

Chemical Engineering Studies on the Decomposition of Amalgam in a Packed Tower in the Chlor-caustic Industry

By

Shiro YOSHIKAWA* and Fumio HINE*

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Part I. The Kinetics and Design of the Tower.**

The kinetics of amalgam decomposition in the case of a local cell consisting of Na-Hg (Y)/NaOH aq. (X)/H₂-graphite, with emphasis on the hydrogen overpotential, chemical engineering considerations of the decomposition tower, and the design of the tower are described.

These studies involve representations concerning the H.T.U. and the N.T.U. of the amalgam decomposition tower which differs from common packed towers where the diffusion process is controlling.

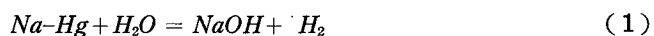
I. Considerations of the Amalgam Decomposition Tower from the Chemical Engineering Point of View.

The decomposition of the amalgam is one of the most important processes in the amalgam type chlorine-caustic industry.

The methods of decomposition have been considered and developed from early days, especially the decomposition tower method used in the de Nora cell in Italy and in Okada's cell in Japan, and they have promoted the amalgam type electrolysis industry of sodium chloride solutions. However, theoretical analyses of the decomposition and of the design of decomposition towers have rarely been published until now.

The amalgam decomposition tower is one kind of packed tower, but this tower differs from common packed towers under the control of the diffusion process, because the decomposition of the amalgam is an electrochemical reaction.

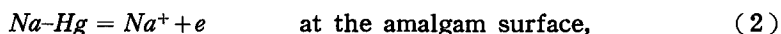
The amalgam decomposer consists of the amalgam and a contact material, such as graphite, and the reaction of the decomposition may be written as follows:



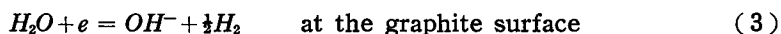
* Department of Industrial Chemistry

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This reaction may be divided into the following two electrochemical processes:

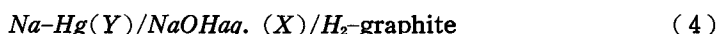


and



and these equations represent the anodic and the cathodic reactions, respectively.

In this paper, the kinetics of the amalgam decomposition is discussed as it takes place in the local cell consisting of



where, X is the activity of the solution of caustic soda, Y is the activity of Na in the amalgam.

1. The Electrochemical Process in the Decomposition of Amalgam.

The schemata of the anodic and cathodic polarization characteristics are given in Fig. 1, in which η_a^0 and η_c^0 are the equilibrium electrode potentials of the amalgam and the hydrogen, respectively.

For example, if the amalgam is kept in contact with the graphite, local current begins to flow between them due to the electromotive force, $\eta_c^0 - \eta_a^0$. This electromotive force is to be considered the driving force for the decomposition of the amalgam, and it is represented by the following equation:

$$E = \eta_c^0 - \eta_a^0 = E_0 + \frac{RT}{F} \log \frac{YW}{X} \quad (5)$$

where, W is the activity of water in caustic soda.

Against this driving force, the reaction resistances are as follows:

$$\overline{PQ} = \pi_h = \eta_c^0 - \eta_c, \quad (6)$$

$$\overline{QR} = JR, \quad \text{and} \quad (7)$$

$$\overline{RS} = \pi_a = \eta_a - \eta_a^0, \quad (8)$$

where, these terms are the hydrogen overpotential of the graphite, the ohmic resistance in the caustic solution, and the anodic overpotential at the amalgam surface, respectively.

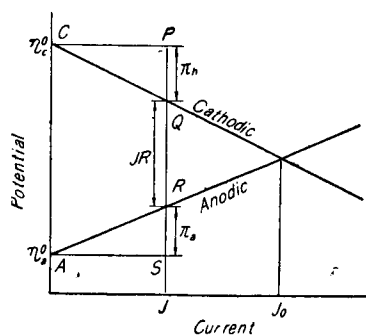


Fig. 1. Schematic profile of the anodic and cathodic polarization curves consisting of Na-amalgam and H_2 -graphite electrodes.

2. Resistances to the Process of Amalgam Decomposition.

The resistances consist of the three kinds of processes given above. Fig. 2 shows an example of the polarization characteristics of both cathodic and anodic surfaces. Nevertheless the cathodic polarization curve has a large slope, while the anodic one is nearly straight, and thus it can be seen that the reaction of the amalgam decomposition is largely a cathodic control process. The hydrogen overpotential may be shown by Tafel's equation

$$\pi_h = a + b \log j \quad (9)$$

where, a and b are constants, and j is the current density; however, for the sake of convenience it will be assumed to a straight line, that is,

$$J = k_h(\pi_h - \pi_h^0), \quad (10)$$

in the range of more than 2 amp/dm² of current density, where k_h is a coefficient. This is shown in Fig. 3. Next, the ohmic resistance between the amalgam and the graphite may be shown as follows:

$$J = k_f(E - \pi_a - \pi_h), \quad (11)$$

where J is the total current of the system and k_f is a coefficient.

