5-1949

Operation Characteristics of the Series System for Electrolytic Refining of Copper

John T. O'Donnell

Recommended Citation

OPERATION CHARACTERISTICS

OF THE

SERIES SYSTEM FOR ELECTROLYTIC REFINING OF COPPER

by

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A Thesis

Submitted to the Department of Metallurgy

in Partial Fulfillment of

the Requirements for the Degree of

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MONTANA SCHOOL OF MINES

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INTRODUCTION

Early Development of Electrochemistry

Near the end of the eighteenth centry, Volta invented the voltaic pile. Sir Humphry Davy almost immediately used the voltaic pile in his experimental work in electrochemistry. Although Sir Humphry Davy contributed much to electrochemistry, his most significant contribution was his student, Michael Faraday. To this genius, electrochemistry is greatly indebted. Not only did Michael Faraday, in 1833, set forth two laws of electrolysis, but he also developed the theory of electromagnetic induction by which electrical energy may be economically generated.[1]

Multiple and Series Systems

In 1865, the first attempt was made to refine copper electrolytically under a patent issued to Elkington. This first attempt used the multiple system and was followed by the series system which was introduced in 1886.[2] There were about thirty electrolytic plants in the world in the latter part of 1892, eleven of which were in the United States. The total annual production of these thirty plants was about 64,000,000 pounds.[3] This production is insignificant with the 1946 United States production of 1,747,000,000 pounds.[4]

[1]Creighton and Koehler, Electrochemistry, Vol. I, p. 1.

[2]Encyclopaedia Britannica, Vol. 6, 1944 Edition, p. 407.

[3]Walker, Arthur L., Learning How to Refine and Cast Copper, "Choice of Methods in Mining and Metallurgy," p. 57.

[4]Minerals Yearbook, 1946, p. 469.

This means that the world production for 1892 was only 3.67 per cent of the present United States production.

The multiple system was used in a majority of the eleven plants, with the Hayden and Smith series systems each used in two plants. The Smith system used horizontal electrodes which soon proved unsuccessful.

At Laurel Hill, Long Island, in 1892, the Nichols Chemical Company started to build an electrolytic plant which used cast anodes in a series system. Previously, only rolled anodes, known as the Hayden series system, had been used. The use of cast anodes became known as the Nichols series system.[5]

Because the Nichols and Hayden series systems were somewhat limited as to the quality and physical characteristics of the anodes used, and required more critical operating conditions than the multiple system, practically all the electrolytic refineries installed the multiple system. Today the series system is used at Laurel Hill, New York, and in part of the American Smelting and Refining operations at Baltimore, Maryland.[6]

In the copper electrolytic refining operation, two main objectives are desired: the first is the production of a metal of desired chemical composition and physical characteristics, and the second is the recovery of the valuable by-products. These objectives are accomplished in varying degrees in both

[5] Walker, op. cit., p. 57.

[6] Creighton and Koehler, Electrochemistry, Vol. II, p. 166.

the multiple and series systems with the factor of economics being an important consideration in the choice of systems used. A. L. Walker,[7] in his excellent article on <u>Learning How to Refine and Cast Copper</u>, states that each system has a number of advantages. He lists the advantages as follows:

1. For a given amount of power more copper can be deposited. While the leakage of current around the electrodes in this system is large, the voltage between plates is much less. The production in the Hayden system is about 140 per cent and in the Nichols cast anode system about 170 per cent of that in the multiple system per unit of power.

2. Less carry of metals in process; electrodes are much thinner.

3. Less scrap produced; about 6.7 per cent in the Hayden system, 10 to 15 per cent in the Nichols and 14 to 18 per cent in the multiple system.

4. Less tank room space required for a given output. Tanks can be placed closer to each other, and there are many more electrodes in each.

5. Much less copper is required for bus bars and conductors.

Advantages of Multiple system are:

1. Ability to treat copper of any quality, no matter how impure or how rich in precious metal.

2. Less loss in previous metals in the cathodes produced-- about 0.35 per cent of the gold and silver in the anodes of the multiple system; 1 per cent in the Hayden system and 2 per cent in the Nichols process, due to the very long cathodes.

3. Ability to handle electrodes and scrap in larger units and with less cost for labor.

4. Requires less care in maintaining the purity of the electrolyte, as it is possible to effect a much better circulation.

5. Cost of casting and preparing anodes much less, especially when compared with the Hayden system, where the plates must be rolled.


[7] Walker, <u>op. cit.</u>, p. 73.

