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By

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Abstract

This investigation deals with the effects of impurites in the electrolysis of sodium chloride solution by mercury process, especially a particular action of magnesium ions, and experimentally points out such an action and its mechanism in the following aspects.

1. Relations between the current and potential.
2. The eddy flow on the electrode surface.
3. Surface tension on the electrode.
4. Potential distribution.

It was noticed by this investigation that the action of magnesium ions has a connection with the polarographic maximum in the relations between the current and potential, and also, reference was made to the cause of the appearance of the maximum phenomenon.

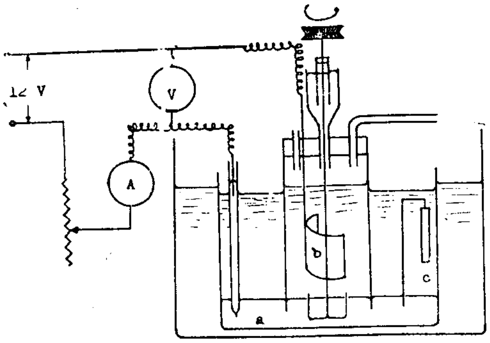
Introduction

Generally it is said that the impurities contained in sodium chloride used in the electrolysis of sodium chloride solution by mercury process retard the current efficiency, but only a few quantitative tests were completed on the nature of the action which the impurities cause. The impurities contained in the solution not only generate hydrogen and cause a loss of the current in the electrolytic cell, but result in the danger of explosion by mingling with chlorine in the anode. The above-mentioned fact is considered relating to hydrogen overpotential, and it was used as the fundamental datum in the practical operation. Relating to the studies on this problem, Dr. T. W. Paterson,1) and Dr. Somiya2) published their works. However, while experimenting, a phenomenon which is unexplainable as the one related to hydrogen overpotential can be found. This is due to the peculiar action of magnesium. This paper presents special researches conducted on this action.

For instance, by comparing the current-potential curves, or measuring the surface tension on electrodes and the distribution of potential, the action is experimentally scrutinized. As a result of the investigation, an interesting conclusion about the peculiar action of magnesium was obtained.

1) The Effects of Impurities on Electrolysis.

Apparatus: shown in Fig. 1.
Current density: 15 A/dm^2.
Temperature: 50°–60°C.
Revolution of Agitator: 50 r. p. m.
Anode: Platinum.
Cathode: Mercury.
Denuding part: Electrode (c) is used to secure constancy of the condition of the cathode surface, that is, Na% = 0.1.
Pure saturated sodium chloride solution: obtained by purifying sea salt solution by Na_2CO_3 and NaOH, pH = 7.0, 310 g NaCl/L.



(a) Mercury Cathode
(b) Platinum Anode
(c) Platinum Denuding Electrode

Fig. 1

Other containable elements were added as impurities to pure saturated sodium chloride solution, and hydrogen gas generating in this electrolysis was measured. Their effects were compared with the percentage of the current loss corresponding to the quantity of hydrogen gas. The results of the experiment are given in Table I.

Table I (a)

Exp. No.	Fe N	Ca N	Mg N	Current loss %	Remarks
2	0	$5\cdot10^{-2}$	0	0.9	
3	0	$5\cdot10^{-2}$	$4\cdot10^{-2}$	4.6	
20	$1\cdot10^{-4}$	0	0	13.5	
4	$1\cdot10^{-6}$	$5\cdot10^{-2}$	$4\cdot10^{-2}$	3.7	
5	$1\cdot10^{-5}$	$5\cdot10^{-2}$	$4\cdot10^{-2}$	4.2	
8	$1\cdot10^{-5}$	$5\cdot10^{-2}$	$4\cdot10^{-2}$	4.8	
9	$1\cdot10^{-5}$	$5\cdot10^{-2}$	$4\cdot10^{-2}$	31.5	No agitation.
6	$1\cdot10^{-4}$	$5\cdot10^{-2}$	$4\cdot10^{-2}$	21.5	No agitation.
32	0	0	$1\cdot10^{-2}$	4.0	Soon after the addition of $MgCl_2$.
33	0	0	$1\cdot10^{-2}$	9.0	Four days after the addition of $MgCl_2$.