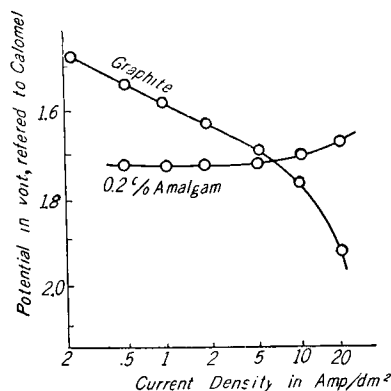


Fig. 2. An example of the anodic and cathodic polarization curves at 80°C in 40% caustic soda solution.

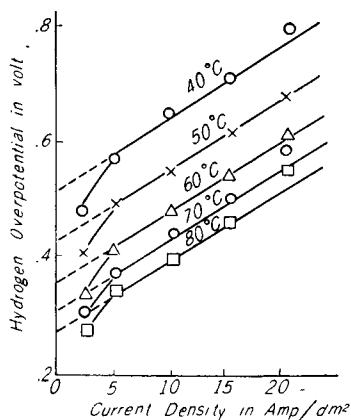


Fig. 3. Hydrogen overpotential of the graphite in 40% caustic soda solution.

II. Mass Transfer in the Tower.

The schema of the amalgam decomposition tower is profiled in Fig. 4. In this figure, symbols on the left-hand side concern the amalgam and those on the

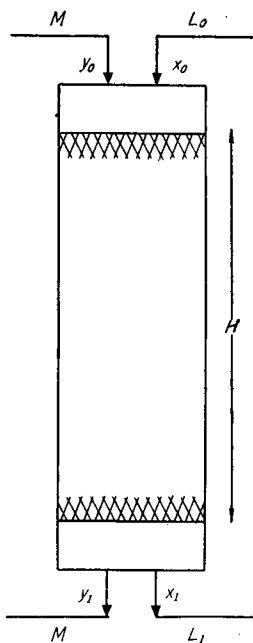


Fig. 4. Mass transfer of the packing tower.

right-hand side the caustic soda. That is, the amalgam, which is M in flow and y_0 in concentration, flows down from the top to the bottom of the tower, and a caustic soda solution of x_1 in concentration and L_1 in flux, should be produced. Then, the mass transfer in the tower may be represented as follows :

$$w = M(y_0 - y) = Lx - L_0x_0 = L_0 - L, \quad (12)$$

the terms of this equation corresponding to the mass transfer of amalgam, caustic soda, and water, respectively.

On the other hand, the electrochemical reaction must follow the so-called Faraday's Law,

$$w = Ih/F \quad (13)$$

where, I is the current per unit length of the tower, and h is the height.

The current per unit length of the tower, I , is represented as follows :

$$\left. \begin{aligned} I &= K_A F S Y \pi_a && \text{anodic reaction} \\ I &= K_F F S (E - \pi_a - \pi_h) && \text{ohmic resistance} \\ I &= K_H F S \pi_h && \text{cathodic reaction} \end{aligned} \right\} \quad (14)$$

or

$$\frac{I}{FS} = KE_h \quad (15)$$

where K_A is the coefficient for mass transfer on the side of the amalgam, K_F is the coefficient for mass transfer in the solution, and K_H is the coefficient for mass transfer in the solution, and K_H is the coefficient for mass transfer at the surface of the graphite. Furthermore E_h and K are shown as follows :

$$E_h = E - \pi_h^0 = E_0 - \pi_h^0 + \frac{RT}{F} \log \frac{YW}{X} \quad (16)$$

$$\frac{1}{K} = \frac{1}{K_A Y} + \frac{1}{K_H} + \frac{1}{K_F \kappa} \approx \frac{1}{K_H} + \frac{1}{K_F \kappa} \quad (17)$$

Then, the total mass transfer for the tower should be obtained as

$$d(Lx) = KE_h S dh \quad (18 x)$$

$$-M dy = KE_h S dh \quad (18 y)$$

or, as integrals :

$$\int_{L_0 x_0}^{L_1 x_1} \frac{d(Lx)}{KE_h} = SH \quad (19 x)$$

$$\int_{y_0}^{y_1} \frac{dy}{KE_h} = -\frac{SH}{M} \quad (19 y)$$

In this equation, K is so greatly a function of the conductivity of the caustic soda solution, that it depends upon the concentration of the solution.

According to eq. (5), the driving force of the tower, E_h , is represented by X , Y and W . Then, E_h may be represented in terms of X , Y and the operating temperature. This relation was obtained by experiment, and the result, as we have understood it, is shown as follows :

$$E_h = \alpha x + \beta_1 y + \beta_2 y^2 + \gamma \quad (20)$$

where x is the concentration of caustic soda and y is the concentration of amalgam, α , β_1 and β_2 are the constants independent of temperature, and γ is a constant which is a function of the temperature. The deviation of γ corresponds to the value of π_h^0 and the correlation between π_h^0 and temperature is shown in Fig. 5.

