

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

L. I. Krishtalik

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A previous communication [1] was devoted to reporting an investigation of the relationship between the permeability of a shaped diaphragm and the pressure in the absence of an electrolytic current. The object of the present paper is to investigate to what extent this relationship continues to apply when current is flowing, or, in other words, to find out how the permeability and, consequently, the alkali concentration, are distributed along the height of the cathode in an operating vertical bath.

This problem was first investigated by Stender and his colleagues [2,3], but only two experiments were carried out, and the region of low pressures was not investigated.†

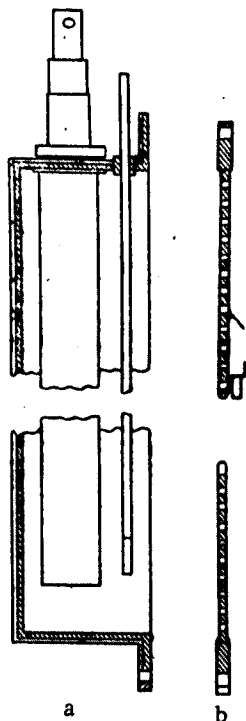


Fig. 1. Laboratory electrolytic vessel. a) Body of bath, in which are inserted from above a graphite anode and a glass tube for the introduction of brine. Addition of brine to the bath was carried out using a Mariott vessel, which maintained constant level of the anode liquid. b) Cathode, on which are shown schematically deflector and tray used for collection of alkali.

EXPERIMENTAL

The experiments were carried out in vertical laboratory electrolytic vessels of height 830 mm. The rubber-lined surface of the bath (Fig. 1a) and the cathode (Fig. 1b), was held together by bolts which were insulated from both halves of the bath.

The cathod portion consisted of a frame, and a cathode plate (Fig. 1b), perforated and welded on to the frame. On the cathode plate was laid an asbestos diaphragm, fastened at the edge by a narrow concrete strip protected by a polyvinyl chloride lacquer, or stuck directly to the frame.

The cathode was divided over its entire height into a number of portions by means of perforated deflectors welded to it between each portion, and collectors with exit tubes (Fig. 1b). The collectors were protected from the entry of alkali from other parts by concrete ridges appropriately arranged. By sampling alkali from various parts of the cathode it was possible to determine its concentration along the height of the bath.

Curves for the distribution of alkalinity were obtained between 3 and 6 times in each 24 hr. Sixteen experiments in all were carried out, with a mean duration of more than 3 weeks. Figure 2 contains a small portion of the data obtained in one of the experiments. It should be pointed out that the overwhelming majority of the something like 1500 determinations which we carried out were in good agreement with the typical curves there given.

* This is paper II in a series of works on the study of electrolytic methods of producing chlorine and alkali in vertical diaphragm electrolytic plant.

† As L. V. Gantman has disclosed to us, experiments were carried out by him in 1947 and 1948, 3 series of experiments being conducted in industrial baths. It was shown that the alkali concentration was constant over the larger part of the cathode, but increased near to the top. These data became known to us only at the end of our own work.

DISCUSSION OF RESULTS

Distribution of Alkali Concentration Along the Height of the Cathode. Figure 2 shows clearly the existence of two zones: a zone of constant alkalinity for high pressures, and one of variable alkalinity for low pressures. The boundary between the two zones lies at a depth of around 30 cm from the level of the anode liquid.

The picture described is obtained for diaphragms made from ordinary asbestos paper (10 experiments), for diaphragms deposited from a salt-alkali suspension (2 experiments), and also for the so-called double-layer diaphragms, or diaphragms consisting of discs of ordinary asbestos paper separated by a thin layer of asbestos-latex paper (3 experiments). All these types of diaphragm are practically free from ingredients forming a stable fiber with each other, and it is for this reason that the nature of the relationship between the permeability and the pressure is practically the same for them all.

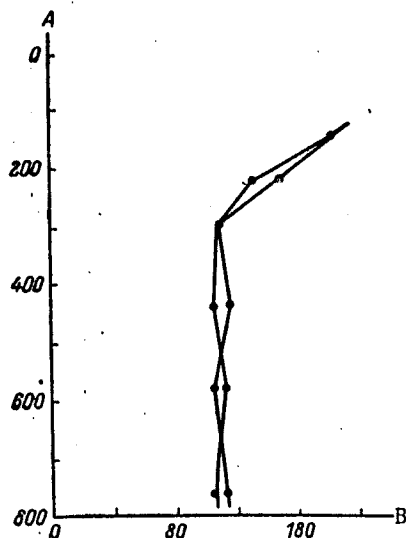


Fig. 2. Distribution of alkali concentration along the height of the cathode. A) Depth from level of anode liquid (mm); B) concentration of sodium hydroxide (g/liter). The data refer to periods of 17 and 25 24-hour periods of continuous electrolysis.

