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Application of Amalgam Metallurgy to the Extraction of Indium

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A Thesis

Submitted to the Department of Metallurgy
in Partial Fulfillment of the
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INTRODUCTION

Indium metal is in group IIIb of the periodic table with an atomic weight of 114.76 and atomic number of 47. This metal was discovered in 1863 by Reich and Rechter while they were working on sphalerite ore with a spectrograph. They isolated the metal in the same year.

The element is scattered widely in nature in minute quantities and is associated with the ores of iron, lead, copper, and zinc. The small amount present in these ores is concentrated in the flue dust and the by-products produced during the smelting of these major base-metals. This is the only commercial source of indium metal.

There are several methods which can be used to extract indium. They are all complicated, requiring several purification steps and an electrolysis. This electrolysis may have to be followed by another electrolytic refining process to obtain 99.99+% pure indium metal.

In view of the greater demand for indium with the progressive development of the metal, simpler methods of recovery are necessary. The author here hopes to apply mercury in the metallurgy of indium in an effort to find a simpler method of extraction.

PROBLEM

The problem is to simplify the extraction of indium and obtain a high purity metal using mercury in the recovery of the pure metal from indium bearing alloy scrap. Other factors such as efficiencies and problems of electrolysis are incidental. Of the four possible methods using mercury, suggested by Hohn (1), that of barrier electrolysis was used in the work.

With this method, two electrolytic steps are necessary to produce a high purity metal. First the removal, by electrolytic means, of indium and more noble metals from a mixed solution by precipitation and collection in a mercury cathode; and then extraction of the indium from the mercury, used as an anode, on an insoluble cathode.

The nobility of metals is referred to as the electronegativity of the metal with reference to another metal. The nobility can be related to half-wave potentials, with reference to the saturated calomel electrode. The half-wave potential increases negatively as the nobility of the metals decrease.

BARRIER ELECTROLYSIS

This method is based on the fact that mercury acts as a barrier during electrolysis. In an electrolytic cell, mercury is made the cathode and the solution containing indium with other impurities is electrolyzed. By controlling the potential, with reference to the saturated calomel electrode (S. C. E.), the indium and metals more noble than indium, are electrolytically deposited from the electrolyte and collected by the mercury cathode. This mercury, containing the metals, is then made the anode in a refining cell containing a pure indium electrolyte. The metals more noble than indium cannot leave the anode until the indium has first been completely removed. Should there be some less noble metals than indium, they will go into the electrolyte; however, they will not deposit on the insoluble cathode until the indium is completely removed from the electrolyte.

Mercury has been introduced into metallurgy by many different men, and Hohn (1) has used the liquid metal in his work on the hydrometallurgy of zinc. He had proposed several methods and principles involved in the process. From this, he introduced the term "Amalgam Metallurgy" (2).

Here, he divided the amalgams into three groups, iron, zinc, and sodium types. The zinc type, with which we are concerned here, has a medium affinity for and good miscibility with mercury. The zinc type group includes indium, copper, lead, tin, cadium, bismith, and thallium. All these metals have a different polarographic reduction and half-wave potential, with reference to the S. C. E. The reduction potentials are slightly more positive than are the half-wave potentials. Taking advantage of these potentials, it is possible to plate out one metal by controlling the reduction potential of the metal with reference to the S. C. E.

PRELIMINARY WORK

Before the final electrolytic tests could be conducted, much preliminary work had to be done.

Electrolyte

To obtain an impure, indium bearing electrolyte, all the scrap alloys of indium were collected. These were as follows:

1. Pb-In
2. Cu-In
3. Mn-In
4. Hg-In
5. Cu-Mn-In
6. Cu-Fe-Ni-Co-In
7. Ag-Ni-Mn-Co-Fe-Al-In

The scraps were dissolved in acid, and partial purification was conducted to obtain a more concentrated indium solution.

The alloys were dissolved individually in a suitable acid and the indium was precipitated as a hydroxide, $In(OH)_3$. Each of these precipitates obtained still contained much occluded metal impurities. Therefore, additional purification was attempted. The copper solution was treated with pure indium metal for cementation of copper. For the solutions containing cobalt and nickel, both zinc and aluminum were used to precipitate indium. This was unsuccessful because the ions of nickel and cobalt hinder the indium deposition. Because of this difficulty, all of the acid solutions were combined. This became the base electrolyte used for all subsequent experiments.

Half-wave Potentials

In order that selective separation of metals can be conducted using barrier electrolysis, the half-wave potentials of the metals must be determined. These potentials were determined by polarography with reference to the S. C. E. This gives a measure of the electronegativity of one metal as compared to another.

For each metal in the electrolyte, the half-wave potential was determined. The potentials were more electronegative in the order - Cu, Pb, In, Zn, Ni, Co, Fe, and Mn, giving potentials of 0.1, 0.39, 0.54, 1.1, 1.19, 1.34, 1.4, and 1.5 respectively. However, the reduction potentials are slightly more positive. Thus, from these results, it can be observed that there exists a working range of potentials whereby indium can be selectively separated.

MATERIAL AND EQUIPMENT

For this work, the material and equipment used are as follows:

Chemicals

The chemicals were used primarily for dissolving and wet purification processes. They included sulfuric acid, hydrochloric acid, nitric acid, and ammonium hydroxide.

Indium
?

Standard Calomel Cell

This cell was constructed according to standards as outlined in "Physico Chemical Experiments" by Livingston, using Hg, KCl, Hg_2Cl_2, and platinum-mercury electrode (Fig. 1).

Coulombmeter

A copper coulombmeter was constructed using copper electrodes and an electrolyte containing 300 gr $CuSO_4$, 100 cc ethyl alcohol, and 2000 cc H_2O. An 800 ml beaker was used as the container.