From the listed advantages the multiple system seems to be the most favored, but the series system has one very important advantage in that it can produce from 1.4 to 1.7 times more copper per kilowatthour than the multiple system. Very little literature is available on the series system, and all that is found refers to the Nichols system as used at Laurel Hill, New York.

Theory of Copper Electrolytic Refining

In theory, the electrolytic refining of copper appears to be very simple; an atom of copper goes into solution from an anode as a copper ion when two electrons are removed from the atom, while at the same time a copper ion becomes a copper atom upon receiving two electrons at the cathode. The impurities may go into solution and either remain in solution or be precipitated; or they may settle to the bottom of the cell as insolubles. The anodic reaction (oxidation) is usually represented by

$$Cu - 2(e) \rightarrow Cu^{++}$$

and the cathodic reaction (reduction) by

$$Cu^{++} + 2(e) \rightarrow Cu$$
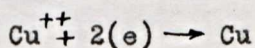
where (e) represents an electron. Under ideal conditions of refining, the above reactions would continue without an external source of power, but such is not the case in practice.

Mr. Lawrence Addicks[8] states in his book, Copper Refining, that "there are a host of resistances and counter electromotive forces to be overcome . . . ." He then breaks down the resistances into those caused by conductors, contacts and

[8]Addicks, Lawrence, Copper Refining, p. 38.

electrolytes. Of the three, electrolytes contribute over one-half of the total resistances. Electrolyte resistance is governed by the distance between the electrodes, and the composition and temperature of the electrolyte. The counter electromotive forces are caused by differences in composition of the electrodes, and by differences in concentration of the electrolyte. Circulation tends to keep the electrolyte in equilibrium.[9]

In order to get a cathode deposit of high purity, the current density has to be closely controlled. Generally, the more electropositive metals (the noble metals) do not go into solution but into the anode mud. However, they may dissolve if a high current density is used. The more electronegative metals are readily dissolved. If undesired metals do go into solution, reagents are usually added to precipitate these metals with the anode mud. Some impurities such as arsenic, nickel, and bismuth (which cannot be successfully removed by precipitation) require the electrolyte to be purified at regular intervals to remove these three impurities before they become too concentrated and contaminate the cathode.[10]

Two systems of electrolytic copper refining are used as has been previously mentioned; the multiple or parallel system and the series system. In the multiple system the anodes and cathodes are alternated through the length of a tank, with the anodes connected to a positive bus bar, and the cathode to a negative bus bar as shown in the diagram on the next page.

[9]Addicks, op. cit., p. 49.

[10]Creighton and Koehler, Vol. II, op. cit., p. 159.
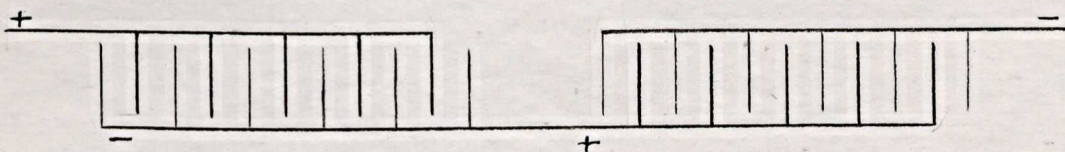
A current of 7,000 to 10,000 amp per tank is evenly distributed by heavy bus bars to the electrodes which are maintained at a cathode current density of 14-33 amp per sq ft. A voltage of 0.2 to 0.8 volts per tank is required.

In the series system, anodes are evenly spaced throughout the length of a tank. No electrical connection to an outside source is used except for the end electrodes, one of which is connected to a positive terminal, and the other to a negative terminal. This connection is shown below.
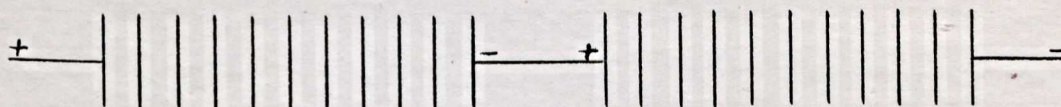
A current of about 76 amp per tank is used at a cathode current density from 18 to 27 amp per sq ft. This current requires a voltage of about 17 volts per tank. Although the current efficiency of the series system is only 70 to 75 per cent as compared to the multiple system, which is 90 to 98 per cent, more copper can be produced per kilowatthour by the series system because of greater voltage drops which occur between wider electrode spacing, and the many electrode connections of the multiple system.[11]

With a greater production per kilowatthour, and with very little data available on the series system, an investigation

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[11] Ibid., p. 166.

into the details of a series system should reveal why it is not used more frequently in the electrolytic refining of copper.