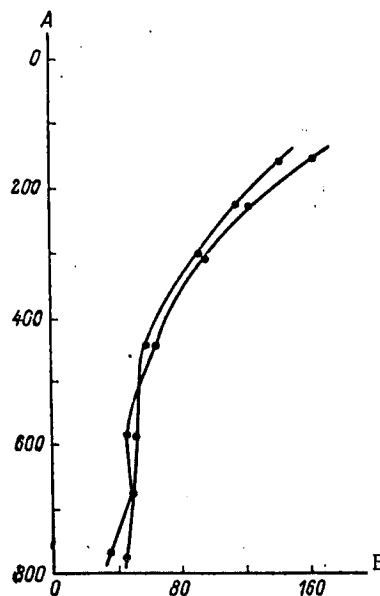


Fig. 3. Distribution of alkali concentration along the height of the cathode. For a bath with asbestos-latex diaphragm. Symbols have the same significance as in Fig. 2.

The position of the boundary between the zones of variable and constant alkalinity is found (Table 1) to be practically independent of the current density, at least within the limits of 400–1200 A/m², and also of the height of the cathode (between 30 and 68 cm),* the height of the level of the anode liquid over the upper edge of the cathode (9–30 cm), and the concentration of the alkali in the constant alkalinity zone (from 60 to 180 g/liter).

The position of the dividing boundary fluctuates somewhat, usually within the limits of ± 5 cm. There is some tendency towards a shift upwards of the boundary with increase in concentration of alkali in the zone of constant alkalinity. If the level of the anode liquid above the edge of the cathode is 30 cm or more, then the zone of variable alkalinity is no longer observed.

Change in current density causes a change in the alkali concentration. The nature of the distribution of alkalinity along the height is, however, practically unchanged: the curve showing the relationship between the alkali concentration and the pressure is shifted in a direction parallel to itself. The nature of the change in alkali concentration with height in the variable alkalinity region may be expressed to a first approximation by the straight line

* Judging from the nature of the relationship between the permeability and the pressure in the absence of a current [1], we should expect a maintenance of the constancy of alkalinity even for appreciably greater cathode height (150 cm and above).

$$C = C_0 + KZ, \quad (1)$$

where C_0 is the concentration in the constant alkalinity zone, and Z is the distance above the point of transition between the zones.

The value of the coefficient of slope, K , varies quite considerably from experiment to experiment, and, within a single experiment, from test to test. The limits of these fluctuations lie between 3 and 8 g/liter · cm. The mean value of K lies close to 5-6 g/liter · cm (Table 1).

Actually, the change in alkali concentration with height is not strictly linear, accelerating somewhat as the height increases. A great increase in the alkali concentration is sometimes observed in a narrow band of with up to 5 cm near the upper edge of the cathode. This phenomenon is attributable to the crystallization of the salt on the upper edge of the cathode because of evaporation of the water from the liquor. Washing the upper portion of the cathode with hot water removes the salt and causes the normal value of K (around 6 g/liter · cm) to be restored.

The picture given above is qualitatively in full agreement with the relationship between permeability and pressure obtained for a shaped diaphragm in the absence of current. Quantitative comparison

(taking account of a correction for the viscosity of the cathode liquid and for the yield with respect to current) shows that, for low pressure, the alkali concentration is somewhat lower than would have been expected on the basis of the data on the permeability of the diaphragm in the absence of current. It seems that, for low pressures, the compressive effect of the pressure, increasing the density of the diaphragm, is small [1], and is unable to compete with the expanding influence of the current.

In the previous communication [1], it was observed that asbestos paper, with an additive consisting of a bonding butadiene latex, is quite distinct in behavior from ordinary asbestos paper. This distinction is preserved when a current is flowing (Fig. 3). The concentration of alkali changes continuously with height - more slowly at great depths, and more rapidly at the upper portion of the cathode, being practically inversely proportional to the pressure.