Potentiometer

A potentiometer was set up as a means of controlling the voltage in the circuit. It consists of

1. Standard cell - 1.0172 volts
2. 2-Dry cells - 1.5 volts each
3. Sensitive galvanometer
4. 1-two-way switch
5. 2 single switches
6. Resistance box
7. Potentiometer

The set up is shown in Fig. 2.

Miscellaneous

Other equipment used in the work is as follows:

1. 2-six volt wet cells
2. Beakers as electrolytic cells
3. Variable resistor
4. Magnetic stirrer
5. Mercury electrodes
6. Platinum electrodes
7. Ammeter
8. Voltmeter

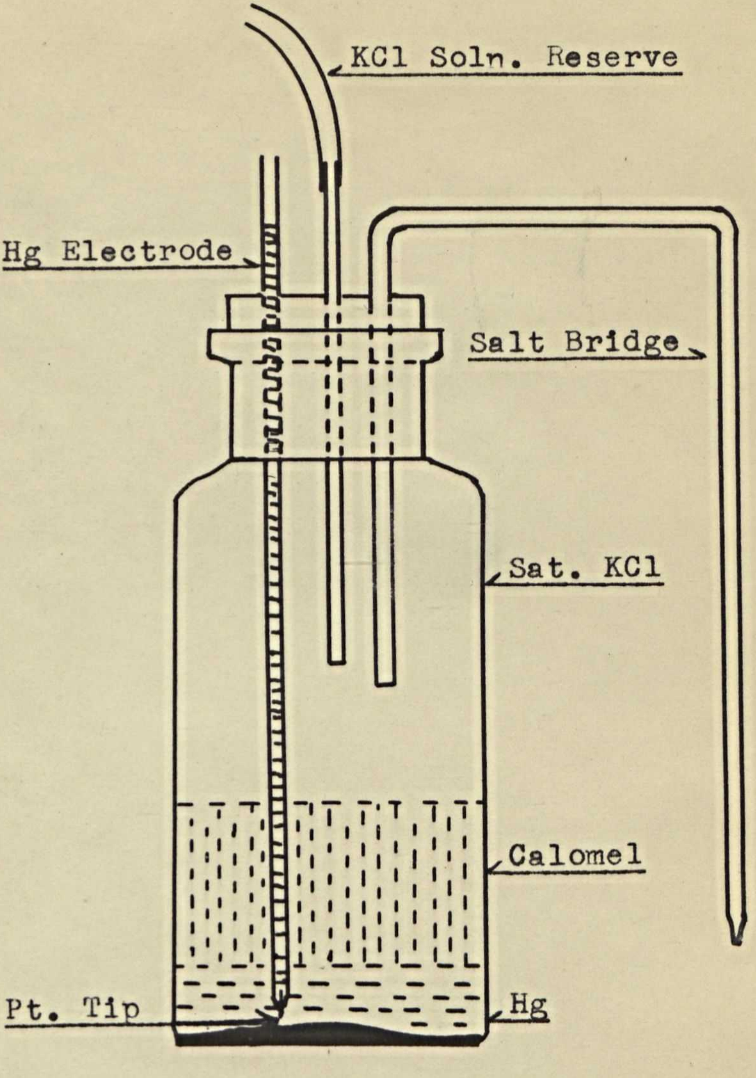
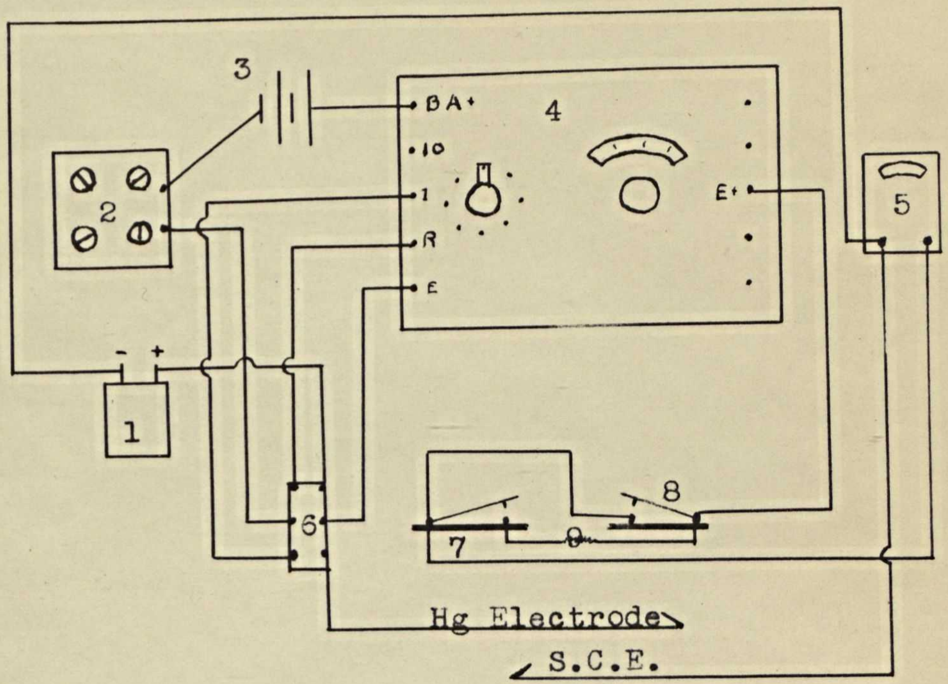


Fig. 1 SATURATED CALOMEL ELECTRODE CELL



1. Standard cell
2. Resistance Box
3. 2-Dry Cells
4. Potentiometer
5. Galvanometer
6. Two-way Switch
7. Switch
8. Switch
9. Resistance

Fig. 2. POTENTIOMETRIC CONNECTIONS

EXPERIMENT No. 1

The equipment was assembled for the electrolytic deposition as shown in Fig. 3. A preliminary experiment was performed to obtain data on which to base succeeding work.

