.3 \cdot 10^{-4}$, $3 \cdot 10^{-3}$, $4 \cdot 3.3 \cdot 10^{-3}$, and $5 \cdot 10^{-2}$).

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Standard Electrode Potential Measurements of Pb/PbCl₂/HCl and Tl/TlCl/HCl Half Cells in Dimethylformamide at 30°C

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ABSTRACT

The potentials of electrodes consisting of metal, solid metal chloride, and a solution of a soluble chloride (anhydrous HCl) in dimethylformamide (DMF) have been measured *vs.* a hydrogen electrode as the reference electrode. Half cells Pb/PbCl₂/HCl and Tl/TlCl/HCl were prepared by contacting pure metal with its associated chloride after forming the solid phase in a glass tube. Elaborate and scrupulous procedure is important for preparing the hydrogen electrode to attain reliable and reproducible measurements in DMF. Standard electrode potentials of -0.3368 and -0.5994V *vs.* SHE in DMF, at 30°C, were attained in DMF for the lead chloride and thallium chloride electrodes, respectively, at 30°C.

Measurements of electrode potentials in nonaqueous solvents have shown complications since 1909, even though some of them were found to be a natural and straightforward extension of the corresponding measurements in aqueous solutions. Pavlopoulos and Strehlow (1) measured the standard potentials of some heavy metals in the solvent formamide, but were unsuccessful in using the Ag/AgCl electrode in the same solvent. The Ag/AgCl electrode in formamide was used for measurements without much difficulty by Mandel and Decroly (2).

Since the unsubstituted amides (with the exception of formamide) are all crystalline solids at room temperature, N,N-dimethylformamide was chosen, which is a powerful solvent for both polar and nonpolar compounds. It has not been investigated as a nonaqueous solvent (3) for the measurement of electrode potentials. It was employed in this paper for the measurement of the standard potential of electrodes of the metal-insoluble salt type *vs.* the hydrogen electrode.

Discussion

In Pavlopoulos and Strehlow's paper (1) the hydrogen electrode was used without adequate descrip-

tion of operational detail. The literature indicates that the level of accuracy of most potentiometric measurements in anhydrous solutions has been insufficient to warrant any distinct choice between alternative methods of preparing the hydrogen electrode. The attainment of a truly reproducible hydrogen electrode actually holds the key to the successful performance in its role as the reference electrode (4) in anhydrous DMF solutions.

A typical laboratory procedure for preparing the platinized hydrogen electrode in aqueous solutions includes cleaning the Pt plate with aqua regia, testing the cleanliness in a 10% solution of H₂SO₄, then electrolyzing it as the cathode in dilute NaOH and H₂SO₄ solutions after electrolyzing it as the cathode for 5 min in a 3% solution of chloroplatinic acid containing 0.5 ml of 0.1N lead acetate in 100 ml solution.

The portion of the procedure most likely to cause a difference in behavior of the hydrogen electrode in aqueous and nonaqueous solutions is the process of platinization. Lead acetate is added to the platinizing solution as an impurity. Purified chloroplatinic acid solutions give only bright Pt deposits upon the platinum plate, which as an electrode can be initially active but decays in activity rather rapidly. Hence the lead acetate has to be retained in the platinizing solution (5). The second factor with prominent importance

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Key words: electrode potentials, metals in DMF.