Table I (b)

Exp. No.	Al N	Ti N	SiO_3 N	Current loss %
2	0	0	0	0.9
15	$1 \cdot 10^{-1}$	0	0	8.0
17	0	$1 \cdot 10^{-1}$	0	5.8
21	0	0	$1 \cdot 10^{-3}$	3.2
23	$1 \cdot 10^{-3}$	0	$1 \cdot 10^{-3}$	4.8
24	$1 \cdot 10^{-2}$	0	$1 \cdot 10^{-3}$	9.0

Calcium ions or magnesium ions do not show much noticeable action soon after their addition if used separately, but their co-existence with iron shows effect to a stronger degree. Magnesium ions act more and more in the course of time after their addition. Ferrous ions alone cause much loss even at above 10^{-4} N. If they co-exists with magnesium and calcium, their effect is seen at 10^{-5} N. Silicate ions make a loss higher at 10^{-3} N. In the experiment on copper and nickel ions, no particular action was seen below 10^{-2} N.

As the action of magnesium varies with the progress of time, the action was investigated from every angle i. e., electrolyzing the solution containing 10^{-2} N magnesium normally purified in factory a figure of 51.0% was obtained as the current loss caused by the generation of hydrogen. After making this solution alkaline by adding sodium hydroxide and removing the precipitate of magnesium hydroxide, the solution was neutralized by adding hydrochloric acid. As a result, the current loss became only 7.8%. Adding the above procipitate and hydrochloric acid, and electrolyzing the solution soon after this operation, the current loss was 21.3%. Five days after, it increased to 75.7%.

It is understood from these facts that the most effective substance may be the products of hydrolysis which are made in a solution of pH. 7 or so, and that hydrolysis of this compound is rather slow. Accordingly, it is explained that the variation of effects corresponds to time.

2) Current-Potential Curve in the Electrolysis of Sodium Chloride Solution.

The results of the observations of the action of impurities through the comparison of current-potential curves are as follows:

In stationary mercury cathode, concentration of sodium amalgam on the surface of mercury varies with time due to the deposition of sodium ions.

Thus it is required to compare the results of measurements in the same periods of time. This is a difficult experiment. Therefore, dropping mercury electrode is used as cathode for the purpose of measuring the constantly renewed surface of the cathode.(Potential is shown refered to sat. calomel electrode hereafter.)

As the surface area of the anode is far larger than that of the cathode, the greater part of electric potential offered is focussed on the polarization of the cathode. Accordingly the relations between the current and voltage thus obtained are those of cathode potential and the current. Using a pure saturated solution of sodium chloride as an electrolyte and adding magnesium chloride, calcium chloride and ferrous sulphate, comparisons of the changes of the current-potential curve are made.

Previously the case in which magnesium chloride was added was shown in Fig. 2. The chain line shows the case of pure saturated sodium chloride solution alone. The dotted line indicates the case soon after the addition of magnesium chloride. The shape of the curves changes slowly according to the progress of time after the addition of magnesium chloride and becomes constant. The full line refers to the constant curve. The intermediate cases are omitted but their curves will appear between the dotted and the full lines.

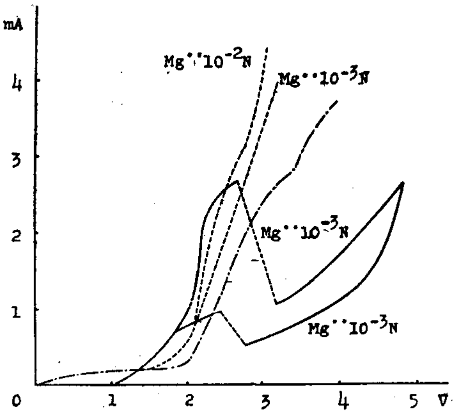


Fig. 2

The time required for the curves to take constant forms is 3 to 4 days. This is one of the distinctive effects that magnesium produces.

It was also shown that by adding calcium chloride and forrous sulphate the curve slope sharpens (Fig. 3) and magnesium flattens it.

It is explainable that the case showing on upward curve is caused by the fall of hydrogen overpotential. The amalgamation of calcium and iron reduces the overpotential. However, the flattening is a special action and the following experiment is for the purpose of learning its cause.