SCOPE OF INVESTIGATION

The object of this investigation was to study the effects of electrode spacing, rate of electrolyte circulation, and current densities upon the deposition and current efficiency of the series system of electrolytic refining of copper. As very little data is available upon which to base this work, the initial requirement of this investigation was the construction of workable series electrolytic cells.

Electrodes to be used in this research work were the basis of an investigation in casting anodes conducted by Mr. R. R. Kupfer. Mr. C. W. Howald was also making an investigation of the effects of impurities in the electrolyte upon the copper deposited. From these three investigations, we hope to obtain data which may be used as a basis of future investigations in the series system of electrolytic refining of copper.

PRELIMINARY WORK

Before any experimental work could be started, equipment
had to be made and readied. It was decided that either one,
two, or three glass tanks would be used in cascade. This re-
quired the construction and forming of: a rigid cell platform,
electrode suspension rods, odd-shaped glass tubing, constant-
level cell siphons, constant head feeder, electrolyte, and
anodes.

Cell Platform

A cell platform was constructed out of packing crates to
the size and shape shown on the following sketch.
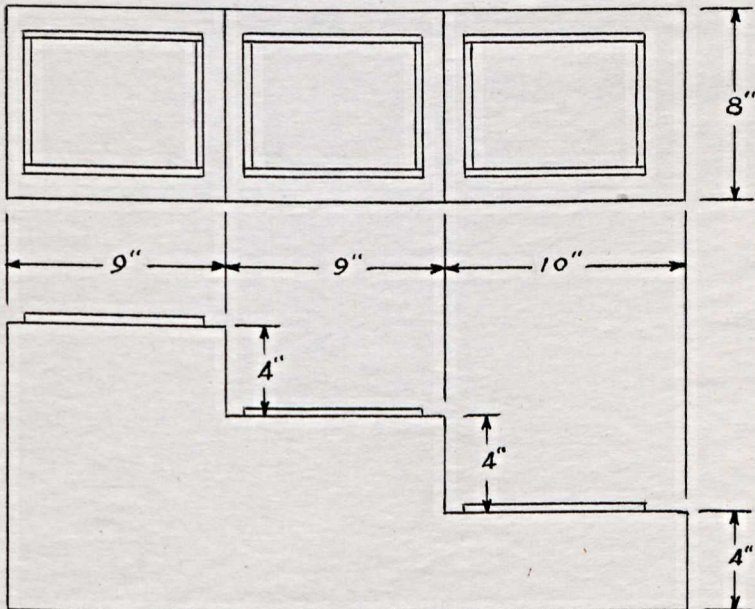
The platform was constructed to provide solid support
for each of the three tanks. After the platform was con-
structed, it was leveled and then nailed to the top of the
laboratory table. Each tank was individually leveled with

copper strips which were nailed into place. A narrow, wood edging held each tank in its proper place on the platform. As the tanks varied slightly in size and shape, they were numbered with tank 1 at the top, tank 2 at the middle, and tank 3 at the bottom. With the tank in its proper place, a horizontal upper edge was always assured. This horizontal edge is necessary to the proper control of the submerged area of each electrode.

Electrode Suspension

Because each anode which Mr. Kupfer was to cast weighed about three-fourths of a pound, it was decided to suspend each anode individually from glass capillary tubing. A short piece of rubber tubing was slipped over each end of the glass suspension rods to give greater friction between the glass rod and the glass tank. Two rubber-covered capillary tubes slightly longer than each tank were placed over and near the ends of the suspension rods. A rubber band pulling downward on the end of each lengthwise rod helped to hold the suspension rods in place. This arrangement can be readily seen in the photographs on the following pages.

