

INVESTIGATION OF THE INFLUENCE OF ELECTROLYSIS CONDITIONS ON THE STABILITY OF GRAPHITE ANODES IN THE CHLORINE CELL *

L. I. Krishtalik

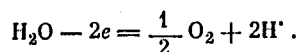
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In the preceding papers [1,2] we determined the effects of individual factors on the wear of graphite electrodes during electrolytic production of chlorine. The purpose of the present investigation was to find the relationships between anode wear and the main technological characteristics of the diaphragm chlorine cell.

Let us calculate the material balance in the anode compartment of the cell.

Acid is formed as the result of the following processes.

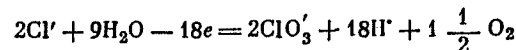
1. Anodic liberation of oxygen:



The amount of acid formed per second by this mechanism is $\frac{1}{F}x$, where I is the current strength; F is the Faraday number; x is the anodic current efficiency for oxygen, expressed as a fraction of unity.

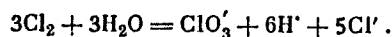
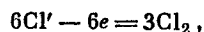
2. The formation of chlorate, whether by a chemical or an electrochemical mechanism, requires six faradays of electricity per mole of ClO_3^- and is accompanied by the formation of six equivalents of acid.

The electrochemical process of chlorate formation is:



(after subtraction of $6e$ and 6H^+ associated with formation of $1\frac{1}{2} \text{O}_2$; this gives $6e$ and 6H^+ for each ClO_3^-). The same is true of any other variant of the electrochemical mechanism.

The chemical process is:



The amount of acid formed by this mechanism is $\frac{1}{F}y$, where y is the current efficiency for chlorate, expressed as a fraction of unity.

3. Hydrolysis of chlorine:



Dissociation of HClO may be in practice disregarded in all cases. The amount of H^+ ions formed as the result of hydrolysis is equal to the amount of HClO :

$$L_a(\text{HClO}) = L_a \frac{K_h(\text{Cl}_2)}{(\text{H}^+)(\text{Cl}^-)}$$

where L_a is the volume of anolyte flowing per second; K_h is the hydrolysis constant of chlorine; the parentheses indicate concentrations.

4. Acid brought in with the salt brine: $L_s(\text{H}^+)_s$, where L_s is the volume of brine flowing through, and $(\text{H}^+)_s$ is the acid concentration in it. For an alkaline brine, this component represents loss of acid [in that case $(\text{H}^+)_s$ must be

* Communication III.

replaced by $(\text{OH}^-)_s$ in all the equations].

Acid is removed in the following ways from the anode compartment.

1. Loss with the anolyte flow: $L_a (\text{H}^+)$.

2. Transference of H^+ ions in the electric field toward the cathode, $\frac{I}{F} l_{\text{H}^+} / (\text{Cl}^-) \lambda_{\text{NaCl}} (\text{H}^+)$, where l_{H^+} is the mobility of H^+ ions in a solution of the given composition and λ_{NaCl} is the equivalent conductance of NaCl under the same conditions; the ratio $l_{\text{H}^+} (\text{H}^+) / (\text{Cl}^-) \lambda_{\text{NaCl}}$ is the transference number of the H^+ ion in the anolyte [the term $(\text{H}^+) (l_{\text{H}^+} - l_{\text{Na}^+})$, in the denominator is omitted, as it is small in comparison with $(\text{Cl}^-) \lambda_{\text{NaCl}}$].

3. Neutralization of acid by the OH^- ions penetrating from the anode compartment, $\frac{I}{F} z$, where z is the loss of current efficiency for alkali (as a fraction of unity) due to transference of OH^- ions from the cathode into the anode compartment. This quantity is determined by the catholyte composition, operating conditions, and uniformity of the diaphragm.