Fig. 4 shows its result. The condition of the treatment of electrolyte is as shown in Table II. When giving treatment (1), the curve became flat gradually soon after the neutralization and at last became (1′). Special attention should be paid to the appearance of polarographic maximum in the curve in this operation. The same in (2). In experiment (3), when filtered by collodium film, no flat curve is seen. From this it can be understood that material which is the cause of flattening is filtered out by the collodium film. The filter paper

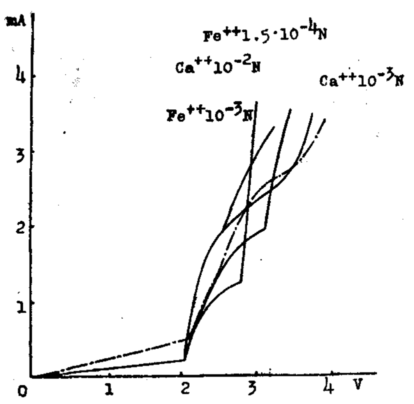


Fig. 3

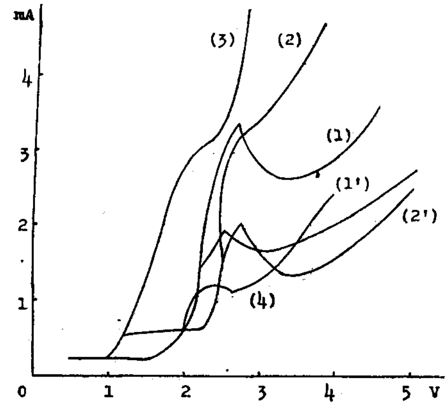


Fig. 4

does not perform such a function. As shown in experiment (4), the addition of gelatin results in such an action. From these facts it is learned that the action of magnesium has a colloidal quality, and that its action is similar to that of surface active substances. That is, it is presumed that colloidal particles from magnesium ions may perform peculiar actions. Considering the appearance of maximum in the process of flattening, this phenomenon is presumed related to the polarographic maximum. The fundamental cause of the magnesium action can be clarified by the explanation of the polarographic maximum phenomenon.

Table II

Exp. No.	Treatment of Electrolyte
(1)	Mg 10^{-3} N Sat. NaCl Solution $\xrightarrow{\text{NaOH}}$ pH=10, precipitate ($Mg(OH)_2$), $Mg(OH)_2$ Sat. NaCl Solution $\xrightarrow{\text{HCl}}$ pH=7, immediately.
(1′)	3 days after the above treatment.
(2)	Mg 10^{-3} N Sat. NaCl Solution $\xrightarrow{\text{Oa}_2\text{CO}_3}$ pH=10, precipitate (Mg-basic carbonate), Mg-basic carbonate Sat. NaCl Solution $\xrightarrow{\text{HCl}}$ pH=7, immediately.
(2′)	3 days after the above treatment.
(3)	Mg 10^{-2} N Sat. NaCl Solution — (Filter with collodium film) — Filtrate.
(4)	Sat. NaCl Solution with 0.01% gelatin.

3) Eddy Flow on Mercury Cathode.

Regarding the nature of mercury as electrode, many experimental results have been gained by the polarograph which used dropping mercury electrode. Among other things, the so-called polarographic maximum in the current-potential curve is a characteristic which does not appear in the case of solid electrodes. It means the current overflow beyond the diffusion current or the limitting current at the moment of deposition of metallic ions or electrolytic reduction and oxidation. It is just as indicated in Fig. 5. with a full line. But if the electrolyte contains some surface active substances, such as pigments, dextrin and gelatin, this maximum does not occur. In such a case the current reaches the limiting current as the dotted line shows. As an important phenomenon in the application of polarograph, various opinions have been offered about the mechanism from which this phenomenon comes. Heyrovsky and coworkers[3] consider that this is by the adsorption of ions or reactant substances, while Stackelberg and Antweiler[4] explain that an eddy flow of electrolyte springs up on the electrode surface and supplies dischargeable substances more readily. But as to which is the real cause, no clear-cut decision has been made. Setting aside the propriety of those explanations, it is found in our experiment that the adulteration of magnesium in the sodium chloride solution is in close relation with the polarographic maximum. Using pure saturated sodium chloride solution and the current density (hereafter abbreviated as C. D.) of 2–2.5 Amp./dm^2, it is observed an eddy flow as given in Fig. 6 (a) takes place on the mercury surface. Above C. D.=3Amp./dm^2, the change become like (b).

