Technical Analysis of the Cell for Na_2SO_4 Electrolysis with Filter Diaphragm and Mercury Cathode*

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The electrolysis of sodium sulfate to obtain H_2SO_4 and NaOH is a very interesting problem, to the viscose rayon industry. On this problem, many investigations⁽¹⁾ have been reported. But nearly all the results^{(3), (4), (5)} showed only the low current efficiencies below 90% when the concentrations of sulfuric acid were higher than ca. 150 g/l. And, for this reason, they have not developed into industrial scales.

The report on the sodium sulfate electrolysis at Bitterfeld in I.G. is given in P.B. Report⁽²⁾. Its best cell has vertical mercury cathode and Pb-10%Ag alloy anode in it, using a diaphragm of micro-porous rubber. At 10 A/dm², 40-50°C., voltage is 4.4. Products are 50% NaOH and 250 g/l H_2SO_4 containing 230 g/l Na_2SO_4 . Its current efficiency is 95-97%. But the detailed conditions of electrolysis and their mutual relations are not described in the report.

Recently, on the electrolysis of sodium chloride solution, Mukaibo⁽⁶⁾ technically analyzed the chlorine cell with filter diaphragm and discussed the rate of flow, current density and the thickness of diaphragm.

The first purpose of this report is to investigate whether such good results are possible or not theoretically and technically with filter diaphragm and mercury cathode. And the second purpose is to find out the optimum conditions of electrolysis.

In this paper, the author has analyzed technically the cell for Na_2SO_4 electrolysis by the Mukaibo's method⁽⁶⁾ and investigated the chief factors which affect the current efficiency of H_2SO_4 and its concentration is represented. The first factor is the current density, the second is the rate of flow of sulfate solution through diaphragm and the third is the thickness of diaphragm.

During the electrolysis, the H^+ in anolyte tends to move to cathode by migration and diffusion and makes current efficiency of H_2SO_4 drop. By adopting the filter diaphragm with mercury cathode, this H^+ is prevented from migration and diffusion from the anode compartment by flowing the neutral sulfate solution through diaphragm and high current efficiency and high concentration of H_2SO_4 can be obtained simultaneously.

Fig. 1 is the model of the diaphragm cell represented with 3 dimensional coordinate. Let us discuss the material balance of H^+ and OH^- in diaphragm, at stationary state. H^+ and OH^- respectively move by diffusion, migration and flow of sulfate solution as shown in Eqs. (1) & (2). When the neutral layer lies in the diaphragm, $k_1 + k_2 = 0$.

Next, the linear differential Equations (4) and (5) of the first order in terms of concentration are derived. Solving these Equations under boundary conditions, we can obtain Eqs. (6) and (7).

Finally Eqs. (8) and (9) are obtained in which the current efficiency of H_2SO_4 and its concentration are expressed as complex exponential function of current density, rate of flow of sulfate-solution and thickness of

Fig. 1 Model of Na_2SO_4 electrolytic cell with filter diaphragm.

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diaphragm.

$$C_1^{\circ} = \frac{D}{v + \frac{n_1^{\circ} D - v}{1 - \exp\left\{\frac{-(n_1^{\circ} D - v)d_1}{K_1}\right\}}} \quad (8)$$

$$cE_{ff}^a = \frac{v \times 10^2}{v + \frac{n_1^{\circ} D - v}{1 - \exp\left\{\frac{-(n_1^{\circ} D - v)d_1}{K_1}\right\}}} = \frac{v}{v + f(v)} \quad (9)$$

As the result of $\lim_{D \rightarrow \infty} \left[\exp\left\{\frac{-(n_1^{\circ} D - v)d_1}{K_1}\right\} \right] = 0$ shown in Eq. (8), the concentration of H_2SO_4 in analyte approaches to a limiting value $\frac{1}{n_1^{\circ}}$ at large current density.

To apply the theoretical and technical results under ordinary conditions of electrolysis, the constants and parameters in Eqs. (8) and (9) are properly estimated by adopting the data from the tables or literatures and measuring the conductivity of mixture of concentrated H_2SO_4 and Na_2SO_4 solution. The value of 2.5^{(7),(8)} is adopted for the porosity (α) of diaphragm. The ratio (a) of the true effective area to the apparent area of diaphragm is estimated as (porosity)^{2/3}. The diffusion constant (K_1) of H_2SO_4 in the mixture of the concentrated H_2SO_4 and Na_2SO_4 has approxi-

Table 1 C_1° and cE_{ff}^a Dependence on v and D , Which was Calculated from Eqs. (8) and (9) at Various Current Densities.

