

AN INVESTIGATION OF THE ELECTROLYSIS OF BRINE IN BATHS WITH FILLED CATHODE SPACE *

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The present article is devoted to the results of an investigation on electrolysis using filled cathode space.

EXPERIMENTAL

The work was carried out in two types of electrolytic vessels. The first type consisted of a bath, the anode part of which was similar to that described earlier [1], while the cathode part is shown in Fig. 1. By means of a number of connecting pipes, it was possible to regulate the level of the cathode liquid. Determination of the yield with respect to current was carried out six times in each 24 h period. The data given below are the mean 24 h period data. In estimating these, values obtained under disturbed conditions are excluded.

Eight experiments in all were carried out with a mean duration of around 40 days. Characteristic data of some of these are given in Figs. 2-4.

The second construction for the electrolytic vessels is shown in Fig. 5. The body of the bath is a faloite vessel, the cathode being fixed into the lid of the bath. The current consisted of a tube of diameter 40 mm, welded from an iron wire grid and closed at the base by means of a rubber bung. The upper part of the cathode was covered with rubber, while the lower portion of height 100 mm constituted the working surface. Around the latter was wound asbestos paper, the upper and lower edges of the diaphragm being fastened by means of asbestos string covered with a polyvinyl chloride resin. Four segments of a hollow graphite cylinder served as anodes. Alkali was introduced into the cathode space by means of a siphon. The baths were maintained at a temperature of 70° by means of a thermostat.

Determination of the yield with respect to current was carried out 1-2 times each day of 24 h. The quantity of electricity passing was determined by means of a mercury ampere-hour meter, calibrated against an ammeter of accuracy class 0.2. The accuracy of direct determination of yield with respect to current was estimated to lie between 1 and 2%. The results of the experiments are shown in Fig. 6.

DISCUSSION OF RESULTS

Concentration of Alkali in Baths with Filled Cathode Space. For a consideration of the question of the concentration of alkali in baths with filled cathode space, we may suppose that for an unfilled space the curve for the distribution of alkalinity with respect to height would correspond to the continuous line in Fig. 7. Let the cathode space be filled to a level lying h_k below the edge of the cathode. Since under the conditions of operation the diaphragm situated above the level of the liquid is in no way altered, the distribution of alkalinity with respect to height in this part should remain unchanged. The part of the diaphragm present below the level of the cathode liquid is present under practically constant pressure, equal to the pressure at the level of the cathode liquid, that is, $h_a + h_k$. Hence, the whole of it should possess a uniform permeability and, therefore, the concentration of alkali at this portion of the cathode should remain constant (Fig. 7, dotted line).

The slope of the upper part of the curve showing the distribution of alkalinity is on the average around 6 g/liter · cm. Hence, with a filled cathode space, the alkali concentration is increased compared with an unfilled space by 6 g/liter ($30 - h_a - h_k$). This increase will occur only in the case when the distance between the level of the anode

*Communication No. 3 in a series of publications on investigations of the electrolytic production of chlorine and alkali in vertical diaphragm.

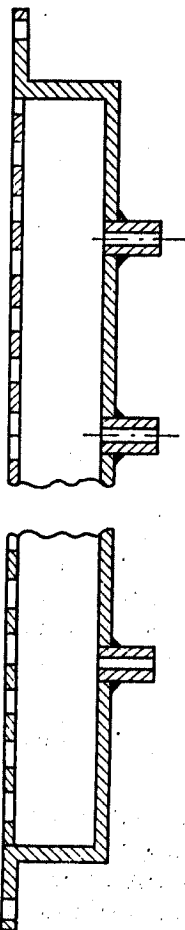


Fig. 1. Cathode portion of the laboratory electrolytic vessel.

liquid and that of the cathode liquid is less than 30 cm ($h = h_a + h_k < 30$). In the opposite case the distribution of alkalinity with respect to height will agree with that for the incompletely filled space, and no meaning can be attached to the filling of the cathode space with the cathode liquid.