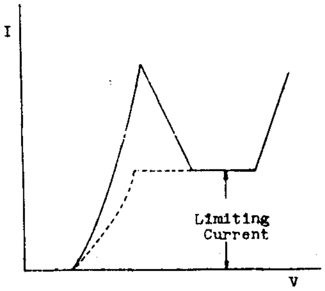


Fig. 5

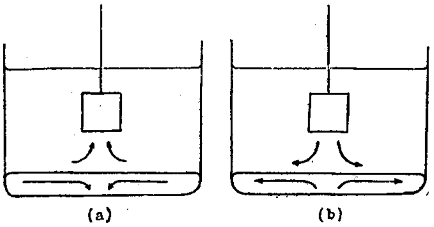


Fig. 6

The velocity of the eddy flow is highest on the mercury surface. If magnesium chloride of about 10^{-2} N is contained in the solution. the same eddy flow occurs till C. D.=2 A/dm^2, but at 3–9 Amp/dm^2 such an eddy flow disappears about 5–6 sec. after the electric current is turned on.

Ferrous ions have no effect on this phenomenon, whereas when copper ions are added an interesting change can be seen ; a small quantity of copper sulphate in the electrolyte induces the flow as shown in Fig. 6 (b) at C. D.=2–4 Amp/dm², and above C. D.=4 Amp/dm², the change becomes like (b) and the flow takes a reverse direction. Even if magnesium ions are added to this solution, an eddy flow does not stop. When copper amalgam (0.0006–0.0083%) is used as electrode instead of pure mercury, the eddy flow occurs even if magnesium is contained. In silver amalgam, magnesium ions do not stop the flow as in the case of copper amalgam.

The results of comparing the flowing velocities at C. D.=10 Amp/dm² are shown in Table III. The measurement of the flow rate is as follows; glass powder is put on the mercury surface and the movement is observed. In the case of pure mercury cathode the existence of magnesium ions stop the flow entirely. In the electrolyte containing magnesium ions, copper amalgam which

Table III

Cathode	Electrolyte	Time for flow in length of 1.5 cm, second
Pure mercury	Sat. NaCl Solution	1.2
»	» 10^{-2} N Mg	∞
»	» 10^{-3} N Fe	1.4
»	» 10^{-2} N Ca	1.7
1% Cu-Amalgam	Sat. NaCl Solution	9.4
0.5%	»	1.8
0.25%	»	1.5
0.10%	»	1.8
0.05%	»	1.8
0.025%	»	1.2
0.012%	»	1.8
0.005%	»	1.0
1% Cu-Amalgam	Sat. NaCl Solution 10^{-2} N Mg	
0.25%	»	4.8
0.05%	»	3.7
0.02%	»	2.8
0.01%	»	6.9
0.005%	»	4.8
0.001%	»	4.8
0.3% Ag-Amalgam	Sat. NaCl Solution	3.3
0.15%	» 10^{-2} N Mg	3.1
0.07%	»	2.6
0.035%	»	1.5
0.017%	»	1.4

contains 0.02% copper has the highest flowing velocity. In the case of silver amalgam, 0.15% silver amalgam has the highest velocity of the flow in the same electrolyte. Comparing the above results with the current-potential curve, an interesting relation can be found. In the case of an electrolyte containing 10^{-2} N magnesium ions the surface flow stops, the slope of current-potential curve becomes flat, and the discharge of sodiums ion is suppressed. The movement on the mercury surface is related to the discharge of sodium ions. If the electrolyte containing 10^{-2} N magnesium holds cupric ions, the flow on mercury surface does not stop, and as shown in Fig. 7, this current-potential curve which is measured by the dropping mercury method is strictly the same as that of the pure sodium chloride solution. This may point to a fact that by the flow on the mercury surface, sodium ions are supplied to the electrode and their discharge becomes easy. These results show that magnesium ions stop the flow on the mercury surface, suppress the supply of sodium ions and make their discharge difficult. As a result, the current-potential curve becomes flat in the magnesium containing electrolyte. Calcium ions or ferrous ions do not have any peculiar effect on the flow on the mercury surface.