Glass Tubing and Cell Siphons

As can be seen from the accompanying photographs, glass tubing had to be bent and formed to many odd shapes. Automatic tank siphons were bent into the shape as shown in the diagram on the following page. These siphons were capable of maintaining a constant level in the tank. If the feed to the tank slowed down or stopped, the siphon would do likewise.
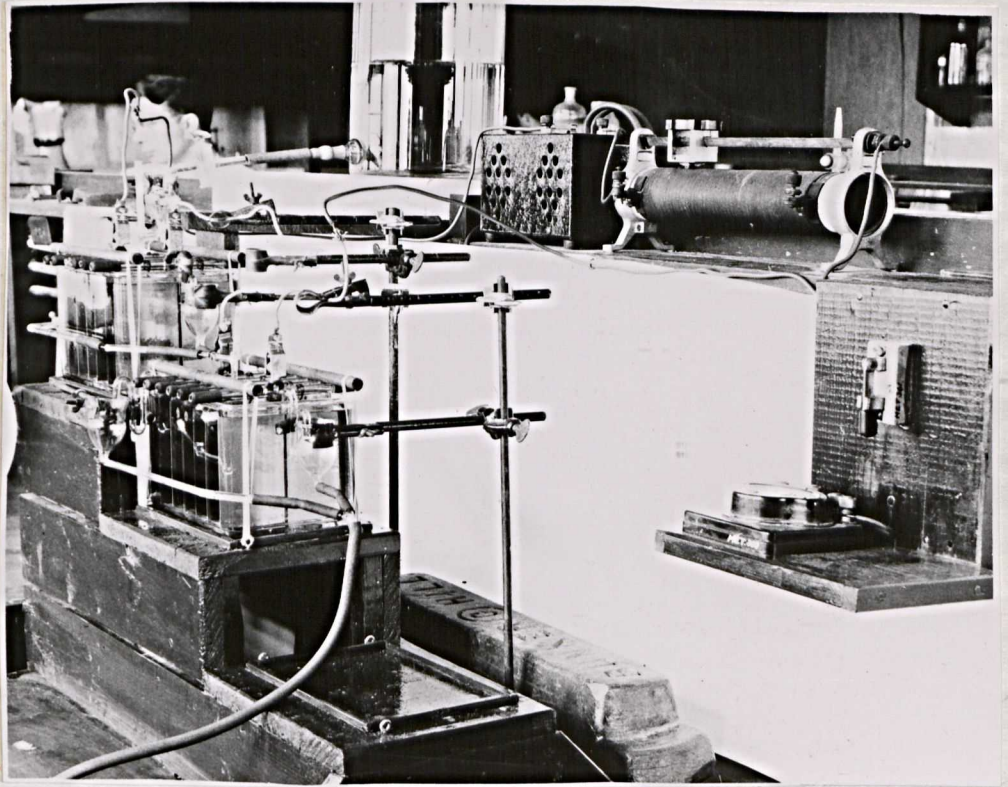
Side and top views of
laboratory apparatus
in operation.
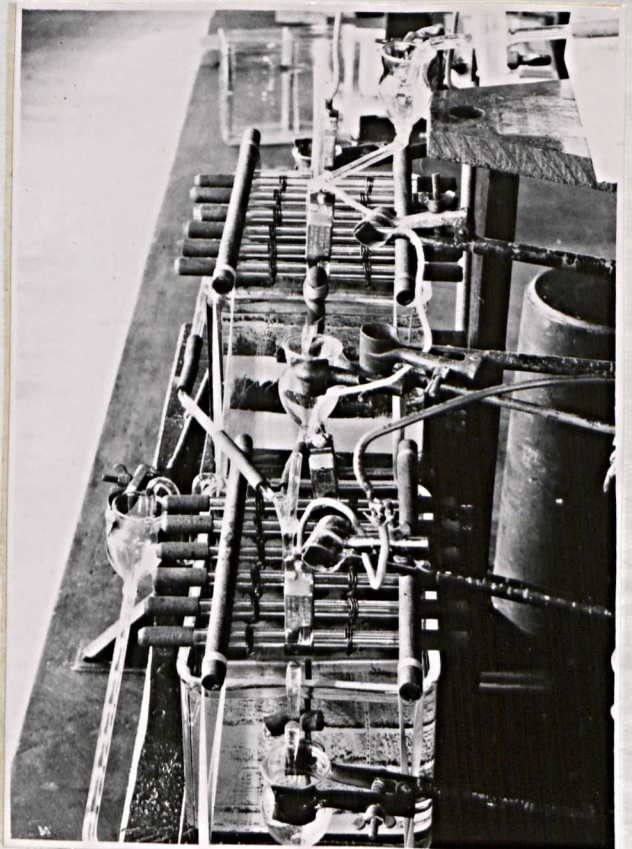
The siphons would also start flowing, after being stopped, when the tank feed again started. I found that a 3/32 in. glass tube siphon would operate continuously with a feed of about $4\frac{1}{2}$ ml per minute and with an unrestricted discharge orfice.
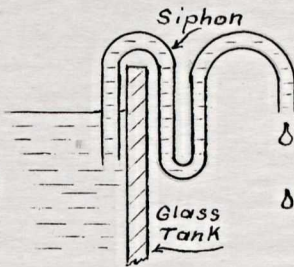
Constant Head Feeders