This suggestion may be confirmed by investigating the effect of changing the anode and the cathode liquid levels, that is, changing the pressure on the diaphragm, on the alkali concentration. Three cases may be considered: 1) $h < 30$, when $\Delta C = 6\Delta h$; 2) $h > 30$, $\Delta C = 0$; 3) transition from $h_1 < 30$ to $h_2 > 30$, for which $\Delta C = 6(30 - h_1)$. The dotted lines in Figs. 2-3 show the concentration of alkali calculated by this method. When the level of the cathode liquid is reduced, that is when the pressure on the diaphragm is increased, the concentration of alkali initially goes down very rapidly. Subsequently, however, the diaphragm is reformed owing to the contraction, and the concentration of alkali is increased to the calculated value. Comparison of the calculated and experimental values for the alkali concentration is given in summary fashion in Fig. 8 (point 1).

The nature of the effect of the levels of the anode and cathode liquids just described on the alkali concentration has also been completely confirmed for industrial baths with filled cathode compartments. In the discussion above, it has been assumed that the pressure on the diaphragm below the level of the cathode liquid is constant. Actually this is not accurate, since the difference between the specific gravity of the anode and cathode liquids means that identical columns of these liquids will exercise different pressures. This effect is small, so that, for example, for pure solutions when the sodium hydroxide is 140 g/liter, it amounts to approximately 6 mm of the anode liquid column per 100 mm of the cathode liquid; but the effect will produce a certain lack of uniformity in the distribution of the alkali concentration with respect to height and should therefore be taken into account, especially in the construction of tall baths [2].

The distribution of alkali concentration with respect to bath height just described for filled cathode spaces should also be found for other diaphragms. The pressure region for which this picture is correct will have a slope of the concentration-pressure curve, of course, determined by the properties of the actual diaphragm chosen.

Yield with Respect to Current and Optimum Conditions for the Use of Electrolytic Vessels with Filled Cathode Spaces. Commencing with the picture described in the previous paragraph for the distribution of alkali concentration with respect to height, it is possible to arrive at an equation for the mean yield with respect to current. It was observed above, however, that when $h + h_k > 30$ cm, the bath operates in the same way as for incompletely filled cathode space. When $h_a + h_k < 30$ cm the width of the zone of intermediate alkalinity is equal to the distance from the level of the cathode liquid to the edge of the cathode, h_k , in distinction from baths with incompletely filled space, where it is determined by the level of the anode liquid, and is equal to $30 - h_a$. Since the shape of the curves for the distribution for filled and incompletely filled spaces is the same, the equations for the former may be obtained by a simple substitution in Eqs. (5) and (5a) in the previous communication [1], of $(30 - h_a)$ by h_k :

$$C_0 \leq 156 \text{ g/l}; \quad A_{cp} = 98 - \frac{1}{H} \left\{ 0.288 [0.0834 (156 - C_0)^2 - (156 - C_0) h_k + 3h_k^2] + (98 - A_0) (H - h_k) \right\}, \quad (1)$$

$$C_0 \geq 156 \text{ g/l}; \quad A_{cp} = 98 - \frac{0.288}{H} [3h_k^2 + (C_0 - 156) H]. \quad (1a)$$

Of course, Eq. (1) is subject to the same limitations as we have considered in the previous article. It may be used for comparative estimation of different electrolytic vessel constructions. Thus, according to Eq. (1), the yield with respect to current in a Giordani-Pomilio bath [3, p. 348], is smaller than in contemporary baths using filled cathode space, since in this bath the level of the cathode liquid is maintained in general further from the edge of the cathode.