In this experiment, lead and copper were deposited from 880 ml of indium-bearing electrolyte. The S. C. E. potential was held at 0.44 volts, and the current at this potential was 0.78 amps. As the copper and lead were depleted, the current decreased steadily, until it became almost nil. This meant that the two elements were completely deposited and collected by the mercury cathode. Having taken out the first two impurities, copper and lead, which are more noble, or have a more positive decomposition potential than indium, the mercury cathode was removed. A fresh mercury cathode was introduced. For the second step, 700 cc of the same electrolyte, copper and lead free, was used. The S. C. E. potential was raised to 0.7455, the voltage range in which indium should deposit and zinc should remain in the electrolyte.

After 24 hours of continuous electrolysis, 19.11 gr of indium had been removed from the electrolyte. The indium could then be removed from the mercury cathode by electrodeposition or by selective solution of the indium as an acid salt. The removal of the indium from the mercury was not done at this time.

The polarograph was used to determine the concentrations of the various metals in the electrolyte.

Stock electrolyte
In - 70.9 gr/l
Pb - 60 mg/l
Cu -100 mg/l

After electrolysis
In - 53.6 gr/l
Pb - not detected
Cu - not detected

Grams of indium removed from the 700 cc of solution is 19.11 gr.

Because of the iron ions in the original solution, a porous crucible, which surrounded the anode, was used to reduce the oxidation of Fe^{++} to Fe^{+++}. The reactions are as follows:

$Fe^{++} - e = Fe^{+++}$ at anode

$Fe^{+++} + e = Fe^{++}$ at cathode

The current efficiency, however, was quite low in spite of the porous crucible. The efficiency was 53.4%; therefore, the crucible was eliminated in the second test.