During the first few runs, feed to the tanks was controlled by a stopcock which was connected into the bottom of a glass bottle. However, as the level of the electrolyte in the bottle lowered, the feed to the tank decreased. To overcome this difficulty, a constant head feeder was made. The idea of this type feeder was brought over from the smelter at Anaconda, Montana, by a fellow student, Mr. Perry Boukind. A diagram of the feeder is shown at the right. The principle of this feeder is very simple. Whether the bottle is nearly empty or full, the cork float will lower or raise the point of intake and discharge simultaneously, thereby maintaining a constant head. For long runs, it was necessary to siphon electrolyte into the feeder from a large reservoir bottle. The intake to the feeder from the reservoir bottle was calibrated to flow one and one-half times as fast as the discharge of the feeder when the reservoir was full. As the head of the reservoir dropped, the feed into the feeder bottle decreased. In operation, the feeder
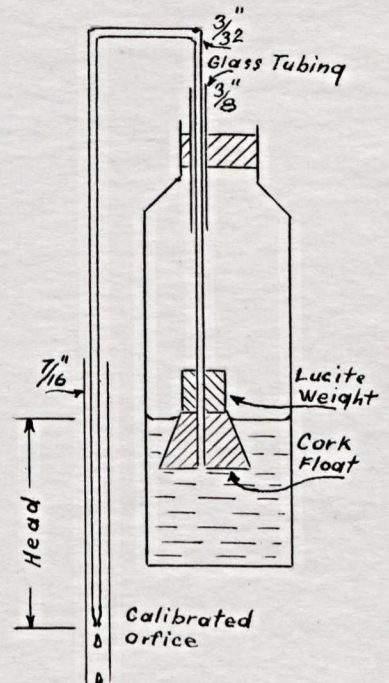
bottle was started about one-fifth full. As the run progressed, the reservoir gradually built up the volume of electrolyte in the feeder, but before the feeder bottle could overflow, the level of the electrolyte in the reservoir was below the top of the feeder bottle. In this manner a $2\frac{1}{2}$-liter feeder bottle was used as a surge bottle for a 8-liter electrolyte reservoir, and at the same time a constant tank feed was maintained. Runs up to 16 hours at 9.2 ml per minute were made without attention, by the use of the system of reservoir and feeder bottle.

Electrolyte

The electrolyte was based upon the Nichols[12] system of electrolytic refining of copper. In this system, the electrolyte is made-up of the following percentages:

$$Cu \quad 2.75 \quad - \quad 2.85\%$$
$$Free \; H_2SO_4 \quad 17.5 \quad - \quad 18.5\%$$
$$Cl \; as \; NaCl \quad 0.0003 \; - \; 0.0005\%$$

In addition to the above, glue and goulac were added to the following amounts for every 50 tons of cathodes deposited.

$$Goulac \quad 1 \; lb$$
$$Glue \quad \; 1 \; oz.$$

The glue and goulac are added to give a better cathode deposition. Calculations for the electrolyte are as follows:

FREE H_2SO_4:

18% H_2SO_4 = 180g H_2SO_4/liter electrolyte

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[12] Harloff, C. S. and Johnson, H. F., "The Nichols Series System of Electrolytic Copper Refining," p. 398.

$\dfrac{x}{1000} = \dfrac{180}{820}$ $x = 219.5g\ H_2SO_4$ for every liter water

$\dfrac{219.5}{1.84 \times 0.95} = 125.5\ ml\ H_2SO_4$ <u>for every liter water</u>

COPPER:

2.8% Cu = 28g Cu/liter

Molecular wt. $CuSO_4 \cdot 5H_2O = 249.63$

$\dfrac{249.63 \times 28}{63.57} = $ <u>$110g\ CuSO_4 \cdot 5H_2O$/liter electrolyte</u>

CHLORINE:

0.0004% Cl = 0.004g Cl/liter electrolyte

$0.004 \times \dfrac{58.5}{35.5} = $ <u>0.00659g NaCl/liter electrolyte</u>

GLUE AND GOULAC:

50 tons = 100,000 lb

1 lb = 1.0×10^{-5} part of 50 tons

Therefore, for a given cathode deposit in (x) grams

Goulac = (x) x 1.0×10^{-5}g

Glue = (x) x 1.0×10^{-5} x $\dfrac{1}{16}$ g

Anodes

As Mr. Kupfer experienced some difficulty in casting anodes, the original anodes were cut from copper sheets. Five runs were made using copper-sheet anodes, and one run with cast anodes. All spacings given in the tests are face to face. The first anodes were cut to 3 by $3\frac{1}{2}$ in. The submerged area was 9 sq in. The next type anodes were cut to $4\frac{1}{4}$ by $4\frac{1}{2}$ in., with 1/8 in. slot through the center of $4\frac{1}{4}$ in. width. This second anode was in

effect two anodes with a total submerged area of 16½ sq in. Diagrams of these anodes follow.
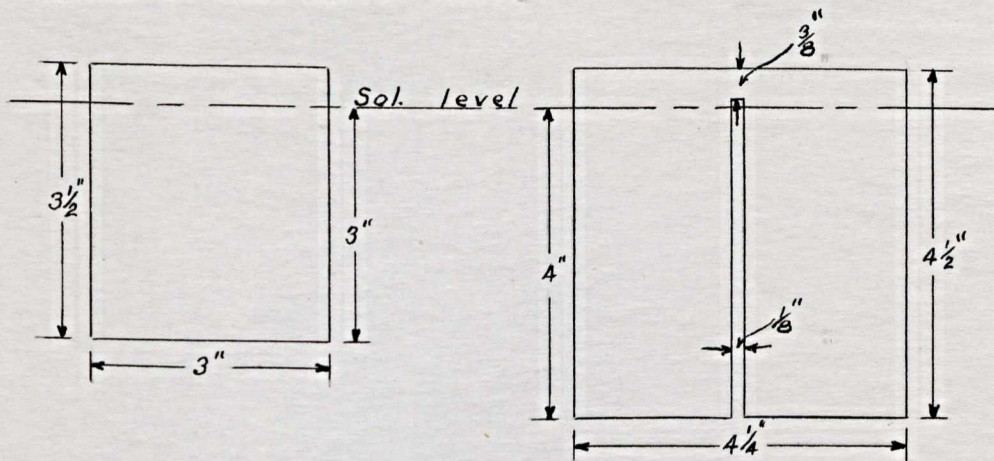
Both of these types of anodes were handled in the follow-ing manner: after all the anodes had been cut with shears to the desired size, two holes of about 1/8 in. in diameter were drilled as close to the top edge as possible. The holes were in the relative positions, as shown on the diagram. The anodes were all filed to equal sizes and the edges smoothed off, after which each anode was made perfectly flat by the use of a smooth surface; a block of wood and a hammer. Each anode was annealed over a Bunson burner to remove stresses. When cool, the anode was dipped into a 1 to 3 solution of HCl, washed in water, and polished with steel wool on a glass surface. The anode was then washed off in water, dipped again into the acid solution, and again washed in water, dried and polished on a flat surface with paper hand towels. The polishing was done immediately after the final wash to prevent oxidation.