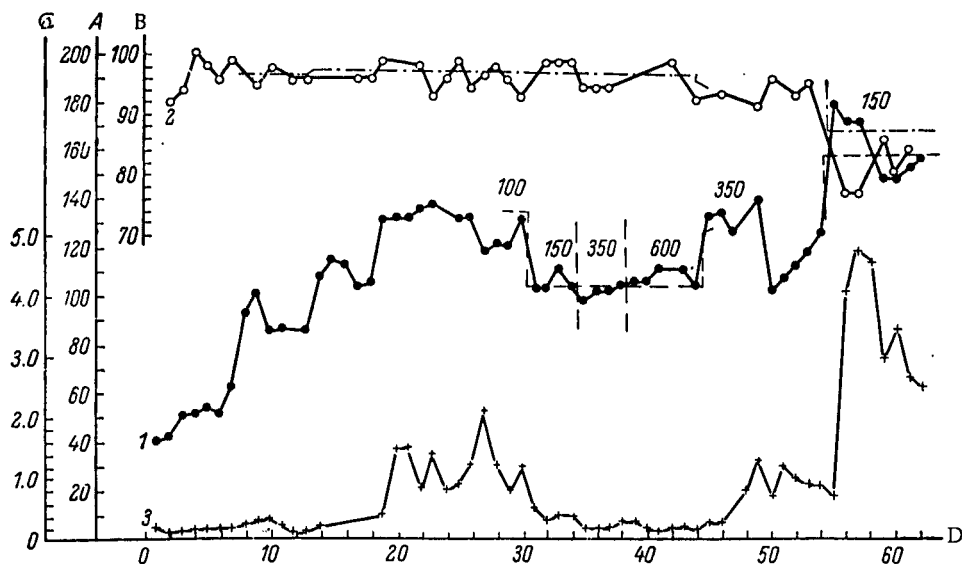


Fig. 2. Change of electrolysis indices with time. A) concentration of sodium hydroxide (g/liter); B) yield with respect to current (%); C) sodium chlorate concentration (g/liter); D) time (24 h days). 1) sodium hydroxide concentration; 2) yield with respect to current; 3) sodium chlorate concentration; Dotted horizontal line denotes calculated value of the alkali concentration; broken and dotted line represents yield with respect to current. The vertical lines denote the point at which the level of the cathode liquid was changed. The numbers lying above curve 1 indicate the position of the cathode liquid level (in millimeters from the edge of the cathode). The level of the anode liquid was 150 mm above the edge of the cathode.

Figure 9 shows the good agreement between the experimental and calculated yields with respect to current when $h_a + h_k < 30$ cm.*

The optimum conditions for operation of baths with filled cathode space are: a) if possible, still more complete filling of the cathode space; b) regulation of the alkali concentration by changing the level of the anode liquid.

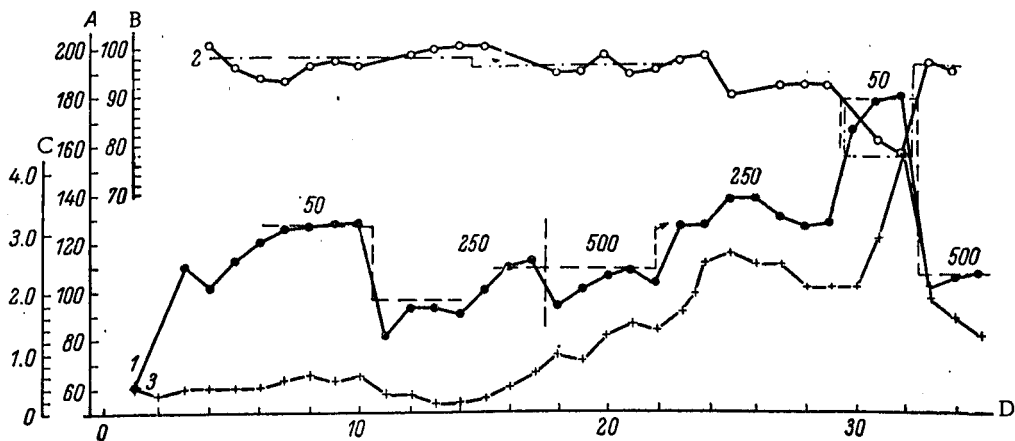


Fig. 3. Change of electrolysis indices with time. Level of the anode liquid was 200 mm above the edge of the cathode, designations the same as in Fig. 2.

*Cf. also Figs. 2-3, where the dotted lines indicate the calculated yield with respect to current.