From the above acid entry and exit items for the anolyte we can derive the acid-balance equation and hence find the steady-state concentration of H^+ ions:

$$\begin{aligned} L_a \frac{K_h(\text{Cl}_2)}{(\text{H}^+) (\text{Cl}^-)} + \frac{I}{F} x + \frac{I}{F} y + L_s (\text{H}^+)_s = \\ = L_a (\text{H}^+) + \frac{I}{F} \frac{l_{\text{H}^+}}{(\text{Cl}^-) \lambda_{\text{NaCl}}} (\text{H}^+) + \frac{I}{F} z \end{aligned} \quad (1)$$

Taking into account that $\frac{L_c C_{\text{NaOH}}}{I} F = A$ (where L_c is the volume of catholyte flowing per second, A is the current efficiency for alkali as a fraction of unity) and expressing all volumes in terms of the brine volume (by means of the relative volumes of the anolyte K_a and catholyte K_c), we transform Eq. (1) as follows:

$$(\text{H}^+) = \frac{\frac{K_h(\text{Cl}_2)}{(\text{Cl}^-) (\text{H}^+)} + \frac{K_c}{K_a} \frac{C_{\text{NaOH}}}{A} (x + y - z) + \frac{(\text{H}^+)_s}{K_a}}{1 + \frac{K_c}{K_a} \frac{C_{\text{NaOH}}}{A} \frac{l_{\text{H}^+}}{(\text{Cl}^-) \lambda_{\text{NaCl}}}} \quad (2)$$

Equation (2) does not give a complete solution to the problem, as the quantities of x , y , and z in it themselves depend on the acidity.

The dependence of anode wear (and therefore of anodic current oxidation under these conditions) on anolyte acidity and sulfate concentration was studied by us earlier [1,2]. It is satisfactorily represented by the following empirical equation:

$$G = 0.5 + \frac{0.94 \cdot 10^{-3}}{(\text{H}^+)} + 0.1065 C_{\text{Na}_2\text{SO}_4} \quad (3)$$

where G is the wear (g/1000 amp-hr). and $C_{\text{Na}_2\text{SO}_4}$ is the sulfate concentration in solution (g/liter).*

The first term of the equation refers, in accordance with the hypothesis put forward earlier, to discharge of water molecules; the third term, to the influence of sulfate on this process; and the second, to discharge of hydroxyl ions.

Equation (3) refers to the wear of new anodes which had not been previously used. Such wear consists almost entirely of chemical wear [1]. Therefore, if G is known, we can determine the fraction of the current consumed for anodic liberation of oxygen, assuming that the entire weight loss is due to removal of carbon in the form of CO_2 .

$$x = 0.0045 + \frac{0.84 \cdot 10^{-5}}{(\text{H}^+)} + 0.00095 C_{\text{Na}_2\text{SO}_4} \quad (4)$$

The formation of chlorate in the chlorine cell has not been studied in detail. The available literature data on current efficiency in chlorate electrolysis are inapplicable in this case because of the very different pH values, tem-

* Anode wear depends directly on the sulfate concentration in the anolyte and not in the brine. Under the usual conditions of diaphragm electrolysis the Na_2SO_4 content of the anolyte is on the average 1.33 times the content in the brine [2]. This is taken into account in Eq. (3).

peratures, etc. In our experiments we carried out a series of determinations of chlorate concentration in the anode and intermediate compartments. It is noteworthy that the ClO_3' concentration is almost the same in both compartments. This may indicate that chlorate is formed electrochemically rather than chemically.

Indeed, if chlorate was formed by the chemical mechanism only, it would be formed mainly in the middle compartment, where alkali enters directly from the catholyte and where the acidity is nearly always lower. Chlorate would enter the anolyte by transference of ions from the middle compartment, and owing to the counterflow it could not accumulate to a considerable extent in the anolyte and its concentration there would be lower than in the middle compartment. Calculation based on the assumption that chlorate is formed only in the middle compartment show that its concentration in the anolyte would be

$$\frac{K_c}{K_a A} \cdot \frac{C_{\text{NaOH}}}{(\text{Cl}')} \cdot \frac{l_{\text{ClO}_3'}}{\lambda_{\text{NaCl}}} \approx \frac{1}{3}$$

of its concentration in the middle compartment.

On the other hand, if all the chlorate is formed electrochemically in the anode compartment it would be carried with the liquid stream through the middle compartment, and, since it does not undergo any changes in the process, its concentrations in the middle and anode compartments would be equal.

In accordance with our data, the dependence of chlorate concentration on anolyte acidity may be represented by the following equation:

$$C_{\text{NaClO}_3} = 0.14 + \frac{0.5 \cdot 10^{-3}}{(\text{H}')} \quad (5)$$

where C_{NaClO_3} is the chlorate concentration in the anolyte (g/liter).

Equation (5) is approximate only, because the chlorate concentration is sensitive to variations in the process conditions and is slow to reach a steady state, so that the experimental points are very scattered.