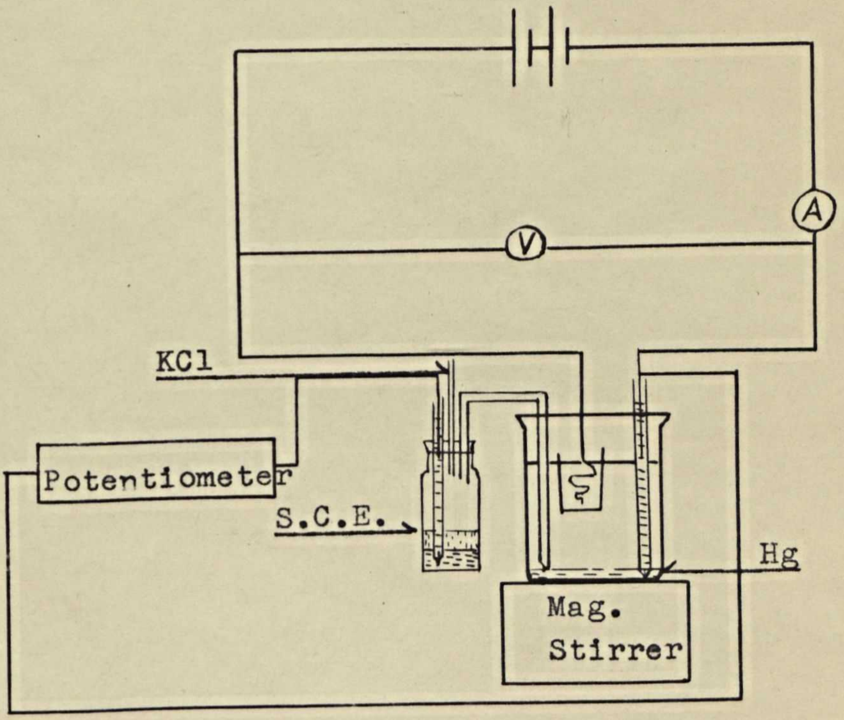


Fig. 3. CIRCUIT for EXPERIMENT No. 1

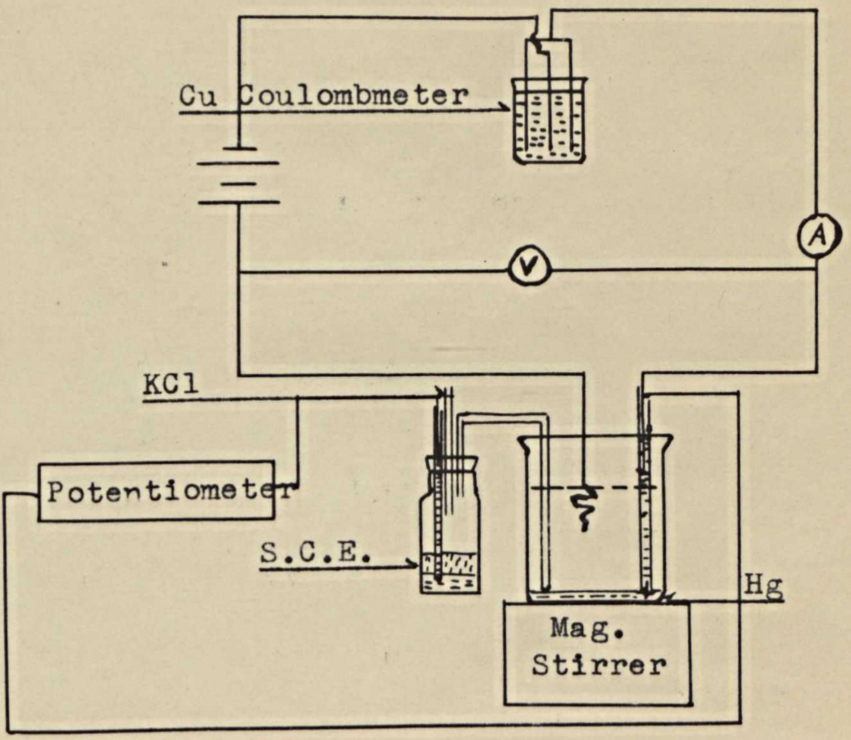


Fig. 4. CIRCUIT for EXPERIMENT No. 2

EXPERIMENT No. 2

The essential apparatus for this experiment was the same as before, except a coulombmeter was installed in series and the protective crucible around the platinum anode was not used, (Fig. 4). Here, more care was taken and periodic samples were obtained to find the amount of indium deposited. This electrolysis was conducted continuously except for the short periods where the copper deposit of the coulombmeter was weighted.

Starting Conditions

The starting electrolytic conditions are

Volume of electrolyte----- 500 cc
Weight of mercury--------- 294 gr
Amperage------------------ 1.4 amps
S. C. E. potential-------- 0.775 volts

Testing

Periodic tests were conducted during electrolysis.

Sample No. 1
Deposition time------ 3 hrs
Sample of electrolyte removed--------- 5 ml
Copper deposited----- 7.0504 gr
S. C. E. potential increased from 0.775 to 0.910 volts. This was reset to 0.8240 volts.

Sample No. 2
Deposition time------ 4.5 hrs
Sample of electrolyte removed--------- 5 ml
Copper deposited----- 1.9496 gr
S. C. E. potential dropped from 0.8240 to 0.637 volts. Reset at 0.6978.

Sample No. 3
Deposition time------ 4 hrs
Sample of electrolyte
removed--------- 5 ml
Copper deposited----- 9.7647 gr
S. C. E. potential increased from 0.6978 to 0.7187 volts. No potential adjustment was made.

Sample No. 4
Deposition time------ 4.5 hrs
Sample of electrolyte
removed--------- 5 ml
Copper deposition---- 11.8878 gr
S. C. E. potential remained at 0.7187 volts.

Sample No. 5
Deposition time------ 3 hrs
Sample of electrolyte
removed--------- 5 ml
Copper deposited----- 5.5190 gr
S. C. E. potential remained the same as above.

Sample No. 6
Deposition time------ 4 hrs
Sample of electrolyte
removed--------- 5 ml
Copper deposited----- 9.8814 gr
S. C. E. potential increase from 0.7187 to 0.7736 volts. This was not changed.

Sample No. 7
Deposition time------ 4 hrs
Sample of electrolyte
removed--------- 5 ml
Copper deposited----- 10.7890 gr
S. C. E. potential increased from 0.7736 to 0.9366 volts. This was not changed.

Sample No. 8
Deposition time------ 1 hr 5 min
Sample of electrolyte
removed--------- 5 ml
Copper deposited----- 2.3083 gr
S. C. E. potential remained at 0.9366 volts.

The above samples were assayed immediately. Because

No. 7 sample showed a low concentration of indium in solution, it was apparent that the indium deposition was approaching completion, and the process was stopped.

Refining

After the collection of the copper, lead, and indium in the mercury cathode, it was removed and was made the anode in a refining cell. A platinum cathode was used. The electrolyte for the refining cell was 200 ml of 50% HCl solution. Electrolysis was started. The hydrogen plated at the cathode and was replaced in the solution by indium. When the solution was saturated with indium in the form of indium chloride, the metal plated on the platinum cathode. When 10.5317 grams of indium was deposited, the color of the electrolyte changed from clear to black. This indicated that all of the indium was removed from the anode, and that other metals were beginning to deposit. This refining process was run for 23 hrs at which time the sudden change of color showed that recovery of indium was complete.

RESULTS

Each of the samples obtained in the second electrolysis was evaporated and then taken up in 0.1 N KCl solution for the determination of the amount of indium that has been recovered. From this, it can be seen that there was a steady decrease in the concentration of indium in the electrolyte, (Table 1).

Table 1

Polarographic Determination on Each Sample

Description	Shunt	x	Wave length in mm	=	Ratio	Conc. in gr/l
Original Stock Sample	500	x	92.2	=	46,100	70.9
Standard In	50	x	65.0	=	3,250	0.25
Sample No. 1	500	x	74.9	=	37,450	57.6
Sample No. 2	500	x	80.5	=	40,250	61.8
Sample No. 3	500	x	62.5	=	31,250	48.2
Sample No. 4	500	x	45.0	=	22,500	32.6
Sample No. 5	500	x	35.3	=	17,650	27.1
Sample No. 6	500	x	16.2	=	8,100	12.5
Sample No. 7	50	x	3.5	=	175	0.27
Sample No. 8	10	x	15.7	=	157	0.24

Method of calculations

$$\text{Conc.} = \frac{\text{Sample Ratio}}{\text{Standard Ratio}} \times \text{Dilution (20)} \times \text{Stand. Conc. (0.25)}$$

Table No. 2

Using the concentrations obtained in Table No. 1, the amount of indium deposited was determined for each period.

