Investigation on the Various Conditions of Electrolysis about the Cell for the Na_2SO_4 Electrolysis with Filter Diaphragm and Mercury Cathode*

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In the previous paper¹⁾, the author technically considered the cell for Na_2SO_4 electrolysis with filter diaphragm and mercury cathode. From the results, the concentration of sulfuric acid and its current efficiency could be theoretically expressed as the functions of the current density, the rate of flow of the sulfate solution through diaphragm and the thickness of the diaphragm, and the refore, their mutual relationships could be culculated and plotted graphically on various conditions of electrolysis by substituting the properly estimated values.

The first purpose of this report is to make sure how much this theory applies to the practical electrolysis under various conditions. The second purpose is to find the optimum conditions of electrolysis and the third is to investigate, technically and electrochemically, important problems for the design of a large scale unit, such as arrangement of diaphragm, economical acid concentration and resulting current efficiency.

In this paper, the electrolysis was performed with diaphragmatic pre-pilot plant 90-ampere cell with rotating mercury cathode. The picture of the electrolyzer and the arrangement of electrolytic system were already shown in Fig. 1 & Fig. 2 in the previous paper²⁾. We used, as anode material, lead alloy containing 2% silver and 1% tellurium which were more durable and cheaper than lead alloy containing 10% silver.

Experiments in this report were performed under the following constant conditions of electrolysis, except the special description.

Current=90 Amp.

Anodic and cathodic current density=
10 A/dm².

Rate of inlet of electrolyte=
38 cc/min. Na_2SO_4 solution
(50°C saturated).

Number of rotating of cathode=14.5 rpm

Amalgan=0.05% Na.

"Rubber diaphragm" was the micro-porous rubber sheet which was treated in Vinylon cloth as described in the previous paper³⁾. First we examined the obtained concentrations of sulfuric acid and its current efficiencies at various rates of flow of sulfate solution through rubber diaphragm with 0.8

Fig. 1 Effects of the rate of flow of sulfate solution and thickness of diaphragm.

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and 1.6 mm thickness, which consisted of only a single sheet.

The results are shown in Fig. 1 and have the same tendency which was calculated and plotted graphically in the previous paper¹⁾. Using a thicker diaphragm, the current efficiency was already high with a lower rate of flow of electrolyte and this is pointed out in the previous paper¹⁾. The experiments about the method of arrangement of diaphragm showed some interesting results on the concentration of sulfuric acid and its current efficiency as described below.

Table 1 Effect of the Tightly Combined Same Diaphragm

Number of sheet tightly combined	Thickness of diaphragm (mm)	A.F. (cc/min/900cm ²)	Concentration of H ₂ SO ₄ (g/l)	cE^a_{ff} (%)	Acid in catholyte (g/l)	Anodic decomposition grade (%)	Voltage (V)
1 Sheet	0.5	11.3	223.0	91.6	H ₂ SO ₄ 0.35	60.1	5.1
2 Sheets	1.0	11.7	227.5	96.7	0.51	58.2	5.4
		10.3	246.3	92.2	0.74	61.8	5.4
		10.0	251.5	91.6	0.75	62.5	5.4
3 Sheets	1.5	10.4	246.1	93.9	0.50	61.7	5.5

When the same two rubber diaphragm were combined together tightly, the concentration of sulfuric acid and its current efficiency were higher than those of the single diaphragm having the total thickness of the two diaphragms as shown in Fig. 1. and Table 1. When the "Grid" was inserted between the combined diaphragms to make a proper diffusion layer (in this case 1.5 mm), the above mentioned tendency was fortunately much more accelerated and the bath voltage did not increase. Fig. 3 shows the concentration distribution of H₂SO₄ and NaOH in the three-sheets-combined diaphragm with two "Grids" inserted in stationary state.

Fig. 2 The effect of insertion of "Grid" between two sheets of diaphragm.

It is desirable to keep the rate of anolyte flow out (A.F.) and the rate of catholyte flow out (C.F.) at the constant rate, but in practical operation it is impossible to keep the both flows at a constant rate on account of the changing of the mercury level or the evolution of the gas bubbles, and so either A.F. or C.F. must be chosen to keep at a constant rate.

Fig. 3 and Fig. 5 show the results obtained from A.F. controlled at the constant rate by using the siphon especially made. The concentration of sulfuric acid and its current efficiency scarcely changed as

Fig. 3 Distribution of acid in the three combined diaphragm with two inserted Grids (form exp. No. 47).

Fig. 4 The case keeping A.F. at constant rate.

Fig. 5 The case keeping C.F. at constant rate.

time passed and were relatively higher than C.F. controlling type. Fig. 6 and Fig. 7 show the case of keeping C.F. at the constant rate. But this controlling type showed a very irregular change of concentration of sulfuric acid and current efficiency and their average values were lower than the above mentioned A.F. controlling type.