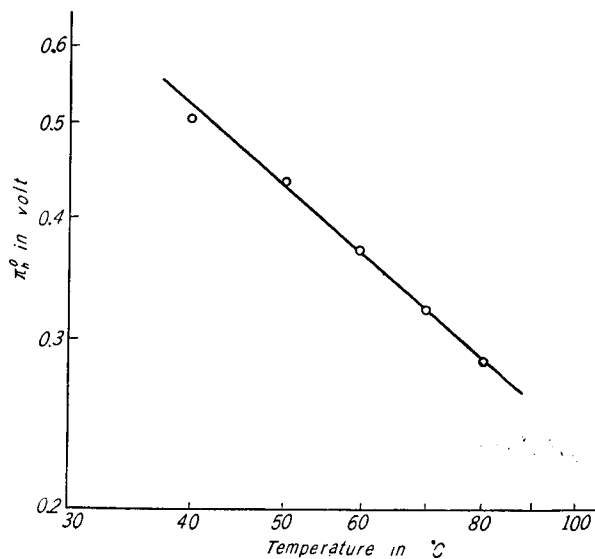


Fig. 5. π_h^0 vs. temperature curve in 40% NaOH.

Now the equations of (19) may be integrated explicitly, and if β_2 is negligibly small, eq. (19 y) may be integrated to

$$\frac{KSH}{M} = \frac{y_0 - y_1}{(\alpha x + \beta y + \gamma)_m} \quad (21)$$

$()_m$ is the logarithmic mean of the term, and the form of the equation is similar to the one for the common packed tower operated by the diffusion control process.

III. How to Design an Amalgam Decomposition Tower.

1. Required Sectional Area.

When the amalgam decomposition packed tower is operated under suitable conditions, the overall coefficient for mass transfer, K , must be a maximum, and the value of K depends upon the flow flux of mercury. This relation has been measured experimentally, and an example of this result is shown in Fig. 6.

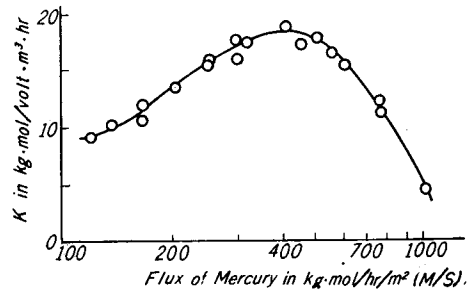


Fig. 6. A relation between K and M/S in 25% caustic soda solution at 50°C. Diameter of the packing: 10mm ϕ .

According to this figure, a suitable flow flux may be in the range between

300 and 450 kg-mol/hr/m², however, we believe it may be operated safely up to 400 kg-mol/hr/m².

2. H.T.U. and N.T.U.

Eq. (19 y) should be transformed into the following equations,

$$\text{H.T.U.} = - \int_{y_0}^{y_1} \frac{dy}{E_h} \quad (22)$$

$$\text{H.T.U.} = \frac{M}{KS} \quad (23)$$

The above two equations may be called the N.T.U. and H.T.U. of the amalgam decomposition packed tower, respectively. We can obtain the required height of the tower from the product of the H.T.U. and the N.T.U. Fig. 7 is the H.T.U. as it relates to the concentration and temperature of the caustic soda. And Figs. 8-13 are certain examples of the relation between $1/E_h$, which is a function of the integral of eq. (22), and the y -value of the caustic soda at several temperatures. For example, if we measure the area under this curve, we obtain N.T.U. under given conditions.

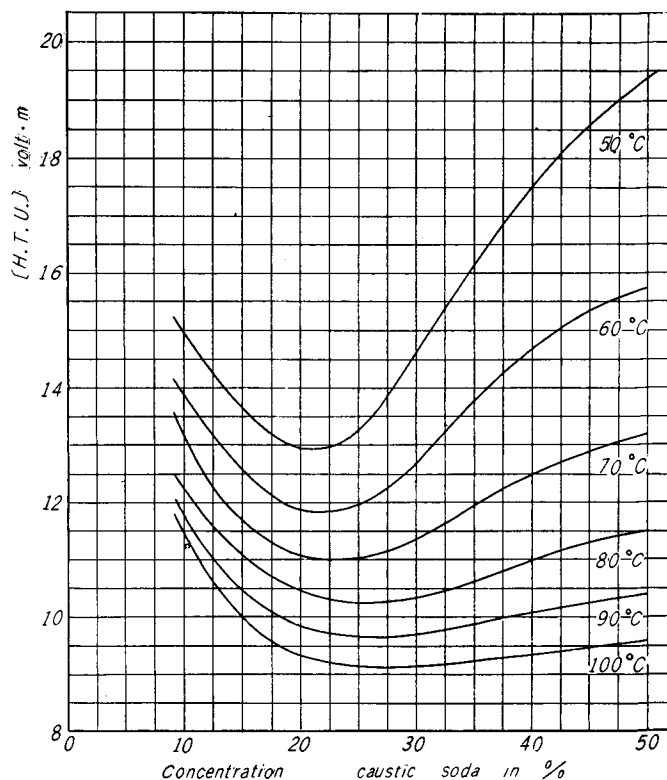


Fig. 7. H.T.U. diagram of the decomposition tower.

3. Operating Temperature and Concentration of Caustic Soda.

It is evident that the higher the operating temperature, the more easily the amalgam is decomposed, because both the H.T.U. and the N.T.U. become smaller at higher temperatures. Next, we may consider two examples of design for the amalgam decomposition tower, which may be annexed to the 100 KA-electrolyzer.