Electrolytic Diagram

A. C. Source

Rectifier

+ —

Variable Resistor

D. C. Ammeter

D. C. Voltmeter

+

—

—

+
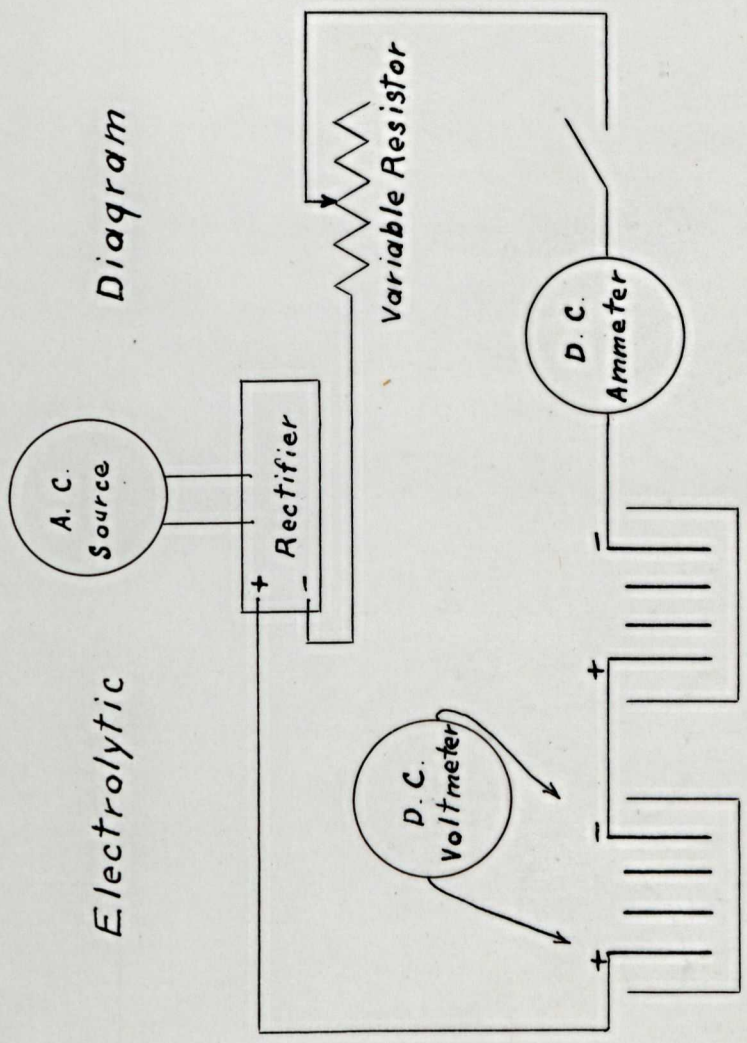
EXPERIMENTAL TESTS, RESULTS AND DATA

After the preliminary work had been finished, which con-
sumed considerable time, the various tests were made. Alto-
gether there were six tests, five of which were made with
copper-sheet anodes, and one with cast anodes. Several of the
tests used two tanks in cascade. The tests with data and re-
sults are given in the following pages.

Test 1

The first test was made to see if a series system of labo-
ratory size would operate. This test is probably an excellent
example of how not to operate a series system for the electro-
lytic refining of copper. Four unweighed anodes of 3-by $3\frac{1}{2}$-in.
sheet copper were placed in a glass tank, and electrolyte of
the previously given composition brought to within one-half
inch of the tank top edge. No circulation was used and a current
density of 26 amp per sq ft was maintained. Anode spacing was
one inch.

At the end of about four hours, the electrolyte graduated
from a light blue at the top to a deeper blue at the bottom.
This was due to the depletion of copper ions in the upper
portion of the tank upon depositing on the cathode, and the
settling to the bottom of the copper ions from the corrosion
of the anodes. This latter effect was noticeably evident in
the fine, sheetlike flow of electrolyte from the bottom of the
anodes. Because of these actions, and because copper sulfate
is heavier than sulphuric acid, the graduation in concentration
remained in effect until the current was turned off, after

which time the electrolyte became equally blue throughout.

The anode corrosion occurred to a greater extent around the bottom of the anode, as shown in the diagram at the right. The cathode deposit was beady and non-adherent, and occurred near the bottom and on both sides of the cathode. The bipolar electrodes were slightly thicker at the bottom and had a more adherent deposit than the cathode.
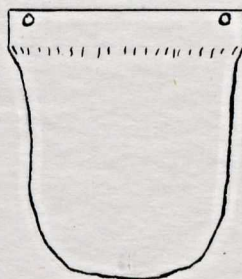
Test 2

Test number two was made to see if the electrode spacing made any difference in the copper deposition. It was thought at this time circulation would be in proportion to that used in commercial plants; that is, a ratio of 3.1 ml per minute for a 2.1 liter tank, as compared to some commercial tanks with a feed of 3.5 gal per minute for a 3260 gal tank.

Two tanks of $7\frac{1}{4}$ by 4 3/4 by 4 3/4 in., inside dimensions, were used in cascade. Electrolyte was brought in to the bottom of the tank at the anode end and discharged by the automatic siphon at the cathode end of the tank. The intake to the siphon was at a point about half the depth of the tank.

The electrodes in the first tank were spaced at $1\frac{1}{4}$ in., and those in the second tank at 1 in. Four, 3-by $3\frac{1}{2}$-in. copper sheet electrodes were used in each tank at a current density of 14 amp per sq ft. Glue and goulac were used in this test which lasted for 18 hours. The results of this test are listed on the following page.

Tank 1

		Before	After	Difference
Anode	No. 1	33.2408g	15.0375g	-18.2033g
	No. 2	31.5451g	31.5110g	- 0.0341g
Bipolar	No. 3	32.9242g	32.8765g	- 0.0477g
Cathode	No. 4	32.9101g	50.7917g	+17.8816g

Tank 2

		Before	After	Difference
Anode	No. 1	32.7402g	14.4902g	-18.2500g
	No. 2	31.4947g	31.4520g	- 0.0427g
Bipolar	No. 3	32.1685g	32.1068g	- 0.0617g
Cathode	No. 4	31.7232g	49.6019g	+17.8787g

The voltage drops across each tank were 0.35v for tank number 1, and 0.33v for tank number 2. No difference could be observed in the cathode deposit of the two tanks. In both cases, the deposit was fine grained and very adherent. Again there was more corrosion around the bottom edge of the anodes, but the cathode and bipolar electrode deposits were more evenly distributed, although still remaining slightly heavier near the bottom.