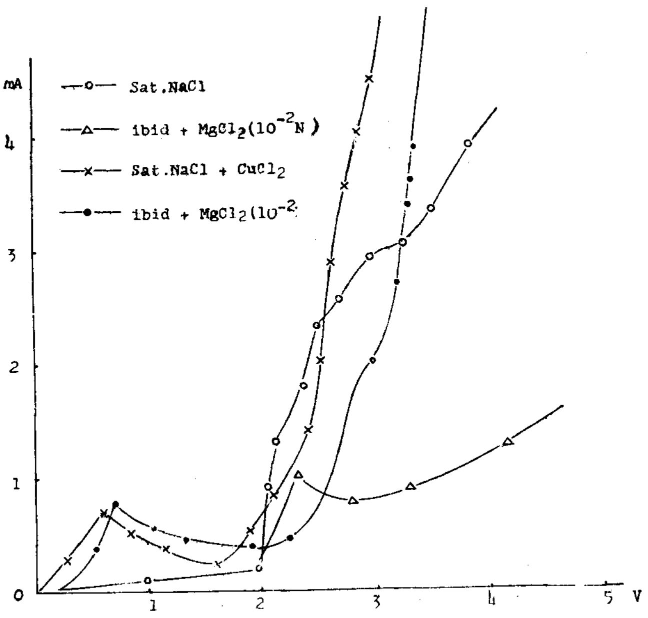


Fig. 7

4) The Surface Tension of Electrode and Potential Distribution.

As stated before, the flow on the mercury cathode surface has its highest velocity on the boundary between cathode and electrolyte. Therefore, the real cause of the flow may be found on the surface of the mercury, that is in the surface tension. The surface tension of mercury varies with the potential. The electrocapillary curve shows this variation of the surface tension which is related to the potential. By measuring the potential distribution on the mercury surface, the relation between the potential distribution and the flowing phenomenon on the mercury surface may be found.

(1) Measurement of the surface tension.

The dropping mercury method[5)] is adopted as a means of measurement. The results are given in Fig. 8. In the case of pure mercury cathode, if the electrolyte contains magnesium, a flat mountain-shaped curve is obtained. The surface active properties of basic salt of magnesium make the electrocapillary curve flat. It shows that the electric charge is decreased by the adsorption of basic salt of magnesium.

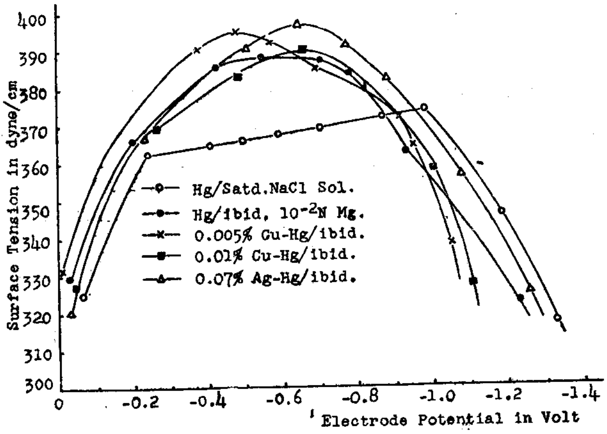


Fig. 8

Using amalgam of copper or silver as cathode, even if the electrolyte contains magnesium ions, a sharp mountain-shaped curve is obtained. It is interesting to note that in the case of amalgam containing 0.01% copper, the maximum point of surface tension deviates to the negative side. The existence of calcium or ferrous ions does not change the shape of the curves. Considering these facts in connection with the flow of mercury, the real cause of the flow can be stated as follows:

In accordance with the distance of the mercury cathode surface from the anode, potential takes various values, i. e. it takes the most negative values at the nearest place to the anode and the most positive at the farthest point. Accordingly, in the case of pure mercury electrode, (a), as shown in Fig. 9. Thus the flow takes a direction in which 2 pulls 1. But in copper amalgam, as shown in (b), if the C. D. is small, (1) pulls (2), and the flow takes a direction in which (1) pulls (2). In other