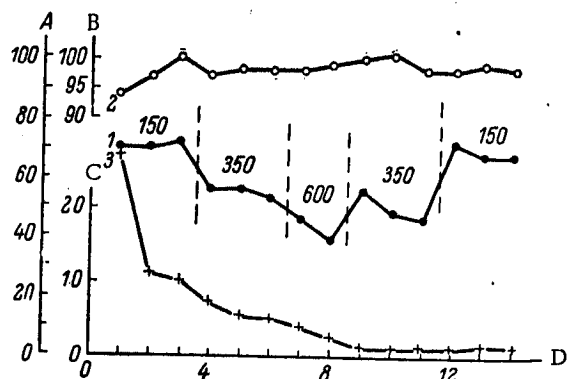


Fig. 4. Change of electrolysis indices with time. Bath containing an asbestos diaphragm. Level of anode liquid is 100 mm above the edge of the cathode. Designations the same as in Fig. 2.

the cathode liquid. However, the concentration of the alkali does depend on the level of the anode liquid, provided that $h_a + h_k$ does not exceed 30 cm. Hence, the given alkali concentration may be satisfactorily maintained by adjusting the level of the anode liquid.

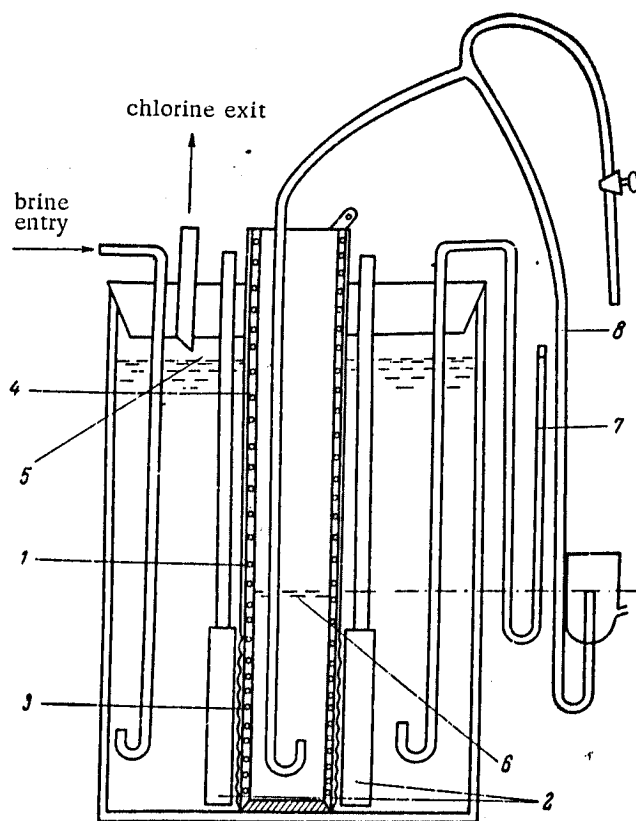


Fig. 5. Laboratory electrolytic vessels. 1) cathode; 2) anodes; 3) diaphragm; 4) rubber coating; 5) anode liquid level; 6) cathode liquid level; 7) index of anode liquid level; 8) siphon for removing alkali.

Reduction of the value of h_k reduces the width of the zone of transitional alkalinity and, due to this, increases the yield with respect to current. For alkali concentration of 135-140 g/liter, and distance between the level of the cathode liquid and the edge of the cathode of ca. 2 cm, the alkali concentration in the upper part of the cathode cannot appreciably exceed the value of 150 g/liter.

For a somewhat wider transitional alkalinity zone, the yield with respect to current is reduced, and it must be emphasized that even a small reduction of the yield with respect to current exercises an appreciable effect on the stability of the anodes [4].

The yield with respect to current in baths with filled cathode space does not depend directly on the level of the anode liquid, since the width of the transitional alkalinity zone is determined by the level of

The optimum conditions given for the operation of a bath with a filter cathode space are valid for baths with any type of diaphragm whose permeability depends on the pressure.

Regulation of the level of the anode liquid to give constant alkali concentration may be carried out automatically if a constant quantity of brine is continuously added to the bath with constant load. By this means, a level of liquid is established in the bath which is satisfactory to ensure the flow of the correct quantity of liquid. This level depends on the state of the diaphragm in the given bath. Constancy of the rate of filtration is also ensured provided that the level of the anode liquid does not exceed 30 cm above that of the cathode liquid. Constant supply of brine to the bath on the large scale is provided for in all contemporary baths operating with filled cathode space [5, 6].

The optimum conditions for the use of baths with filled cathode space indicate definite requirements which should be fulfilled in the construction of the electrolytic vessels. In the first instance the equipment for removing the alkali should permit the maintenance of a high cathode liquid level. In the second place, the space above the cathode should be high enough to permit a gradual increase of the level of the anode liquid to the value of 30 cm. This condition is taken into account in the construction of the bath BGK-17, which has been shown to operate as a very effective type of electrolytic vessel [5].