Dimension; $C_1^{\circ} \times 10^3$: Normality, cE_{ff}^a : %

$\begin{matrix} D \\ c_1^{\circ}, \\ cE_{ff}^a \\ v \end{matrix}$	7		10		12		14		16		20	
	$c_1^{\circ} \times 10^3$	cE_{ff}^a	$c_1^{\circ} \times 10^3$	cE_{ff}^a	$c_1^{\circ} \times 10^3$	cE_{ff}^a	$c_1^{\circ} \times 10^3$	cE_{ff}^a	$c_1^{\circ} \times 10^3$	cE_{ff}^a	$c_1^{\circ} \times 10^3$	cE_{ff}^a
0	6.86	0	6.93	0	6.92	0	6.92	0	6.92	0	6.92	0
20	6.73	30.9	6.91	18.5	6.91	18.5	6.91	15.9	6.92	13.9	6.92	11.1
40	6.40	58.8	6.89 ₅	27.0	6.89 ₅	37.0	6.90 ₅	31.7 ₅	6.92	27.8	6.92	22.3
60	5.81	80.1	6.83	54.9 ₅	6.83	54.9 ₅	6.89	47.5	6.91 ₅	41.7	6.92	33.5
80	5.03	92.5	6.67	71.5	6.67	71.5	6.83	62.8	6.89 ₅	55.4	6.92	44.7
100	4.25	97.6	6.34	85.0	6.34	85.0	6.68	76.8	6.84	68.8	6.91	55.6
120	3.60	99.3	5.82	93.6	5.82	93.6	6.38	88.0	6.75	81.4	6.88	66.4
140	3.10 ₅	99.9	5.20	97.6	5.20	97.6	5.90	95.0	6.41	90.2	6.84	77.0
160	2.72	100.0	4.63	99.3	4.63	99.3	5.34	98.2	5.97	96.0	6.70	86.2
180	2.42	100.0	4.14	99.9	4.14	99.9	4.81	99.5	5.45	98.6	6.43	93.1

$d_1'/K_1 = 12.5$ 1/cm·h, $n_1^{\circ} = 0.1446 \times 10^3$ cc/g-eq, $v = 0 \sim 180$ cc/m²/min, $D = 7 \sim 20$ A/dm² = $2.611 \times 10^{-3} \sim 7.46 \times 10^{-3}$ g-eq/cm²/h

Table 2 Influence of the Thickness of Diaphragm, Which was Calculated from Eqs. (8) and (9)

Dimension; d : cm, v : cc/m²/min, $c_1^{\circ} \times 10^3$: N, cE_{ff}^a : %

$\begin{matrix} d \\ c_1^{\circ}, \\ cE_{ff}^a \\ v \end{matrix}$	0.2		0.3		0.4		0.5		0.6	
	$c_1^{\circ} \times 10^3$	cE_{ff}^a	$c_1^{\circ} \times 10^3$	cE_{ff}^a	$c_1^{\circ} \times 10^3$	cE_{ff}^a	$c_1^{\circ} \times 10^3$	cE_{ff}^a	$c_1^{\circ} \times 10^3$	cE_{ff}^a
0.12	5.60	18.2	5.76	18.5	5.79	18.6	5.80	18.7	5.80	18.7
0.24	5.47	35.0	5.70	36.7	5.77	37.1	5.79	37.4	5.80	37.3
0.36	5.28	51.0	5.59	54.0	5.71	55.1	5.77	55.6	5.78	55.8
0.48	5.04	64.8	5.39	69.4	5.57	71.6	5.67	72.9	5.72	73.6
0.60	4.73	76.1	5.06	81.8	5.28	85.0	5.40	86.9	5.72	92.0
0.72	4.38	84.6	4.68	90.4	4.84	93.4	4.93	95.1	5.00	96.5
0.84	4.02	90.6	4.24	95.5	4.33	97.6	4.38	98.7	4.42	99.3
0.96	3.67	94.5	3.81	98.0	3.86	99.3	3.88	99.7	3.88	99.9
1.08	3.35	99.0	3.43	99.2	3.45	99.9	3.45	99.9 ₅	3.45	100.0

$\alpha = 3.0$, $d_1'/K_1 = 6.0 \sim 18.0$ 1/cm·h, $n_1^{\circ} = 0.1725 \times 10^3$ cc/g-eq, $D = 3.73 \times 10^{-3}$ g-eq/cm²/h = 10 A/dm²

mated to the one in the water⁽⁹⁾. The value of $\Delta\kappa/\Delta t$ also has approximated to the temperature coefficient of conductivity of H_2SO_4 . The value of n_1° in Eqs. (1)' and (2)', namely "proportional constant about the migration", is calculated from the observed specific conductivity.