We must now consider the chlorate balance in the anolyte in order to find the current efficiency for chlorate from its concentration.

The number of moles of ClO_3' formed per second is $\frac{I}{6F} y$ (it is assumed here that six faradays of electricity are consumed per mole of chlorate). At the same time $\frac{l_{\text{ClO}_3'}}{(\text{Cl}') \lambda_{\text{NaCl}}} \cdot \frac{I}{F} (\text{ClO}_3')$ moles of chlorate is transported by the current to the anode. The liquid stream takes away $L_a (\text{ClO}_3')$ moles.

Hence

$$\frac{l_{\text{ClO}_3'}}{(\text{Cl}') \lambda_{\text{NaCl}}} \cdot \frac{I}{F} (\text{ClO}_3') + \frac{I}{6F} y = L_a (\text{ClO}_3');$$

the usual rearrangement gives:

$$y = \frac{1 - \frac{C_{\text{NaOH}}}{A} \cdot \frac{K_c}{K_a} \cdot \frac{l_{\text{ClO}_3'}}{(\text{Cl}') \lambda_{\text{NaCl}}}}{\frac{C_{\text{NaOH}}}{A} \cdot \frac{K_c}{K_a}} \cdot 6 (\text{ClO}_3') \quad (6)$$

Substituting the usual values of $C_{\text{NaOH}} = 3$, $(\text{Cl}') = 4.5$, $A = 0.95$, $K_a = 0.98$, and $K_c = 0.9$, and taking $\frac{l_{\text{ClO}_3'}}{\lambda_{\text{NaCl}}} \approx 0.5$, we have

$$y \approx 1.08 (\text{ClO}_3') \approx 0.01 C_{\text{NaClO}_3} \quad (6a)$$

where (ClO_3') is the chlorate concentration in the anolyte (M), and C_{NaClO_3} is the same concentration in g/liter.

In other words, it follows from Eq. (6a) that the current efficiency for chlorate (%) under the usual electrolysis conditions in a diaphragm cell is numerically equal to the NaClO_3 concentration in the anolyte (g/liter). From Eqs. (5) and (6a) we have

$$y \approx 0.0014 + \frac{0.5 \cdot 10^{-3}}{(\text{H}')} \quad (7)$$

The relationship between current efficiency for chlorate and anolyte acidity is analogous to the relationship for oxygen liberation. This analogy may be due to the existence of similar stages in both anode processes.

Equation (7) is not very precise quantitatively, but this cannot introduce a large error into calculations of acidity, because the contribution of chlorate formation to the total acid balance is less than the contribution of oxygen liberation.

The value of z can be determined from the current efficiency for alkali.

Alkali can be lost in three ways.

First, there is the loss due to neutralization of alkali by acid (HCl and HClO) and chlorine brought with the electrolyte stream from the anode into the cathode compartment; the magnitude of this loss is:

$$\frac{F}{I} L_a [2(\text{Cl}_2) + (\text{HClO}) + (\text{H}')] = A \frac{K_a}{K_c C_{\text{NaOH}}} \left[2(\text{Cl}_2) + \frac{K_h(\text{Cl}_2)}{(\text{Cl}')(\text{H}')} + (\text{H}') \right].$$

Second, there is the loss of alkali by neutralization by the H^+ ions introduced into the catholyte under the influence of the electric field; in other words, the fraction of the current which is expended for transference of H^+ ions from the anode into the cathode compartment represents the net loss $l_{\text{H}^+}(\text{H}') / (\text{Cl}') \lambda_{\text{NaCl}}$.

Third, there is the loss due to transference of OH^+ ions from the catholyte into the anolyte (z).

Hence the current efficiency for alkali, as a fraction of unity, is

$$\begin{aligned} A &= 1 - A \frac{K_a}{K_c C_{\text{NaOH}}} \left[2(\text{Cl}_2) + \frac{K_h(\text{Cl}_2)}{(\text{Cl}')(\text{H}')} + (\text{H}') \right] - \frac{l_{\text{H}^+}}{(\text{Cl}') \lambda_{\text{NaCl}}} (\text{H}') - z = \\ &= \frac{1 - \frac{l_{\text{H}^+}}{(\text{Cl}') \lambda_{\text{NaCl}}} (\text{H}') - z}{1 + \frac{K_a}{K_c C_{\text{NaOH}}} \left[2(\text{Cl}_2) + \frac{K_h(\text{Cl}_2)}{(\text{Cl}')(\text{H}')} + (\text{H}') \right]} \end{aligned} \quad (8)$$

It is easy to express z as a function of the acidity if the experimental value of the current efficiency is known.