Several operating conditions are as follows:

concentration of caustic soda	40% (wt)
concentration of amalgam, top	0.20% (wt)
bottom	0.002% (wt)
temperature	50 and 90°C.

Table 1 shows the results of calculations, and from this table, we can see how profitable operation is under higher temperatures. Also we find that the concentrations of caustic soda need not be considerable at high temperatures. The results are due to the conductivity characteristics of the caustic soda solution.

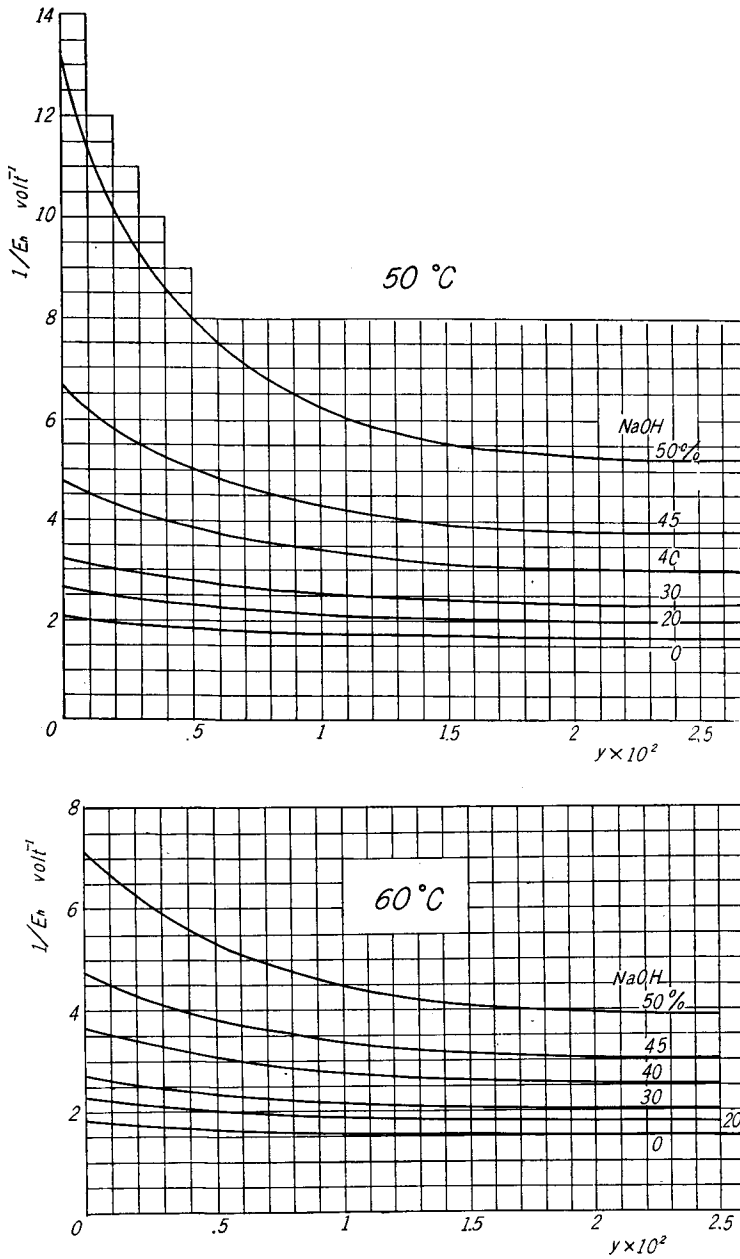


Fig. 8-9. N.T.U. diagrams of the decomposition tower at 50 and 60°C.