The Deposition of Indium and Concentration
of
Electrolyte for Each Sample

Description	Concentration gr/500 cc of In	Deposition gr of In
Original conc.	35.37	0.00
Sample No. 1	28.80	6.57
Sample No. 2	30.90	-2.10(loss-solution)
Sample No. 3	24.10	6.80
Sample No. 4	16.30	7.80
Sample No. 5	13.50	2.80
Sample No. 6	6.25	7.25
Sample No. 7	0.15	6.12
Sample No. 8	0.12	0.02
	Total	35.26

Table No. 3

A table of the amounts of current that was consumed for each time period based on the coulombmeter at 100% efficiency.

$$\text{Amps} = \frac{96{,}500 \times \text{Wt. of Cu}}{\text{Time in sec.} \times \text{Gr. Equiv. Wt.}}$$

	Current in Amps
Sample No. 1	1.323
Sample No. 2	0.548
Sample No. 3	2.061
Sample No. 4	2.230
Sample No. 5	1.555
Sample No. 6	2.082
Sample No. 7	1.855
Sample No. 8	1.780

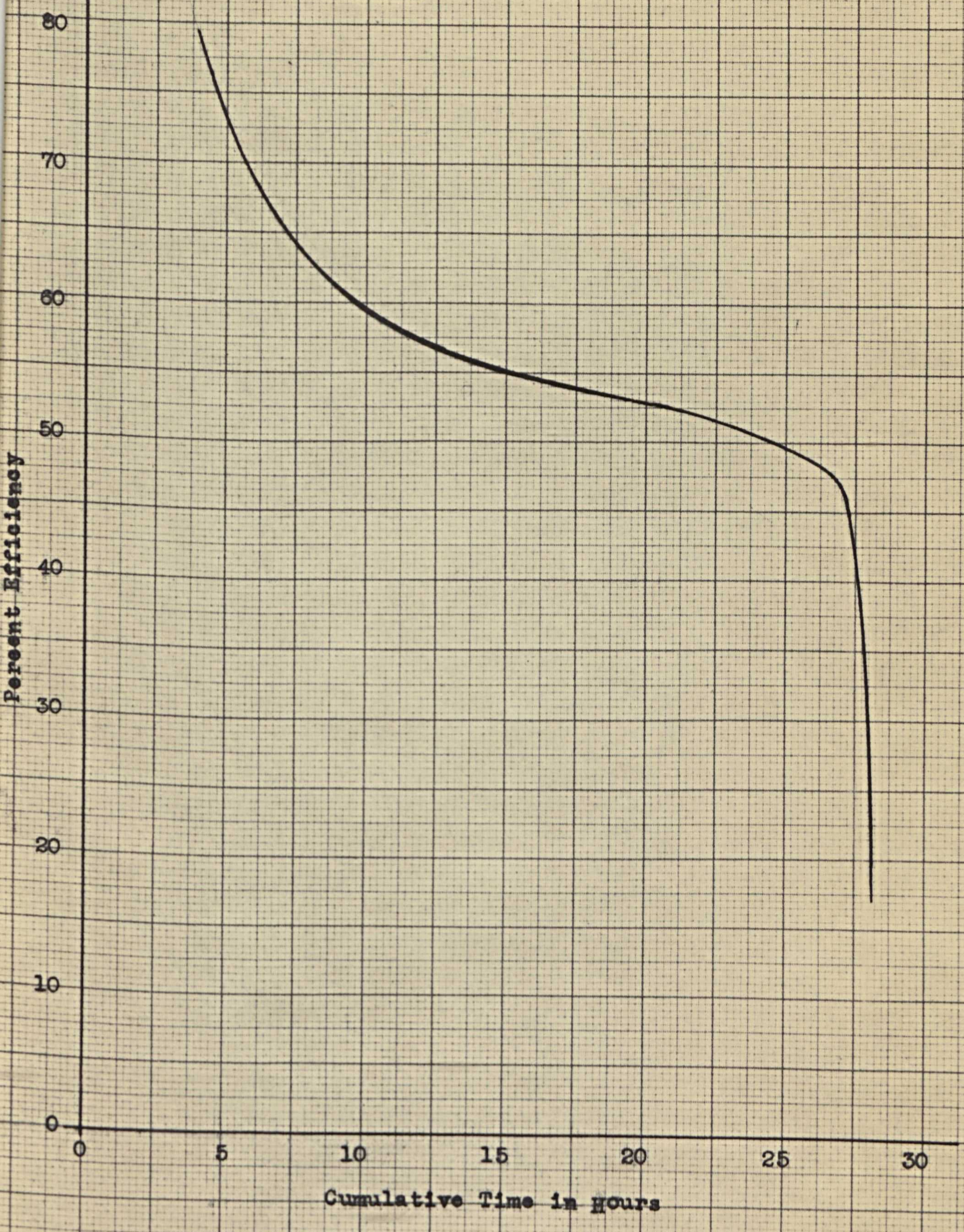
Note - loss shown by sample No. 2. The current during the period of deposition between sample No. 1 and sample No. 3 was too low allowing resolution.

Current Efficiency

Using the copper coulombmeter in the circuit, and assuming its efficiency to be 100%, curves were plotted to obtain electrical efficiency for indium deposition. Using the data on Table 4, the graphs (Fig. 5 and 6) are plotted.