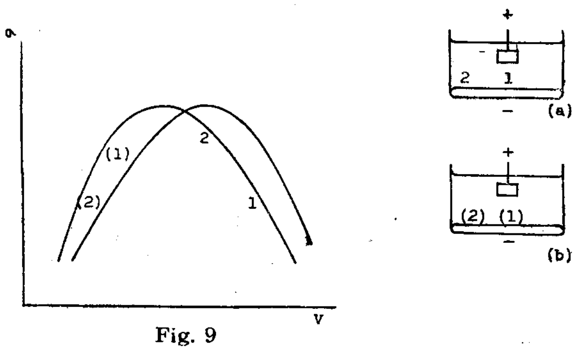
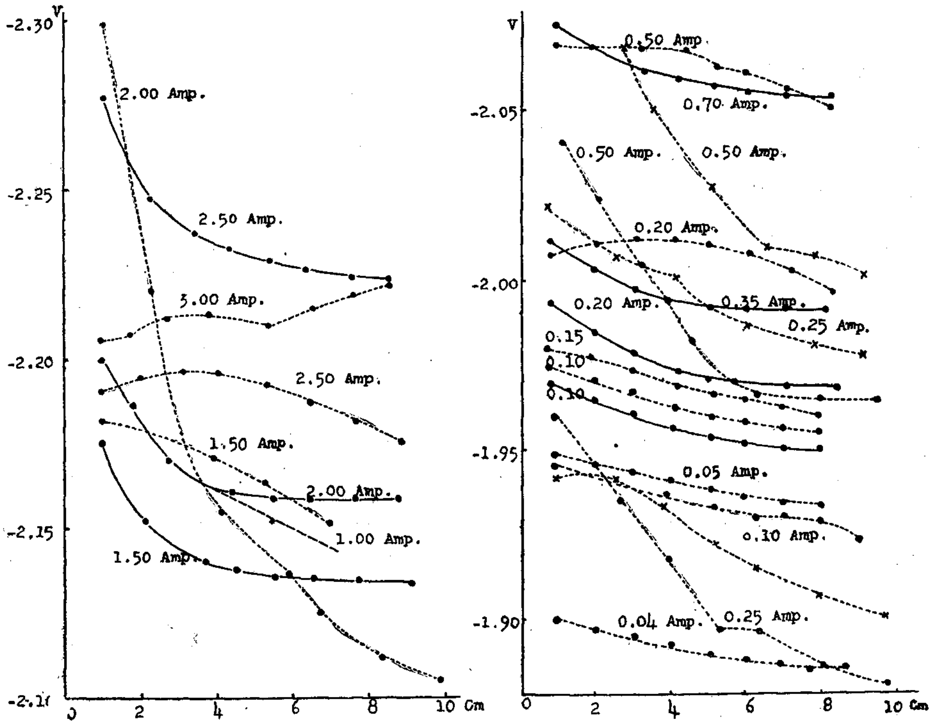


Fig. 9

words, the flow takes a reverse direction. But when the C. D. becomes larger, potential takes a more negative value, and the condition becomes the same as with pure mercury cathode and the direction of the flow is reversed. If the electrolyte contains magnesium ions the difference of value is small. This makes the flow slower but does not stop it entirely. Regarding this matter, an explanation may be given by taking into consideration the measurement of potential distribution.

(2) Measurement of potential distribution.

Using two calomel electrodes, the potential difference between different points on the mercury cathode surface and the reference point (just under the anode) is measured. And then potential distribution is determined. The results of measurements are shown in Fig. 10 (a) and (b).



(a) (b)

Fig. 10

In this figure, the ordinate axis refers to the distance from the reference point on electrodes, and the horizontal axis to potential. In case the flow is rapid, an anticipated large potential distribution is obtained (full line), except in the case where the current is small. Whereas, in the experiment, it may be perceived that in case the flow stops potential distribution difference is equalized (2.5Amp. and 3.0 Amp in dotted line). A more interesting fact is that when the cathode surface is vigorously agitated, the potential distribution becomes unequal. (Fig. 11)

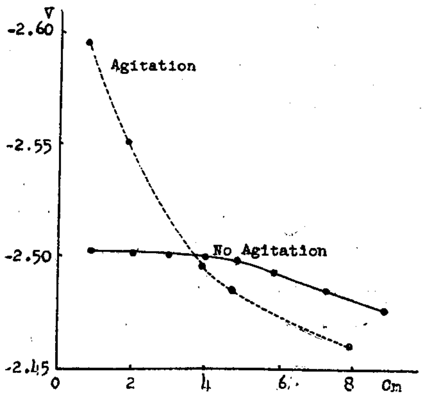


Fig. 11

(3) Consideration.