In baths with filled cathode space, the pressure on the diaphragm is relatively small, and is there-

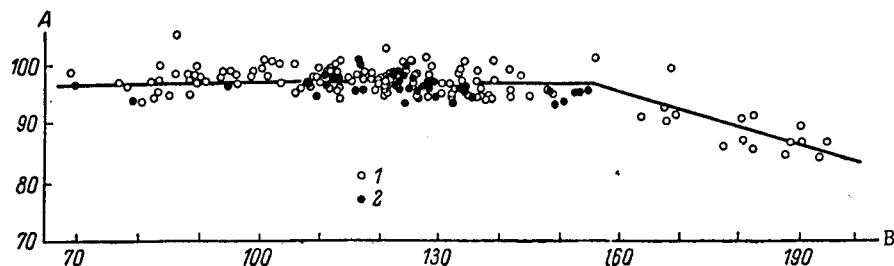


Fig. 6. Relationship between the yield with respect to current and the alkali concentration. A) yield with respect to current (%); B) concentration of sodium hydroxide (g/liter). Diaphragm used in the baths: 1) ordinary asbestos; 2) asbolatex (3% latex).

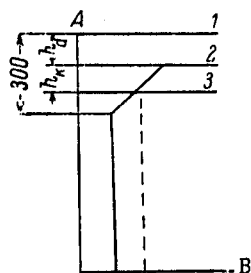


Fig. 7. Diagram of the distribution of alkali concentration with respect to cathode height in an incompletely filled (solid line) and completely filled (dotted line) cathode space. A) depth from level of anode liquid (mm); B) alkali concentration (g/liter). 1) anode liquid level; 2) edge of cathode; 3) cathode liquid level.

fore particularly sensitive to fluctuations in the levels of the anode liquid. If any disturbance occurs in the supply to the bath or in the permeability of the diaphragm, the change in level of the anode liquid will occur more rapidly the smaller the area of the free surface of the anode liquid for unit yield of the bath, since defect or excess of brine will be compensated through a corresponding change in the volume of the anode liquid above the cathode. In baths with current supply from above, a considerable part of the horizontal section above the cathode is occupied by the anode caps, because of which these baths are less stable in operation than those with current supply from below.*

Estimation of the individual components of the potential balance shows that the difference in potential between baths with filled and with incompletely filled cathode space lies within the limits of hundredths of a volt, while, depending on the conditions of operation, in the first place the potential could be either higher or lower than in the second. In practice, both reduction and increase in potential may be observed.

The principal advantage of baths with filled cathode space, compared with electrolytic vessels of the other type, consists in the fact that higher alkali concentrations may be obtained without loss of yield with respect to current. Moreover, electrolysis using filled cathode spaces permits regulation of the alkali concentration, so that the most favorable levels may be obtained throughout the entire operation.

As a result of attaining high and controllable alkali concentrations, electrolysis using filled cathode spaces has nowadays become the basic method used in all contemporary baths.

periments carried out in cylindrical laboratory electrolytic vessels, described at the commencement of the present article, have permitted the determination of yields with respect to current during the operation of baths under optimum conditions, that is, with completely filled cathode space. Part of the experiment was carried out with the space practically unfilled, but with a level of the anode liquid more than 30 cm above the edge of the cathode, which corresponds to the optimum conditions for this case.

As we can see from Fig. 6, our data (represented by points), within the limits of experimental error, are in agreement with those of the most accurate investigation of the horizontal diaphragm electrolytic vessel, carried out by G. Angel [7], (represented by the curve).

Published work reveals a widespread opinion that horizontal electrolytic vessels are fundamentally different from vertical ones because of the stratification of the electrolyte on the basis of specific gravity [3, 8-10], a point of view expressed in such quotations as: "The use of a diaphragm in itself is not the fundamental theoretically significant difference between the various processes. This is rather the method of arranging the electrodes" [3, p. 300].

*Amongst those who have worked in the domestic chlorine industry, the first to direct attention to the great stability in operations of baths with current supply from below was V. S. Ioffe.