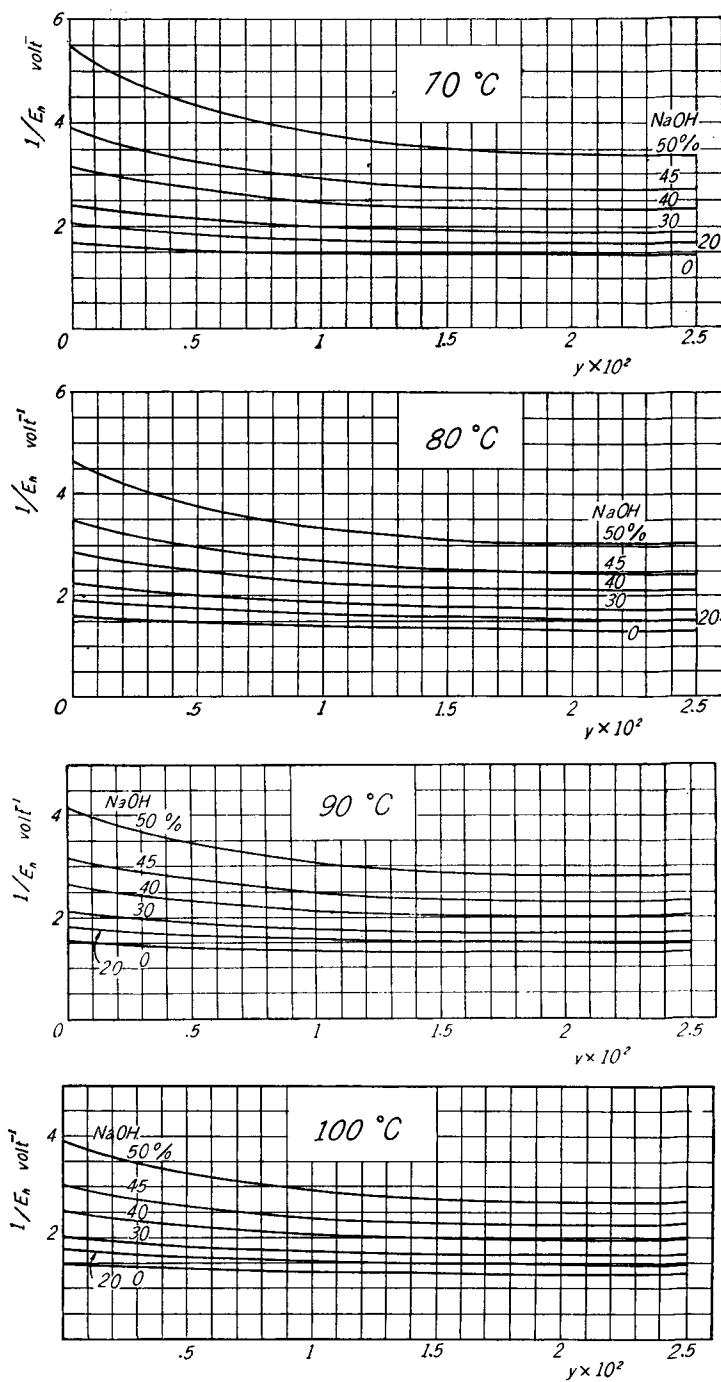


Fig. 10-13. N.T.U. diagrams of the decomposition tower at 70 to 100°C.

Table 1. Required Volume of Packed Tower (with 100 KA-electrolyzer).

Operating Conditions Required	Uniform Concentration of Caustic Soda		Exist Concentration Gradient of Caustic	
	50°C	90°C	50°C	90°C
H.T.U. (volt. m)	17.53	10.16	—	—
N.T.U. (1/volt)	6.35×10^{-2}	3.95×10^{-2}	—	—
Height (m)	1.11	0.40	1.01*1	0.58*2
Volume (m ³)	0.726	0.262	0.610	0.352

*1 $\frac{SH}{M} = 30.50 \times 10^{-4}$ (m³/kg-mol/hr)

*2 $\frac{SH}{M} = 17.47 \times 10^{-4}$ (m³/kg-mol/hr)

4. Estimation of Practical Towers.

At last these operating conditions are estimated from six kinds of amalgam decomposition towers which are in practical operation in our country.

Table 2. Operation Data of Practical Towers.

	A	B	C	D	E	F
Diameter of Tower (mm)	600	500	400	600	500	380
Height : 1st Column (mm)	520	1,000	520	900	700	700
2nd Column (mm)			260	500		
Diameter of Packings (mm)	10 & 15	10 & 15	10	15	10	10
Weight of Packings (kg)	145	200	110	400	150	90
Current of Electrolyzer (KA)	15	23	24	24	15	15
Temperature (°C)	92.4	103.4	92.4	122	100~110	100~110
Concentration of Caustic Soda (%)	47.5	50.2	48	48	44~48	44~48
Concentration of Amalgam : (%)						
Top	0.218	0.454	0.211	0.256	0.20~0.25	0.20~0.25
Bottom of 1st Column	0.0005	0.000	0.008	0.000	0.00	0.00
2nd Column			0.0015	0.000		
Flow Flux of mercury (lit/min)	7.34	5.33	12.1	9.86	7.9~6.4	7.9~6.4
Theoretical :						
Sectional Area*1 (m ²)	0.0735	0.0542	0.123	0.100	0.090~0.064	0.090~0.064
Height (m)	0.550	1.075	0.548		0.493~0.618*2	0.493~0.618*2
Compared with Theoretical Values						
Sectional Area (%)	385	362	102.2	283	217~307	125~177
Height of 1st Column (%)	94.5	93.1	95.0		142~113	142~113
Total (%)			142.1			

*1 The flow flux is assumed as 98.6 lit/min/m² (400 kg-mol/hr/m²)

*2 [H.T.U.] = 9.4 [volt·m]

These towers have the following peculiarities:

A : Large sectional area and low height.

B : Great height with concentrated amalgam

C : Narrow section, consisting of two columns and a comparatively low height for each column.

D : Two big columns, each column rather high, and the whole operated at high temperature.

E and F : With sectional areas differing from each other, but with other conditions the same.

The diameter of the towers, A, B, D and F are large, but their heights are rather low. Details are shown in Table 2. It is concluded that high and thin packed towers are to be recommended in general for the following reasons:

- (1) the overall coefficient of amalgam decomposition K is large near the critical flux of amalgam,
- (2) the distribution of amalgam in a thin packed tower is more uniform,
- (3) operating temperature can be maintained easily, and
- (4) even if the amalgam floods, the high tower will carry out the decomposition of amalgam.