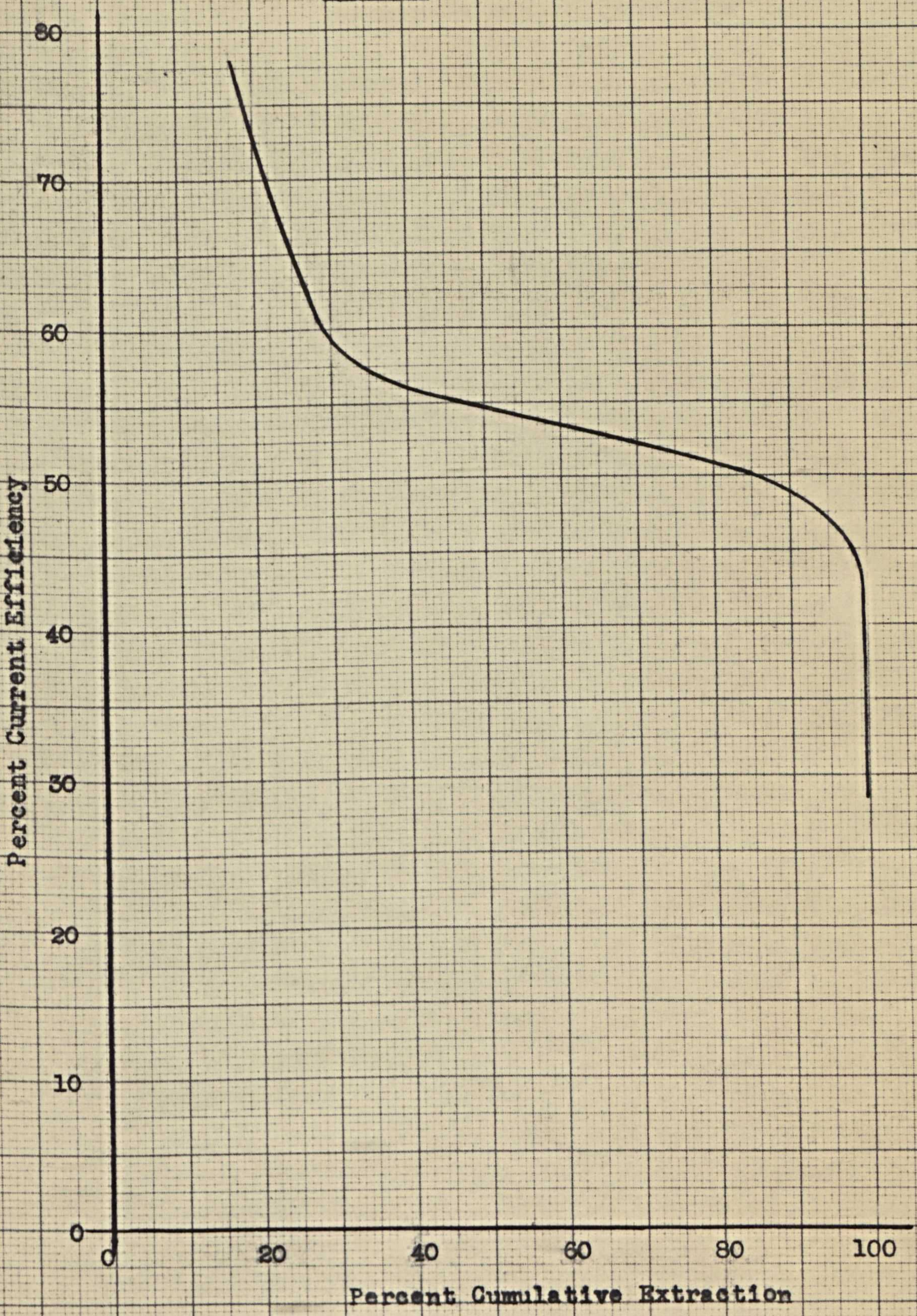
Table No. 4

Time in Hrs	Cumulative Time in Hrs	Cumulative % Extraction	Current Efficiency
4.5	4.5	18.6	75.2
3.0	7.5	----	----
4.0	11.5	31.0	57.7
4.5	16.0	52.6	54.4
3.0	19.0	60.8	43.6
4.0	23.0	81.0	61.0
4.0	27.0	99.1	47.2
1.1	28.1	99.9	0.7



<u>Fig. 5.</u> CURRENT EFFICIENCY

Fig. 6. CURRENT EFFICIENCY



PURITY TESTS

To determine the purity of the indium metal recovered, tests for copper and iron were conducted. The indium metal obtained on final electrolysis was dissolved in HCl. This $In(Cl)_3$ was evaporated to dryness to eliminate the excess acid. The pure chloride was then dissolved in KCl solution so that, with dilution to 100 cc, the solution would be 0.1 N KCl.

Iron

A colorimetric determination was conducted to determine the amount of iron present. Using the ammonium thiocynate method (3), standards of 100, 10, 1, 0.01, 0.001, 0.0001 ml/l iron were prepared. A blank was also prepared.

By comparing the indium sample against the standards, it was established that there was less than 0.001 mg/l, or 0.000001% Fe was in the indium metal.

Copper

The copper was determined polarographically. The same standards were prepared. With lower concentrations, inconsistant results were obtained. Because of this, four standards were run (Table No. 5), and a graph (Fig. 7) was made to determine by interpolation the amount of copper present. It was determined that about 0.00089 gr of copper was present in the 10.1549 gr of indium. This is 0.00876% copper.