TABLE 1. Characteristics of the Distribution of Alkalinity Along the Height of the Cathode for a Bath Containing a Diaphragm Made from Ordinary Asbestos Paper

Exp. No.	Current density (A/m ²)	Height of cathode (cm)	Level of anode liquid (cm)	Alkali concentration C_0 , g/liter	Depth of transition point (cm)	Slope of curve, K (g/liter·cm)
50	400	61	9	90	30	6
28	570	68	13	80	30	5
25	570	68	13	100	33	4
50	600	61	9	110	27	5
33	600	45	16	60	33	—
27	650	68	13	110	33	6
28	680	68	13	100	30	4
56	700	61	9	160	28	3
57	700	61	9	160	28	7
29	730	68	13	80	30	5
50	800	61	9	135	28	4
29	800	68	13	100	30	5
27	800	51	30	90	30	—
26	800	55	26	110	30	2
24	800	68	13	120	30	4
30	900	56	25	100	30	5
32	900	30	30	100	30	—
32	900	30	16	110	30	6
34	900	30	15	100	30	3
22	1050	61	9	170	26	8
27	1200	51	30	120	33	—

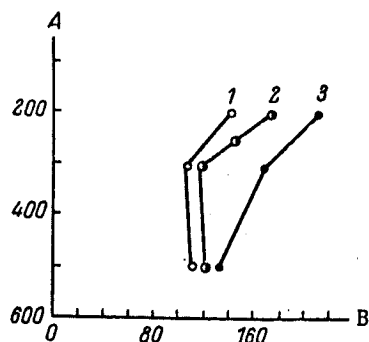


Fig. 4. Effect of clogging of the diaphragm with calcium hydroxide on the distribution of alkali concentration along the height of the cathode. Symbols the same as in Fig. 2. 1) Up to great clogging of the diaphragm with calcium hydroxide; 2) after washing the diaphragm; 3) after 30 24-hr periods of electrolysis of brine containing Ca^{2+} in concentration of 100-150 mg/liter.

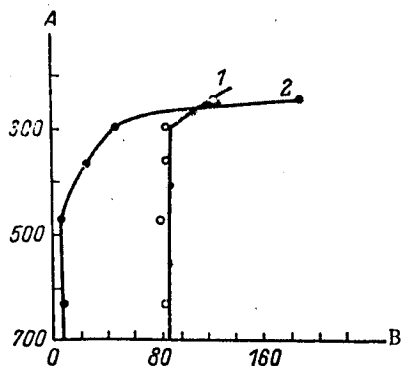


Fig. 5. Effect of sudden change in the distribution of current density on the distribution of alkali concentration along the height of the cathode (in an experiment imitating the condition of large-scale anode corrosion). Symbols the same as in Fig. 2. 1) Anode of normal length. 2) Short anode (lower edge of anode located at a depth of 250 mm, upper edge of cathode at 200 mm).

distribution curve became greatly distorted: at the upper portion a concentration of 200 g/liter was reached, while at the lower half the value did not exceed 10 g/liter (Fig. 5). It should be observed that this picture, obtained in two independent experiments, remained unchanged for a period of 26 days.

Yield with Respect to Current in Electrolytic Vessels with Partially Filled Cathode Space. In actual industrial electrolytic vessels with incompletely filled cathode space, the height of the level of the anode liquid above the upper edge of the cathode is considerably smaller than 30 cm and, therefore, a considerable portion of the cathode operates at a high alkali concentration. Under these conditions, an excessively high alkali concentration (of the order 180-200 g/liter or more) is attained at the upper part of the cathode, and the yield with respect to current at this part of the cathode goes down rapidly, resulting in a diminished yield with respect to current in the bath as a whole.

The different nature of the distribution of alkalinity with respect to height is the immediate cause of the difference in yield with respect to current in the use of ordinary, and asbestos-latex, diaphragms in electrolytic vessels with incompletely filled cathode space, which is found in industrial investigations. In the latter case, for the same mean alkali concentration, the region of high alkalinity is considerably wider, and the concentration itself is appreciably higher, which leads to a larger current loss.

Knowing the distribution of alkali concentration described above along the height of the cathode, and knowing also the relationship between the yield with respect to current and alkalinity [4], we are able to calculate the mean yield with respect to current in the bath.

Any portion of the cathode, of height dx , may be considered as an independent electrolytic apparatus with an infinitely small cathode, the diaphragm of which exists under constant pressure, and has a permeability which is uniform over the whole of its surface.