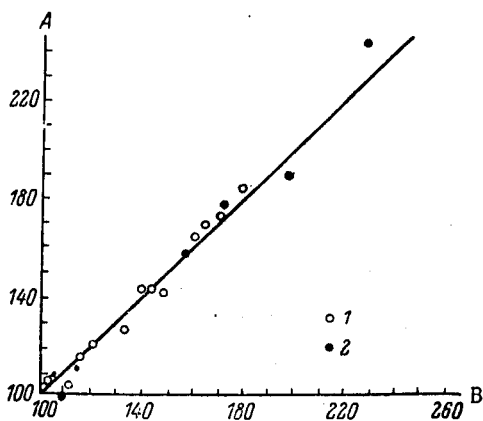


Fig. 8. Comparison of the experimental and calculated values of the alkali concentration (g/liter). A) experimental; B) calculated values of the concentrations. 1) without adjustment of diaphragm; 2) after adjustment of diaphragm.

difference in behavior between these two types of diaphragm in industrial electrolytic procedure [1], in these experiments both forms of diaphragm have given results comparable with one another (Fig. 6). As we have observed above, these results are in agreement with the figures given by G. Angel, obtained using a Billiter diaphragm (consisting of barium sulfate to which asbestos had been added). It follows clearly that the yield with respect to current is independent of the material and the structural type of the diaphragm.

In speaking of the independence of the yield from the structure of the diaphragm we are thinking only of the difference in the geometry of the pores of the diaphragm. Uniformity of structure is, of course, important. If individual portions of the diaphragm have appreciable difference in permeability, the concentrations of alkali at parts of

the cathode are found to be appreciably higher, while the yield with respect to current is appreciably lower than the mean value. The overall result is that the yield with respect to current in the bath as a whole is reduced.

Giordani [11] has stated that yield with respect to current depends strongly on the porosity of the diaphragm. To support this point of view, he gives two experiments, in one of which the diaphragm, made of asbestos fabric, was very porous, while in the second "a diaphragm of the same material was artificially made less porous by various additives". The yield with respect to current in the first experiment was considerably lower than in the second.

It is clear, however, that these experiments are quite indecisive. Asbestos fabric is characterized by a great lack of uniformity in its structure: the very large pores between the threads exist side by side with extremely fine pores within the threads [12]. As we have already indicated, it is the non-uniformity of the pores which led to a substantial drop in the yield with respect to current. The addition of additives, however, not only reduced the porosity, but also made it more uniform, with a corresponding increase in yield with respect to current.

"Adjustment" of the Diaphragm. The experiments described above on the effect of changing the levels of the

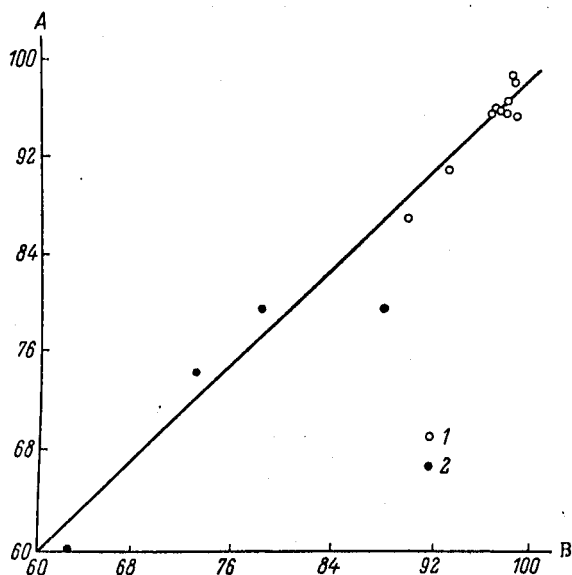


Fig. 9. Comparison of experimental and calculated values of yield with respect to current (%). A) experimental; B) calculated values of yield with respect to current. 1) without adjustment of diaphragm; 2) after adjustment of diaphragm.