Table No. 5

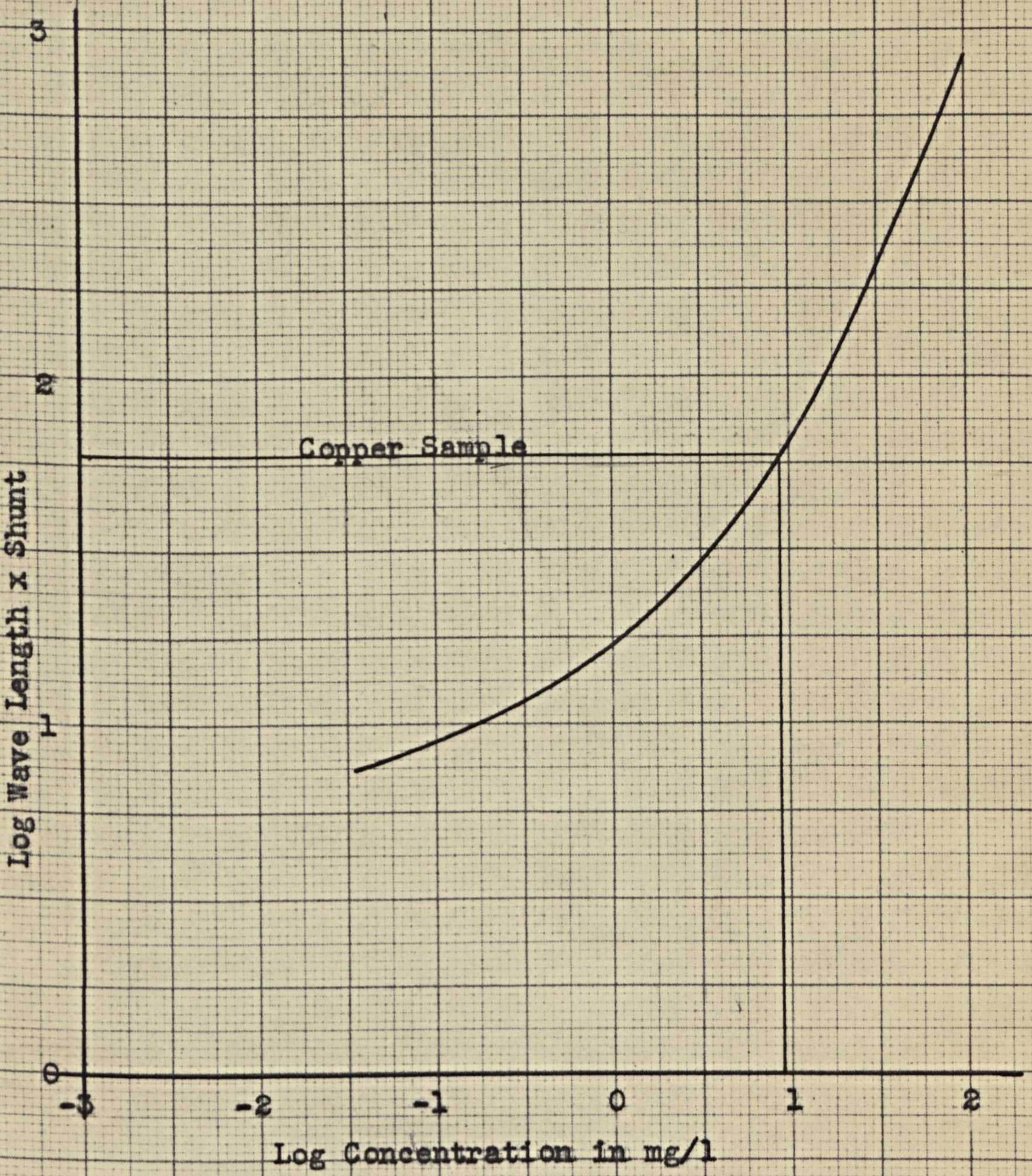
Polarographic determinations on four copper standards and the indium sample.

Conc. mg/l	Wave Length Times Shunt	Log Wave L. Times Shunt	Log Conc.
100	856	2.932	2.0
10	75	1.875	1.0
1	17	1.230	0.0
0.1	9.5	0.977	-1.0
In Sample	61.5	1.788	0.95(from graph)

From the graph, it was determined that the log concentration is 0.95 to give a concentration of 8.9 mg/l of copper, or 0.89 mg in the 100 cc sample of indium. The percent of copper is determined by

$$\frac{0.00089\text{ gr}}{10.1549\text{ gr}} \times 100 = \underline{0.00876\%\text{ Cu}}$$

Fig. 7. COPPER DETERMINATION



DISCUSSION

It is evident from Table 2 that there is a loss of indium in Sample No. 2. This is probably caused by the low current that was passing in that period of time. Because of this low current, the indium was being redissolved into the electrolyte.

Another fact that was evident during refining is that the indium must be removed periodically from the cathode. The metal plates in the form of trees, Plate No. 1, which grow towards the mercury and would cause a short circuit if allowed to contact the mercury. Not only that, but the indium is contaminated by the mercury. This was found when on dissolving the indium for purity tests, a small drop of mercury remained after the indium had gone into solution.

Indium Balance

In in electrolyte = In in electrowinning = In on refining

In in electrolyte------	35.37 gr
In on electrowinning	
Spent electrolyte-	0.12 gr
Deposited----------	35.29 gr
Total	35.41 gr
Difference---	0.04 gr
% difference-	0.113%
In on refining	
Deposited out-----	10.5317 gr
In the electrolyte	24.52
Total	35.0517
Difference---	0.3183 gr
% difference-	0.905%