From the above facts, the phenomenon of an eddy flow on a mercury surface is proved to be caused by the unequality both of potential distribution and of the surface tention. When the flow stops, both the potential distribution and the surface tension become even. The equalization of potential is caused by the following process: The potential distribution on the cathode surface is due to the current distribution, and the current intensity depends on the strength of electrical field and on the diffusion of the ion. When the agitation on the cathode surface is violent or the C. D. is small, the migration of the ion caused not so much by the free diffusion as by the electrical field. Therefore, the current density shows its distribution in proportion to the strength of electrical field, and potential difference becomes unequal in accordance with the distribution. On the contrary, when the agitation on the cathode surface is calm or the C. D. is large, on account of small concentration of the ion consequent upon the reaction, the greater part of migration of the ion is caused by free diffusion, Therefore, the current density is not influenced by the strength of electrical field. As a result, the distribution, and accordingly the potential difference, become equal. When the eddy flow stops, such conditions may exist. In the case of the pure mercury electrode and the electrolyte of sodium chloride solution containing Mg the change of surface tension which relates to the potential difference is small as stated before. Accordingly, the eddy flow is slow and the quantity of sodium ions supplied by that eddy flow is small. So when electrolysis continues, the concentration of the ion on the cathode surface becomes dilute and the most part of ions reaches the cathode surface by free diffusion. The current and potential are distributed equally. The condition on this occasion is that the discharge of sodium ions can not exceed the so called diffusion current, and if more electric current is transmitted the surplus current is applied to the discharge of hydrogen ions and this generates hydrogen gas. In the condition where the eddy flow is violent, the current flows continuosly with unequal distribution, owing to the ample supply of sodium ions. The distribution of cathode surface tension also becomes unequal, the eddy flow continues, and the supply and discharge of sodium ions are effected smoothly.

Conclusion

Summarizing the results of the above experiments:

(1) Calcium and ferrous ions are deposited in the cathode mercury and make amalgams of these elements. These amalgams reduce the hydrogen overpotential of mercury and promote the generation of hydrogen gas.

(2) The hydrolysis products of $MgCl_2$ are adsorbed in the surface of the electrode and as a result the difference of its surface tension is equalized. The eddy flow caused by this difference of surface tension is diminished. Therefore, the supply of sodium ions is apt to delay. Thus the original cause of the eddy flow of mercury is lost. The sodium ions are supplied to the electrode surface only by the diffusion, and the deposition of sodium ions corresponds to the diffusion current. The rest of the current will be used to discharge hydrogen ions. In the electrolysis of electrolyte containing magnesium ions the liberation of a large quantity of hydrogen gas is due to this phenomenon.

References

1) T. W. Walker and O. S. Paterson; Trans. Am. Electrochom. Soc. **3**, 185 (1903).
2) S. Somiya; J. of Ind. Chem. Japan **26**, 534 (1923).
3) J. Heyrovsky and R. Simuneck; Phil. Mag. **7**, 951 (1929).
4) M. v. Stackelberg; Angew. Chem. **50**, 418 (1937).
M. v. Stackelberg, H. J. Antweiler, Kieselbach-Bonn; Z. Elektrochem. **44**, 663, 901 (1938).
M. v. Stackelberg; ibid. **45**, 466 (1939).
5) Tate; Phil. Mag. (4) **27**, 176 (1864).
H. Dunken; Z. phys. Chem. B **47**. 195 (1940).
W. D. Harkins and F. E. Brown; J. Am. Chem. Soc. **41**, 499 (1919).
S. R. Craxford and H. A. C. Mckay; J. Phys. Chem. **39**, 545 (1935).