To determine the yield with respect to current in the bath as a whole (A_m), the yields are required at each portion of height $dx(A)$, averaged over the entire height of the bath:

$$A_m = \frac{\int_0^H A dx}{H} \quad (2)$$

At the portion A (from $x = 0$ to $x = H + h_a - 30$) (Fig. 6). The concentration of alkali is equal to C_0 and the yield with respect to current to A_0 . When the concentration of alkali is changed from C_0 to 156 g/liter (which corresponds to the transition point in the concentration-current yield curve [4]), the yield with respect to current hardly

* It has been shown by means of special experiments that prolonged immersion of the diaphragm in alkali (up to 12.5 months) has no effect on the nature of the relationship between its permeability and the pressure in the absence of current.

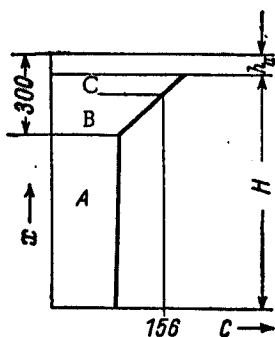


Fig. 6. Diagram of the distribution of alkali concentration along the height of the cathode [as deduced from Eq. (5)].

changes at all and may be taken equal to 98% (part B). The coordinates of this part are from $x = H + h_a - 30$ to $x = H + h_a - 30 + \frac{156 - C_0}{6}$, which follows from Eq. (1). The value of K taken for this equals $\frac{156 - C_0}{6}$ g/liter · cm.

On part C (from $x = H + h_a - 30 + \frac{156 - C_0}{6}$ to $x = H$), the yield with respect to current changes with alkali concentration changes in accordance with the equation [4]

$$A = 98 - 0.288 (C - 156), \quad (3)$$

while the concentration of alkali depends on the height:

$$C = C_0 + 6 (x - H - h_a + 30). \quad (1a)$$

Hence, in this part

$$A = 98 + 0.288 (156 - C_0) + 1.728 (H + h_a - 30) - 1.728x. \quad (4)$$

From Eqs.(2) to (4),

$$A_m = 98 - \frac{1}{H} \{ 0.288 [0.0834 (156 - C_0)^2 - (156 - C_0) (30 - h_a) + 3 (30 - h_a)^2] + (98 - A_0) (H + h_a - 30) \}. \quad (5)$$

Cases may be encountered for which the alkali concentration in the upper point, C_{max} , may not exceed 156 g/liter, that is, C_0 does not exceed $156 - 6(30 - h_a)$. Under these conditions A_m is practically identical with A_0 .

A somewhat different situation is found when C_0 exceeds 156 g/liter. In this case the portion B disappears, and the yield with respect to current in portion A depends on C_0 according to Eq. (3), while the coordinates of portion C lie between $x = H + h_a - 30$ and $x = H$. For this case,

$$A_m = 98 - \frac{0.288}{H} [3(30 - h_a)^2 - (C_0 - 156)H]. \quad (5a)$$

Equations (5) and (5a) give the relation between the yield with respect to current and the cathode height, H , the height of the level of the anode liquid above the upper edge of the cathode, h_a , and the concentration of alkali in the constant alkalinity zone, C_0 . The last named is close to the mean concentration in the bath, C_m .

In Eq. (5) a number of assumptions are involved, in particular the postulate of a linear relationship between the alkali concentration and the height, and the equal distribution of current density, and no account is taken of the possibility that the upper edge of the cathode might become clogged up. These assumptions, as well as the unavoidable imperfections of operation of industrial baths, lead to the fact that the calculated yield with respect to current should be higher than that obtained in practice, and, in particular, should be higher than the yields obtained over the whole period of operation. We may be certain, however, that the yields calculated by means of Eq. (5) will be reliable relative characteristics of the particular bath construction employed. This suggestion is confirmed by the data in Table 2, in which the calculated yields with respect to current are compared with the industrial indices for a number of electrolytic vessels. It must be admitted that the data given in Table 2 for incompletely filled cathode chambers were obtained under conditions which are not strictly comparable, but in spite of this, they indicate clearly the applicability of the calculated yields with respect to current for comparative estimates of different bath constructions.