Thus, Table 1 was obtained under various current densities, in which the current efficiencies of obtaining H_2SO_4 and their concentrations were calculated from Eqs. (8) and (9) at various rate of flow of sulfate solution through diaphragm and plotted altogether in Fig. 2. The influence of thickness of diaphragm is shown in Table 2, which was calculated from Eqs. (8) and (9).

The thickness of diaphragm gave an interesting effect on the current efficiency. The current efficiency increased at the rate of percolation of the electrolyte through diaphragm and then approached to the limiting value. Using a more thick diaphragm, the current efficiency is already high with lower rate of flow of electrolyte. And this phenomenon is especially remarkable when the current efficiency is between 90% and 97%, as shown in Table 2, which is important to practical electrolysis. Then the tightly combined diaphragm is made, which consists of several same sheets and H^+ and OH^- concentration distributions are analyzed by pipetting out the electrolyte between them. The results are shown in Fig. 3: the distribution curve of H^+ concentration is concave upwards and that of OH^- concentration is convex upwards, satisfying the demands of this theory.

Summary :

(1) The author technically analyzed the cell for Na_2SO_4 electrolysis with filter diaphragm and mercury cathode under stationary state. The linear differential equation of migration, diffusion and the rate of flow of catholyte were solved with a few approximations. And the current efficiency of H_2SO_4 and its concentration were able to be expressed as the complex exponential functions of the current density, thickness of diaphragm and the rate of flow of catholyte.

(2) Under ordinary conditions of current densities and thickness of diaphragms, the current efficiency of H_2SO_4 and its concentration were calculated and were plotted against the rate of flow of catholyte. And we found it is possible to obtain the current efficiency of H_2SO_4 95% and its concentration of 250 g/l at the same time.

(3) The concentration of H_2SO_4 can not exceed the limiting value of $(n_1^\circ)^{-1}$, however high is the current density.

(4) The effects of the thickness of diaphragm are remarkable when the current efficiency is 90-97%.

It is desirable to set the neutral layer at the end of diaphragm or in its neighbouring position.

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Fig. 2 Concentration of H_2SO_4 in anolyte and current efficiency dependence on flow of catholyte at various current density.

Fig. 3 H^+ , OH^- distribution in filter diaphragm at stationary state.

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Literature :

- (1) H.V. Atwell, T. Fuwa, *Ind. Eng. Chem.*, **15**, 617 (1923);
E.R. Waston, *J. Soc. Chem. Ind.*, **42**, 251 (1923);
W.W. Stender, I.J. Seerak, *Journ. Electrochem. Soc.*, 493 (1953);
G. Grube, S. Stainoff, *Z. Electrochem.*, **44**, 640 (1938);
R. Torigai. et al, *Denki-Hyōron*, **26**, 431, 519, 601 (1938), *This Journal*, **6** A. 333 (1938);
T. Okuno, W. Sakai, *J. Chem. Soc. Japan (Indust. Chem. Section)* **42**, 86 (1939),
This Journal, **9**, 32, 381 (1941) **10**, 123, 129 (1942);
Maeshima, *This Journal*, **11**, 351 (1943).
 - (2) FIAT. Final Report No. 831 June (1946).
 - (3) R. Torigai. et al, *Denki-Hyōron* **26**, 431, 519 (1938).
 - (4) T. Okuno, *J. Chem. Soc. Japan (Ind. Chem. Sect.)* **47**, 919 (1939).
 - (5) G. Grube. et al, *Z. Elektrochem.* **44**, 640 (1938).
 - (6) T. Mukaibo, *This Journal*, **20**, 482 (1952).
 - (7) T. Matsuno, *This Journal*, **20**, 97 (1952),
J. Chem. Soc. Japan (Ind. Chem. Sect) **52**, 281 (1949), **60**, 951 (1957).
 - (8) S. Sanada, *J. Chem. Soc. Japan (Ind. Chem. Sect)* **42**, 625 (1939).
 - (9) Landolt, "Physikalish Chemishe Tabellen" Hw. I. 248.
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