**Part. II. On the Estimation of the Graphite Packing
in an Amalgam Decomposer.***

The amalgam decomposition tower is a kind of packed column. The height is given by the product of H.T.U. and N.T.U., where H.T.U. and N.T.U. are as follows:

$$\text{H.T.U.} = \frac{1}{K} \frac{M}{S} \quad (1)$$

$$\text{H.T.U.} = - \int_{y_0}^{y_1} \frac{dy}{E - \pi_h^0} \quad (2)$$

and

$$\frac{1}{K} = \frac{1}{K_A Y} + \frac{1}{K_H} + \frac{1}{K_F \kappa} \approx \frac{1}{K_H} + \frac{1}{K_F \kappa} \quad (3)$$

Thus, the H.T.U. is, determined by the geometry which occurs between the graphite packings and the amalgam drops, and the N.T.U. is determined by the hydrogen overpotential of the graphite. Hence, the performance of the graphite packings may be estimated from these physical and electrochemical characteristics if they are established empirically.

I. H.T.U. and N.T.U. of the Amalgam Decomposition Tower.

According to the result of Part I, the height of a packed tower which is required to decompose an amalgam from concentration of y_1 to y_0 is represented by the product of H.T.U. and N.T.U., where the H.T.U. and N.T.U. of the amalgam decomposer are as follows:

$$\text{H.T.U.} = \frac{1}{K} \frac{M}{S} \quad (1)$$

$$\text{N.T.U.} = - \int_{y_0}^{y_1} \frac{dy}{E - \pi_h^0} \quad (2)$$

and

$$\frac{1}{K} = \frac{1}{K_A Y} + \frac{1}{K_H} + \frac{1}{K_F \kappa} \quad (3)$$

$$\approx \frac{1}{K_H} + \frac{1}{K_F \kappa} \quad (4)$$

We may consider the variations of H.T.U. and N.T.U. under the conditions of constant concentration of caustic soda solution and of constant flow flux of the amalgam in a packed tower as shown in Fig. 4.

The values of K_A , K_F and K_H are complicated functions of M/S , which is the flow flux of the amalgam per unit cross-sectional area, where K , the overall

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coefficient of mass transfer as shown by eq. (4), is approximately proportional to M/S . Therefore, the H.T.U. is independent of M/S , and is a certain constant.

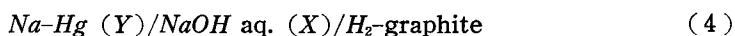
The term $1/K_A Y$ in eq. (3) may be neglected because the value of the coefficient K_A is much greater than the others even after decomposition is finished. So K can be calculated from eq. (4).

The value of K_H is the slope of the hydrogen overpotential against current density curve, and it seems to be constant for the range of current density beyond 2 amp. per dm^2 . It is also independent of operating temperature, the concentration of caustic soda, and the manner of the graphite packing.

The conductivity of caustic soda, κ , should be constant under constant temperature and concentration of solution.

Since the value of K_F may depend upon the geometry between the graphite packings and amalgam drops, the value of K_F may vary with the manner of graphite packing. Accordingly the variation of H.T.U. corresponds to the value of K_F .

On the other hand, E is the electromotive force of the local cell:



and while it is independent of the graphite, the value π_h^0 is a function of the characteristics of the graphite because of the intersection of the hydrogen overpotential diagram as shown in Fig. 3.

Then the value of π_h^0 affects the value of y_1 , which is the concentration of the amalgam at the bottom of the tower, and hence the N.T.U. should be a function of π_h^0 or the hydrogen overpotential of the graphite packing.

Consequently it is evident that the H.T.U. and N.T.U. have the physical and electrochemical properties respectively. For instance, the performance of the tower will be affected by the nature of the packing if the packing used is controlled by the physical property, and on the contrary it will be necessary to increase the surface area of the graphite packing if the electrochemical property is important.

Fig. 14 shows the hydrogen overpotential curves for several materials. The hydrogen overpotentials of iron and nickel are about 200 mv lower than that of graphite, so iron and/or nickel might be better than graphite for decomposition packing if they do not amalgamize from the electrochemical point of view. However, they are soon covered by amalgam in practice, and hence the coefficient K_F may tend to zero which would mean the H.T.U. diverges from the practical value.