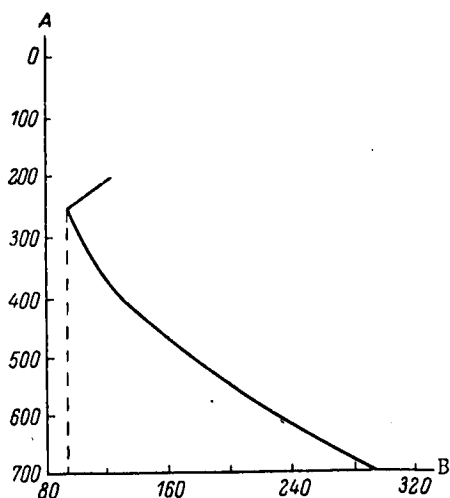


Fig. 10. Calculated distribution of alkali concentration along the height of cathode before adjustment of diaphragm (dotted line) and after adjustment (solid line). A) depth from level of anode liquid (mm); B) alkali concentration (g/liter).

anode and cathode liquids on the concentration of alkali were carried out under such conditions that irreversible change in the diaphragm did not lead to any appreciable deviation from the simple picture of alkali distribution set out in Fig. 7. In 1950-1951, Yu. S. Puzyrev observed on industrial baths that if at a certain time a change was made from a filled cathode space to an incompletely filled space, subsequently reverting to the previous level of the cathode liquid, the concentration of alkali appreciably increased. This phenomenon was called "adjustment".

The reason for this lies in the irreversible contraction of the diaphragm under the effect of a large pressure. This is supported by the following calculations. If we know the effect of inelastic deformation in the absence of current [13], it is possible to calculate the nature and distribution of alkali with respect to height. An example of a curve obtained in this way is given in Fig. 10. For comparison, the dotted line gives the curve which is found before raising the level of the cathode liquid, that is, using an incompletely filled cathode space. Knowing the distribution of concentration of alkali with respect to height, it is possible to find the mean yield with respect to current, and the mean alkali concentration in the bath.

The agreement between the calculated and experimental values, as we can see from Figs. 8 and 9, is entirely satisfactory, especially if account is taken of the large value of the effect previously mentioned,

and the not very good reproducibility of the diaphragm properties. It should be noted that very large errors in the calculation would be involved if no account was taken of the irreversible changes.

It is a characteristic fact that the second change in the level of the cathode liquid leads to the previous value of the alkali concentration (Fig. 3). This would not be so if increase in the alkali concentration was due to appreciable chemical alteration in the nature of the diaphragm. This is to be expected in view of the explanation already given of the irreversible processes occurring in the diaphragm as consisting of a reorientation of the fibers involving a closer packing [13].

Negative effects of short-period adjustment are less clearly expressed, but are nevertheless appreciable, and for this reason this procedure is not to be recommended. Particular attention should be paid to eliminating the possibility of accidental adjustment of the diaphragm. If the bath for any reason is changed during operation so as to acquire an incompletely filled cathode space, it may be impossible subsequently to increase the level of the cathode liquid. Cases are known when such an oversight has caused considerable damage.

As has been previously observed [13], using asbestos paper with appreciable additions of latex, the change in orientation of the fibers is made very difficult. Hence, deformation of such diaphragms is small and is of a completely reversible, elastic character. This is shown by the fact that, in baths using asbolatex diaphragms, the diaphragm adjustment phenomenon is not found (Fig. 4).

CONCLUSIONS

1. It has been shown that in baths with filled cathode space, the alkali concentration below the level of the cathode liquid is almost constant, while above this it changes in the same way as with the incompletely filled space. When the distance between the levels of the anode and cathode liquid is less than 30 cm, the alkali concentration in the bath with filled cathode space is higher than in the bath with incompletely filled space.

2. Optimum conditions have been found for the operation of a bath with a filled cathode space to be: a) where possible, a greater degree of filling of the cathode space; b) regulation of the concentration of alkali by a change in the level of the anode liquid. Electrolysis with filled cathode space, in comparison with the working of a bath with incompletely filled space, is advantageous in that it allows the obtaining of a higher and regulatable concentration of alkali, while maintaining an equally good yield with respect to current.

3. It has been shown that there is no difference in principle between the operation of electrolytic vessels with the vertical and horizontal electrodes, and it has also been shown that it is possible to obtain maximum yield with respect to current using a vertical electrolytic vessel.

4. The yield with respect to current has been shown to be practically independent of the material and structure of uniform diaphragms.

CONCLUSIONS

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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.