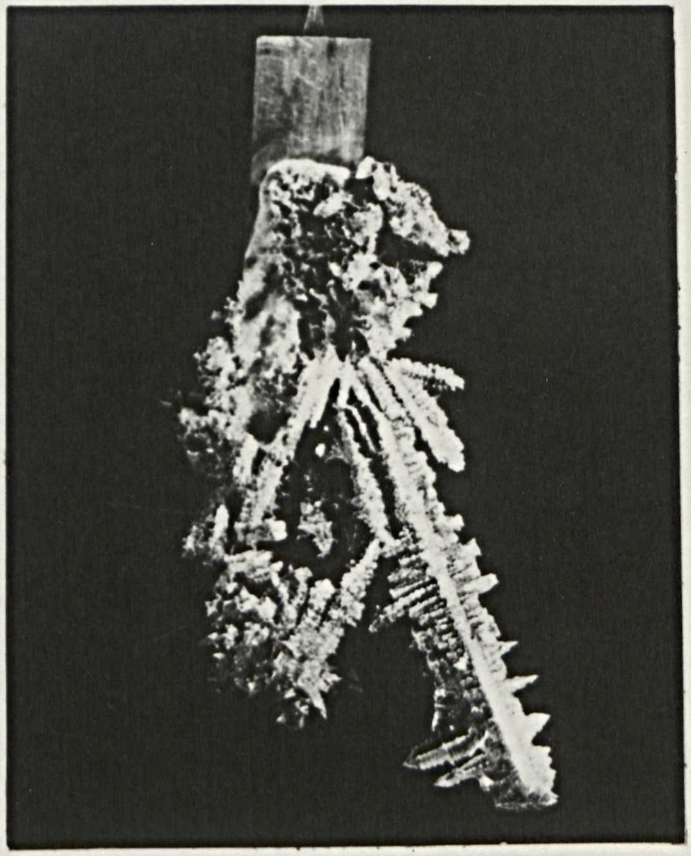


PLATE NO. 1. INDIUM TREES

CONCLUSION

From this investigation, it was found that indium can be recovered by an amalgam metallurgy process. By using mercury as a barrier electrode, a good grade of indium was extracted by using two electrolytic steps. This barrier electrolysis method depends on the polarographic half-wave potential with reference to the saturated calomel electrode. The potential is just above that of lead at 0.44 volts, and below that of zinc at about 1 volt. The deposition of indium can be obtained in this range of voltages regardless of concentration. Although the current efficiency is not high, it probably can be increased by varying the conditions of electrolysis.

RECOMMENDATIONS

Future work on this problem could include

1. Establish the optimum conditions for high current efficiency.
2. Varying the electrorefining conditions to obtain a smooth indium deposit, and eliminate the growth of trees which causes short circuiting and picking up mercury from the anode.
3. The application of the method on an industrial basis.
4. The application of barrier-electrolysis to the raw material such as calcines and flue dusts.

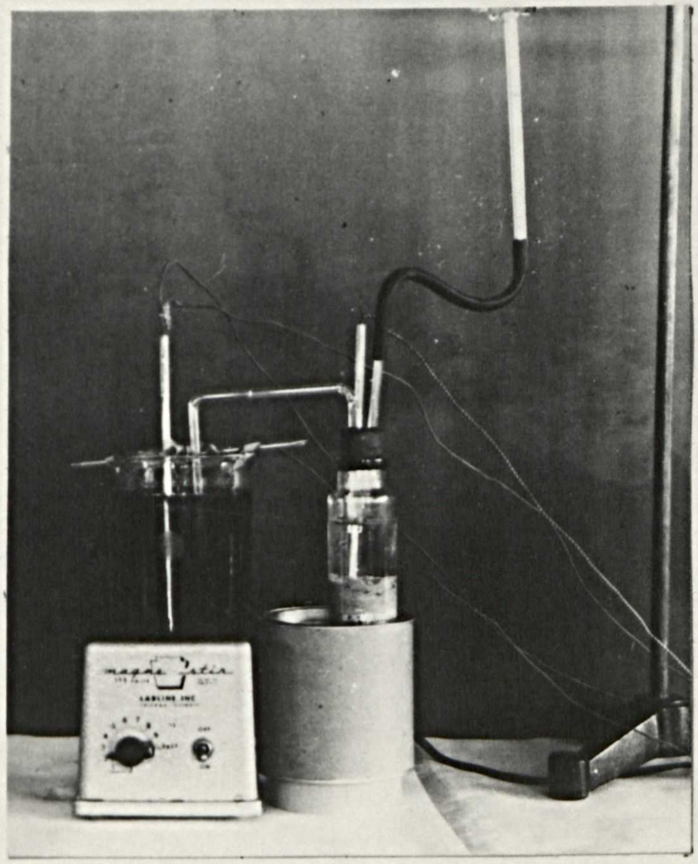


PLATE NO. 2. ELECTROWINNING CELL

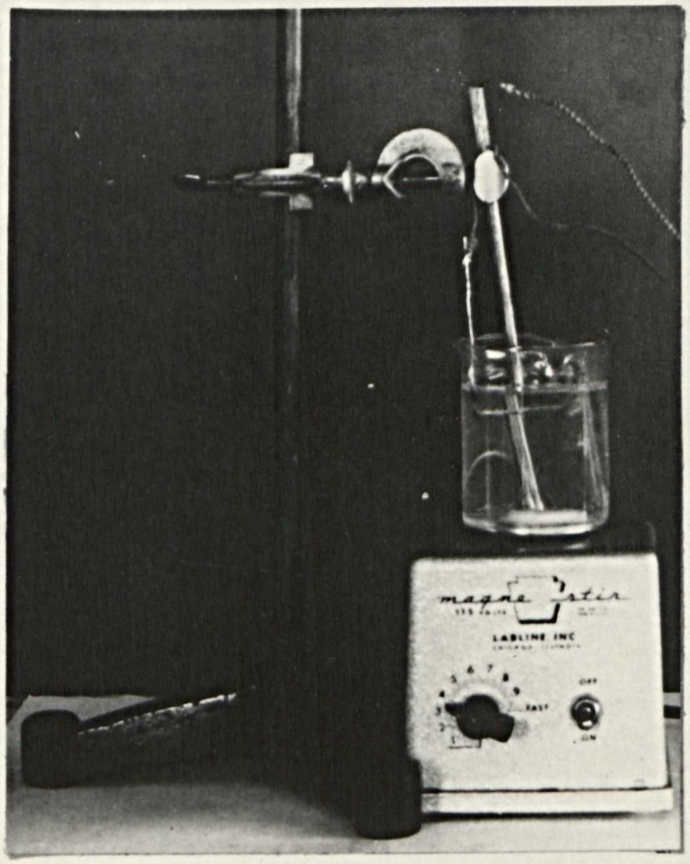


PLATE NO. 3. REFINING CELL

ACKNOWLEDGMENTS

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