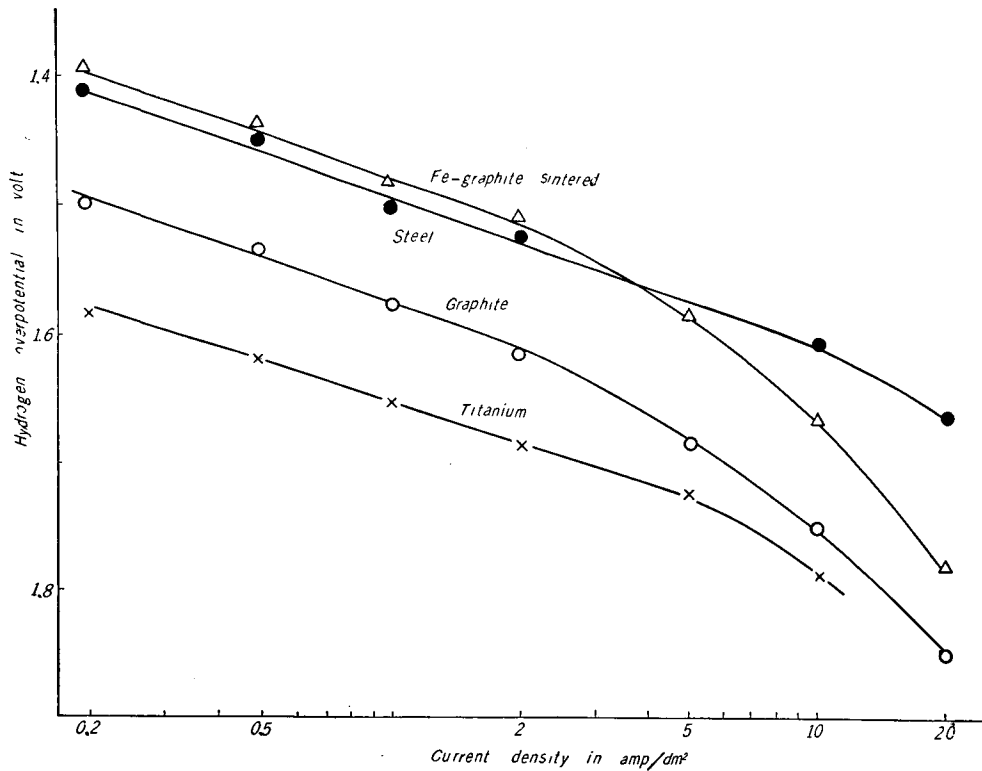


Fig. 14. Hydrogen overpotential curve in 40% NaOH at 60°C.

II. Test of Performance of the Graphite Packing.

It is clear that both H.T.U. and N.T.U. are important for estimating the performance of the graphite packing as explained above.

In the first place, the hydrogen overpotential should be obtained and both π_h^0 and K_H determined. For example, π_h^0 of graphite in 40% of caustic soda under various temperatures is shown in Fig. 5.

So the electromotive force of the local cell represented by eq. (5) may be follows:

$$E = -0.910x + 11.0y - 270.0y^2 + 0.9060 + 0.0005(70-t) \quad (6)$$

where

- x : NaOH kg-mol/H₂O kg-mol
- y : Na kg-mol/Hg kg-mol
- t : temperature in °C (30 < t < 100)

and the diagram of $1/(E - \pi_h^0)$ vs. y can be drawn under given conditions. An example is shown in Fig. 15.

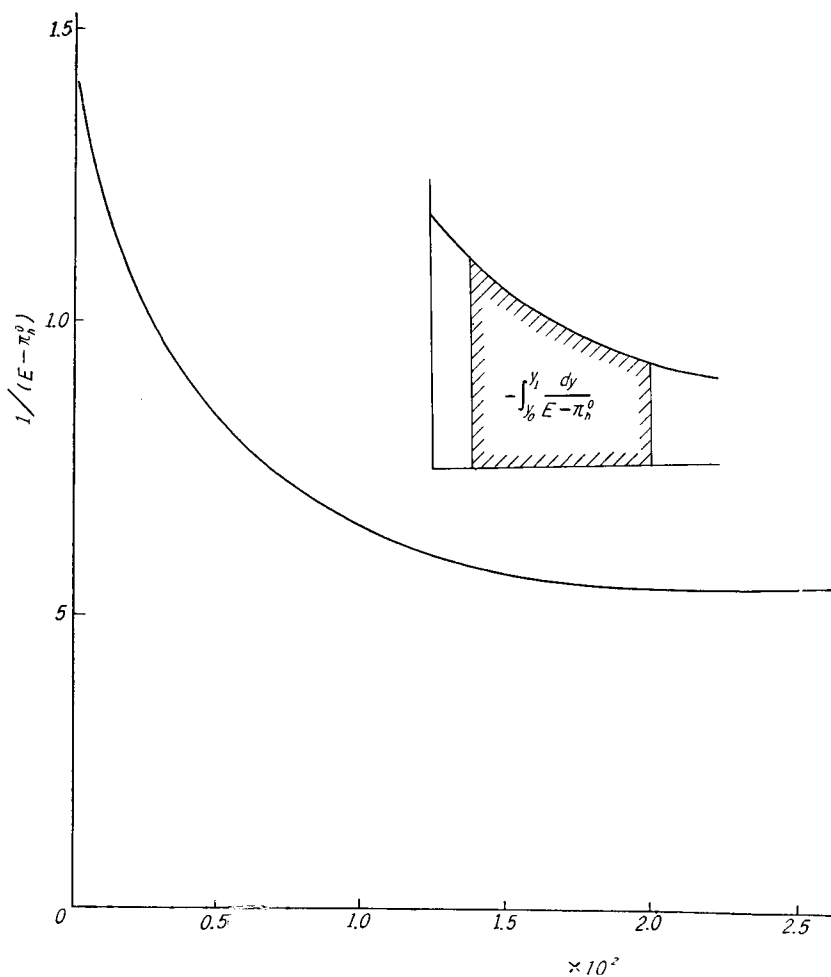


Fig. 15. N.T.U. diagram of graphite ball (10mm ϕ) at 40°C.

Next we may consider the decomposition test. A model of the tower for test of the graphite packing is shown in Fig. 16. The amalgam distributor, which is 2mm ϕ holed steel plate, is set about 5 cm distance from the top of the packing column.

About 15 liters of the amalgam is prepared in the head tank and about 20 litres of caustic soda solution in the other tank.