From what has been set out above, it is clear that, in the operation of vertical diaphragm baths with incompletely filled cathode chambers, the level of the anode liquid plays a very important part. The lower the level of the anode liquid, the wider is the zone of variable alkalinity ($30 - h_a$), and the higher the concentration of the alkali at the upper cathode portion, and the more noticeable is the fall in the yield with respect to current. It must be emphasized that the first indices for the series of baths considered in Table 2 were obtained for those with low anode liquid level.

For constant value of the anode liquid level and of alkali concentration, the current loss in the variable alkalinity zone is constant also. But these factors shows a smaller influence on the mean value of the yield with respect to current, the lower the fraction of the cathode surface which occupies this zone. It follows that, for constant anode liquid level, the yield with respect to current will be greater in baths with the highest cathodes.

The results given above permit of arriving at the optimum conditions for the operation of vertical diaphragm electrolytic vessels with incompletely filled cathode chambers, the level of the anode liquid being maintained at

approximately 30 cm above the edge of the cathode. Under these conditions the zone of variable alkalinity disappears. We should note that, for baths operating under optimal conditions, the height of the cathode has no effect on the yield with respect to current.

The reasoning developed above is concerned with the operation of baths with ordinary asbestos diaphragms. As we have seen for the case of asbestos paper with the addition of latex, the use in baths with incompletely filled cathode chambers of diaphragms giving a less uniform distribution of alkali concentration with respect to height leads to a reduction in the yield with respect to the current, so that such a procedure is inadvisable.

TABLE 2. Comparative Characteristics of Different Electrolytic Vessels with Incompletely Filled Cathode Chambers [3, 5, 6]

Type of electrolytic vessel	Alkali concentration (g/liter)	Yield with respect to current(%)	
		practically attained	calculated from Eq. (5)
Cylindrical bath with two cathodes	100-110	94-95	96
Cylindrical bath with single cathode (Kh-2, Vors)	110	94-95	95.5
Bak-Mak-Rei	70-100	94-95	94.5-95.5
Krebs	100-110	90-92	92
Dzhari	130	90-92	92
Nelson	100-120	90±2	91-92

It has been indicated above that during prolonged operation of electrolytic vessels the normal picture of the alkalinity distribution may suffer distortion from a variety of causes.

Clogging of the diaphragm by calcium hydroxide leads to a considerable increase in the nonhomogeneity of the distribution of alkali concentration with respect to height, and, therefore, to a reduction of the yield with respect to current (which, according to our data, may go as far as to 5%).

A further cause of nonuniformity of alkalinity distribution with respect to height may be the suddenly occurring nonuniformity in the distribution of current density arising from substantial corrosion of the anode.

Determinations of the yield with respect to current in laboratory baths with composite anodes, giving some form of imitation of different degrees of anodic corrosion, have shown a reduction of yield with respect to current of from 1 to 10%.

In distinction from the effect of clogging of the diaphragm, the limiting corrosion of the anode has a great effect on the yield with respect to current, both with baths containing incompletely filled cathode chambers, and those in which the chambers are completely filled.

SUMMARY

1. The nature of the relationship between the permeability of an asbestos diaphragm and the pressure described in a previous communication [1] is maintained also when current is flowing. At the cathode a zone of constant alkalinity and one of variable alkalinity are formed, with the boundary between them lying at a level of approximately 30 cm from the level of the anode liquid. The position of this boundary is practically independent of the current density, the height of the cathode, the level of the anode liquid above the edge of the cathode, and the concentration of alkali in the constant alkalinity zone. Above the 30 cm level the alkali concentration increases on the average by 5-6 g/liter per centimeter increase in height.

2. Starting from the nature of the distribution of alkalinity with respect to cathode height, and from the relationship between the yield with respect to current and the alkali concentration, equations have been derived which connect the yield with respect to current with structural parameters in vertical diaphragm baths with incompletely filled cathode chambers. The equations give good agreement with experiment, and may be employed for preliminary evaluation of new constructions.

It has been shown that the optimum conditions for the operation of a bath with incompletely filled cathode space involve arranging the height of the anode liquid at about 30 cm above the upper edge of the cathode.

3. Clogging of the diaphragm with calcium hydroxide leads to a less uniform distribution of alkali concentration with respect to height, and so to reduced yield with respect to current.

4. The great nonuniformity of distribution of current density with respect to cathode height, which is due to great corrosion of the anode, involves also a great nonuniformity in the distribution of alkalinity with respect to height, and hence again reduced yield with respect to current.

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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.