Having found the dependence of x , y , and z on the anolyte acidity, we can now represent in explicit form the dependence of anolyte acidity on the electrolysis conditions. It is given by the following equation:

$$(\text{H}') = \frac{2 \frac{K_h(\text{Cl}_2)}{(\text{Cl}')} + \frac{K_c}{K_a} C_{\text{NaOH}} \frac{f+g}{A}}{\frac{K_c}{K_a} C_{\text{NaOH}} \left(\frac{1}{A} - 1 \right) - \frac{K_c}{K_a} C_{\text{NaOH}} \frac{m+n+SC_{\text{Na}_2\text{SO}_4}}{A} - 2(\text{Cl}_2) - \frac{(\text{H}')_g}{K_a}}, \quad (9)$$

where $m = 0.0045$, $S = 0.00095$ and $f = 0.84 \cdot 10^{-5}$, constants of Eq. (4); $n = 0.0014$ and $g = 0.5 \cdot 10^{-5}$ are constants of Eq. (7).

These two sets of constants themselves depend on the chloride concentration of the anolyte, so that Eq. (9) does not give the direct relationship between acidity and chloride concentration. The influence of temperature on acidity is also determined by its influence on these quantities, i.e., on the rates of the anode processes, and to some extent by its influence on K_a and K_c because of evaporation of water.

The main technological factor influencing anolyte acidity is the current efficiency. This conclusion follows directly from Eq. (9), because many of the terms of that equation depend on A , and the term containing $(\frac{1}{A} - 1)$ is especially sensitive to it.

The strong influence of current efficiency on anolyte acidity becomes understandable on the following considerations: even at such a relatively high current efficiency as 94% about 5 g of alkali per liter of incoming brine enters the anolyte, and this is considerably higher than the alkalinity of the brine itself. It is obvious that such amounts have a strong influence on anolyte acidity.

Figure 1 shows calculated values of anolyte acidity plotted against current efficiency; the remaining quantities have the following values: $C_{\text{NaOH}}=3.0$, $(\text{Cl}^-)=4.5$, $C_{\text{Na}_2\text{SO}_4}=0$, $K_a=0.98$, $K_c=0.9$, $(\text{Cl}_2)=0.007$, $K_h=1.2 \cdot 10^{-3}$.

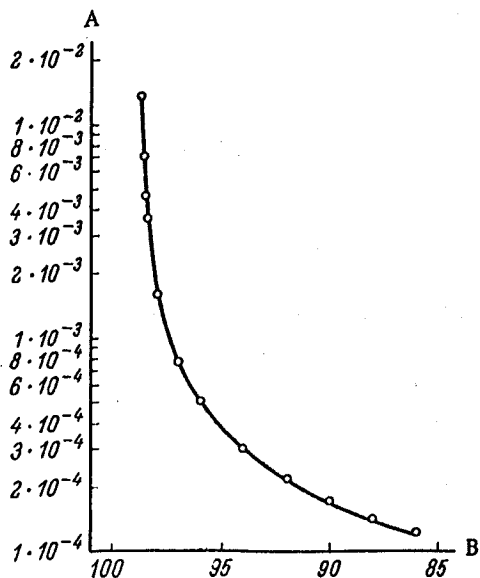


Fig. 1. Calculated values of anolyte acidity in relation to current efficiency. A) Acidity (H^+) (M); B) current efficiency (%).

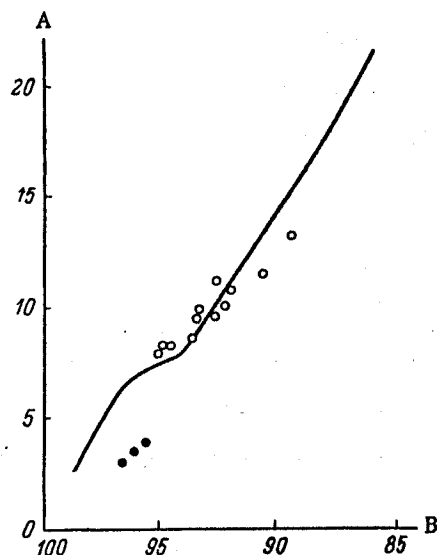


Fig. 2. Calculated (curve) and industrial (points) values of anode consumption in relation to current efficiency. A) Anode consumption (kg/ton NaOH); B) current efficiency (%).