Then the following five terms, namely,

- (1) concentration of caustic soda (to be kept constant),
- (2) operating temperature (to be kept constant) at inlets and outlets of amalgam and caustic, and top and bottom of the tower,

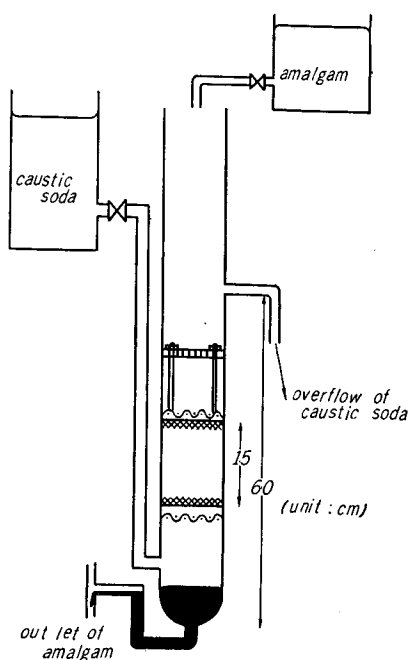


Fig. 16. Amalgam decomposer.

- (3) concentration of amalgam (to be kept constant at inlet),
 - (4) height and sectional area of packed column, and
 - (5) flow flux of amalgam (kept constant in the range of 30-100 lit/min/m²)
- are observed. On the other hand, observation of the amount of hydrogen gas generated by decomposition, the state of contact between graphite and amalgam, and other factors are recommended for reference.

The N.T.U. will be calculated from these empirical data. Because the area between y_0 and y_1 of the plot $1/(E-\pi_k^0)$ vs. y represents the N.T.U. (see Fig. 15). So that the H.T.U. may also be calculated as follows:

$$\text{H.T.U.} = \frac{H}{\text{N.T.U.}} \quad (7)$$

where H is the height of the column.

Some examples are shown in Fig. 17. Now we may calculate both the H.T.U. and N.T.U. for specimen C as an example.

Operating conditions :

temperature	$30 \pm 1^\circ\text{C}$
amalgam flux	72.2 lit/min/m ²
concentration of caustic soda	28.94% (wt)
weight of packing	160 gr
height of packing column	15 cm
concentration of amalgam	
inlet	0.274% (wt)
outlet	0.250% (wt)

then

$$\begin{aligned} \text{N.T.U.} &= 1.135 \times 10^{-2} && (1/\text{volt}) \\ \text{H.T.U.} &= 13.22 && (\text{volt}\cdot\text{m}) \end{aligned}$$

are obtained.

III. Estimation and Discussion.

According to the definition of N.T.U. of the amalgam decomposition tower, it is concluded that (a) the value does not change for different kinds of graphite, because the values of π_h^0 are not different, (b) the physical properties, for instance, the size of the packing, and the form of column should be reconsidered for improvement of the ability of the tower, and also (c) the tower should be operated in a high temperature range if it is wanted to decrease the value of π_h^0 .

The stability of the packing can be known by the decomposition data of time dependence such as in Fig. 17. That is to say, in this figure specimen A goes down slightly though specimen C remains constant after 20 min. On the other hand, specimen F or G goes up gradually and seems unstable. So it is not recommended for practical purpose even if its ability is better in the initial period.

There is a certain value of H.T.U. for each packing tower, and it is controlled by the state of flow of the amalgam and also affected by the diameter of the tower.

The value of H.T.U. of the steel-made packing tower is usually higher than that of the glass-made empirical tower. So that we cannot use the value obtained empirically with a glass-made tower for design.

Last of all, it is concluded that we can estimate the performance of the graphite packing by the decomposition test if the following conditions are satisfied, that is,

- (1) the types of specimen are not so different from each other,
- (2) the concentration of the amalgam at the inlet is high, and
- (3) the difference in concentration between inlet and outlet is not very large.

The first condition means that π_h^0 may be nearly equal and the others that the N.T.U. may be proportional to the decomposition rate of the amalgam.

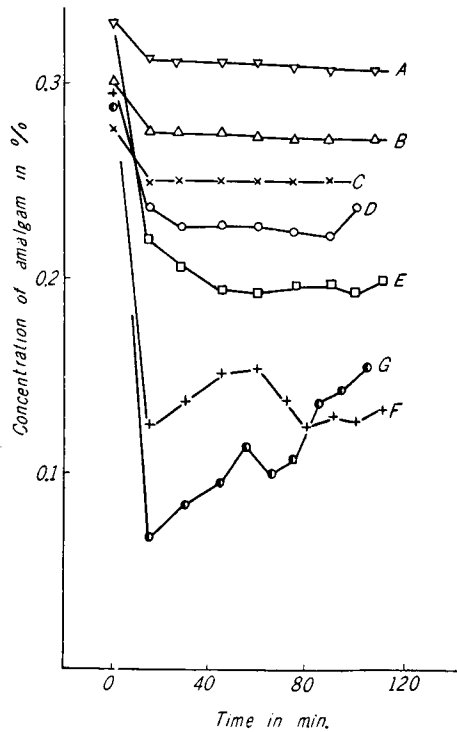


Fig. 17. Decomposition test in 30% NaOH at 30°C.

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