Next the effect of partial overflow of catholyte from 40 to 80 vol % was tested. The partial overflow of catholyte is a very important practical process to obtain the high concentration of sulfuric acid and its high current efficiency. The overflowed catholyte is re-saturated with sodium sulfate crystal and is reused. The results are shown in Table 3 and Fig. 8. From Fig. 8, we have found that the partial overflow of catholyte must be kept above 65 Vol-% for the safety operation. And, at overflow ratio 65 Vol-%, the concentration ratio of Na_2SO_4 vs. H_2SO_4 in anolyte was ca. 80 : 100.

The concentration of electrolyte (Na_2SO_4 solution) in feed which varied from 420 to 360 g/l gave a remarkable effect in electrolysis as shown in Table 4. Current efficiency drops with decrease of concentration of Na_2SO_4 . In practical operation, we must use Na_2SO_4 solution containing 420 g/l or above it.

Fig. 6 Effect of partial overflow of catholyte

Table 2. The Effect of Insertion of Grid between two Sheets of Diaphragm

Case	Voltage (V)	A.F. (cc/min/900 cm ²)	Concentration of H ₂ SO ₄ (g/l)	Acidity of Catholyte (g/l)	Elect. Exp. No.
Without "Grid"	5.36	10.4	255.3	NaOH 0.25	No. 43 ³⁾
	5.27	9.7	262.9	H ₂ SO ₄ 0.68	
With "Grid"	5.3	10.4	263.0	NaOH 2.23	No. 44 ³⁾
	5.3	10.0	270.6	" 1.51	
	5.35	9.7	276.2	" 1.14	
	5.3	9.4	276.6	" 0.52	

Table 3 Effect of Partial Overflow of Catholyte

$D_A=D_C=10\text{ A/dm}^2$, A.F.=10.4 cc/min 900 cm², Feed= Na_2SO_4 420~425 g/l, Temp=46~50°C, Diaphragm=Combined Diaphragm with inserted Grid.

Overflow of Catholyte (Vol%)	Exp. No.	Concentration of Feed (Na_2SO_4) (g/l)	Analysis of Anolyte				E.F. (cc/min)	C.F. (cc/min)	Analysis of Catholyte		Concentration Ratio in Anolyte. $\frac{\text{Na}_2\text{SO}_4}{\text{H}_2\text{SO}_4}=100$ (%)
			H ₂ SO ₄ (g/l)	cE_{ff}^a (%)	Na ₂ SO ₄ (g/l)	Decomposition Grade (%)			Na ₂ SO ₄ (g/l)	Acidity (g/l)	
40.3	No. 48-3	—	241.9	91.6	176.3	66.6	18.3	7.4	304.3	H ₂ SO ₄ 1.11	72.9
48.6	—2	424.8	246.4	93.4	184.1	66.2	21.2	10.3	325.4	" 0.84	74.7
60.0	—4	425.0	251.1	95.2	196.6	64.9	26.8	15.8	341.4	" 0.66	78.3
71.0	No. 47-1	417.1	257.1	97.4	211.9	63.8	37.6	26.7	362.4	NaOH 1.66	82.4
79.6	No. 48-5	425.0	261.4	99.1	228.2	62.4	42.5	42.5	379.8	" 1.63	87.3

Table 4 Effect of the Concentration of Electrolyte.
 $D_A=10\text{ A/dm}^2$, A.F.=10.4 cc/min, 900 cm², Temp=47-50°C
Diaphragm=Combined Diaphragm with inserted "Grid".

Elect Exp. No.	Concentration of Electrolyte (Na ₂ SO ₄) (g/l)	H ₂ SO ₄ (g/l)	cE_{ff}^a (%)	E.F. (cc/min)	C.F. (cc/min)	Overflow of Catholyte (Vol %)	Na ₂ SO ₄ in Anolyte (g/l)	Acidity of Catholyte (g/l)	Voltage (V)
No.50-1	417.5	260.7	98.8	37.2	26.0	70.7	216.3	NaOH 2.12	5.4
-2	391.0	249.8	94.7	38.0	27.1	71.3	191.5	" 1.84	5.4
-3	391.5	250.7	95.0	30.4	19.5	64.1	188.9	H ₂ SO ₄ 0.19	5.3
-4	359.9	236.5	89.6	37.4	26.5	70.7	175.5	" 0.72	5.35
-5	360.0	237.5	90.0	31.1	20.2	64.9	172.5	" 0.68	5.35
-6	412.3	258.0	97.7	36.0	25.1	69.7	203.9	NaOH 2.58	5.4

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