If the acid concentration in the anolyte is known, we can calculate the chemical wear of the anodes from Eq. (3). To find total wear from chemical wear we must take into account the relationship between mechanical and chemical losses which was determined earlier [1].

Anode consumption is influenced by the magnitude of the nonutilizable electrode residue, in addition to the direct wear of the anodes. It is assumed here that this residue is 40% of the anode weight.

In Fig. 2 the calculated anode consumption (kg/ton of 100% alkali) is plotted against current efficiency. The inflections on the curves are due to changes in the ratio of mechanical to chemical wear. At a low current efficiency, i.e., at high wear, this ratio is almost constant. It then begins to increase appreciably, and as a result the decrease of anode wear with increase of current efficiency slows down. Subsequently, at low values of wear, the ratio of the two types of loss alters relatively little and anode wear again diminishes in proportion to the decrease of chemical wear. The expression used in the calculations for the relationship between mechanical and chemical wear is not quite accurate, but the qualitative picture and orders of magnitude are fairly reliable, so that the inflections on the anode consumption-current efficiency curves are significant.

It follows from Figs. 1 and 2 that in a cell with an ideal diaphragm, in which there is virtually no penetration of alkali into the anolyte (current efficiency about 99%), the anolyte acidity becomes established at a high enough level (above 0.01 N) to ensure minimum anode wear. The anode consumption in such a cell is about 2 kg per ton of 100% NaOH.

Decrease of current efficiency leads to a decrease of anolyte acidity and hence to intensified anode wear. The relationship between current efficiency and anode wear has been frequently observed. We need only mention the occurrence of the so-called "high-voltage" cells, well known to practical men of the chlorine industry; in general, most of these cells prove to be cells with excessively high alkali concentrations and therefore with low current efficiencies.

However, in this case we are concerned not merely with qualitative correlation of anode consumption with current efficiency, but with a quantitative evaluation of the direct relationship between them. According to our calcu-

lations, in the range of current efficiencies obtained in practice a change of 1% in current efficiency alters the CO_2 content on the average by 0.3%, and the anode consumption by 0.5-1.5 kg per ton of alkali (Fig.2).*

The points in Fig.2 represent industrial data obtained under various cell operation conditions. A high degree of precision in comparison of these values cannot be expected because of the different types of cells used, different methods of calculation, and certain differences of brine composition, temperature, etc. It must, however, be emphasized that in general the agreement with calculated values is quite satisfactory both in regard to the absolute magnitude of anode consumption and in regard to its dependence on current efficiency.**

Therefore the above theory of anode performance in the chlorine cell is confirmed by the results of industrial practice.

It must be pointed out that the average current efficiency does not fully characterize anode wear. For example, at 94% current efficiency the calculated anode consumption is 8.0 kg/ton NaOH. If in 80% of the cells the current efficiency is 95%, while the average value of 94% takes in the operation of the other cells at 90% current efficiency, the anode wear is found to be 8.75 kg/ton NaOH. If most of the cells operate at a still higher current efficiency (96%) while in a smaller group the yield falls to 85%, the average graphite consumption reaches 9.75 kg/ton NaOH at the same average current efficiency (94%).

SUMMARY

The acid balance in the anolyte and the balance of current-efficiency losses were computed; the results were used for deriving equations representing the relationship between anolyte acidity (and therefore anode wear) and the technical process parameters of electrolysis. It is shown that current efficiency for alkali is the factor with the greatest influence on graphite consumption.

LITERATURE CITED

1. L. I. Krishtalik, G. L. Melikova, E. G. Kalinina, *ZhPKh*, 34, 7, 1543 (1961).
2. L. I. Krishtalik, G. L. Melikova, E. G. Kalinina, *ZhPKh*, 34, 7, 1537 (1961).

* Anode consumption alters not only because of changes in the proportion of current expended for formation of CO_2 but also owing to variations in the ratio of chemical to mechanical wear.

** The black points below the curve relate to cells with impregnated anodes, where the anode consumption is lowered still further.

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