With a theoretical deposit of 18.68g for each cathode, there was an average current efficiency of 95.7 per cent for the end cathodes. However, this percentage could not be used as typical of the bipolar electrodes because as yet no method was used for measuring the amount of copper deposited on those electrodes.

An electroanalysis of the electrolytic copper content before and after this test showed the per cent copper to be the same in both cases.

The third test was made using six 3- by $3\frac{1}{2}$-in. electrodes,
spaced at one inch in a $7\frac{1}{4}$- by 4 3/4- by 4 3/4-in. tank. The
cathode sides of the electrodes were coated with vasoline to
provide a plane of weakness from which the deposited copper
could be stripped and weighed. Glue and goulac were added to
the electrolyte. The test lasted for 17 hours at a current
density of 18 amp per sq ft. The electrolyte at 4.5 ml per
min was again brought in to the bottom of the tank at the anode
end and discharged at the cathode end. However, the intake to
the automatic siphon was placed one-half inch below the surface.
The purpose in raising the point of outlet was to try to create
better circulation through the upper portions of the tank so
that the heavier copper ions would not by-pass the bipolar
electrodes. Results of this test follow.

		Before	After	Difference
Anode	No. 1	32.4099g	9.7977g	-22.6122g
	No. 2	32.7523g	32.7480g	- 0.0043g
Bipolar	No. 3	32.6895g	32.6800g	- 0.0095g
	No. 4	32.6050g	32.5935g	- 0.0115g
	No. 5	32.3143g	32.3142g	- 0.0001g
Cathode	No. 6	32.5792g	54.6461g	+22.0669g

The small loss of weight on the bipolar electrodes was
probably due to the added weight of vasoline. Although care
had been used in applying the vasoline, the copper deposited
was so irregular and patchy that it could not be stripped from
the cathodes. However, during this test observations were
made of the voltage drops across the electrodes, which indi-
cated that the copper ions from the anode were largely by-
passing the bipolar electrodes. An average of the three

readings made is shown below.

| Anode | 0.17v | 0.09v | 0.09v | 0.09v | 0.16v | Cathode |

|← ——————————— 0.60v ——————————— →|
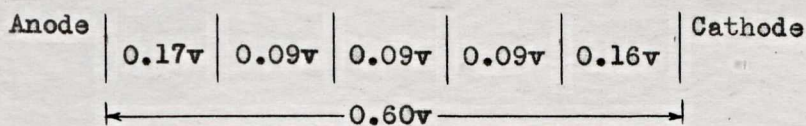
An electroanalysis of the copper percentage showed the
copper content to be the same after the run as at the begin-
ning. The cathode current efficiency was 97.3 per cent.
Copper deposited continued to be fine grained and adherent.
No treeing was observed.

Test 4

This test was made to determine the effects of agitation
upon the voltage drops across the electrodes. Tank number 1
was readied and operated under the same conditions as in test
number 3, except that agitation was used. Agitation was cre-
ated by a motor-driven solid glass rod with a short, 90° bend.
The glass rod operated between the two middle electrodes and
at the center of the tank. The tip of the rod was almost
touching the bottom of the tank. The speed of the rotation was
such that the agitation created almost made the electrodes swing.

Tank number 2 was operated at the same time but with the
electrodes at 7/16 in. spacing to see if there would be any de-
crease in the voltage differences between the cells with close
spacing.

In both tanks, the cathodes were greased with vasoline,
and then wiped off with a paper hand towel. This test, using
the two tanks, lasted for $7\frac{1}{2}$ hours. Voltage drops observed be-
tween the electrodes are shown on the next page.

Tank 1 (One-inch spacing)

Anode | 0.13v | 0.08v | 0.08v | 0.08v | 0.16v | Cathode

|←————————— 0.53v —————————→|

Tank 2 (7/16-in. spacing)

Anode | 0.09v | 0.06v | 0.05v | 0.75v | 0.12v | Cathode

|←————————— 0.40v —————————→|
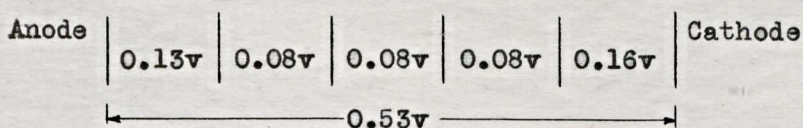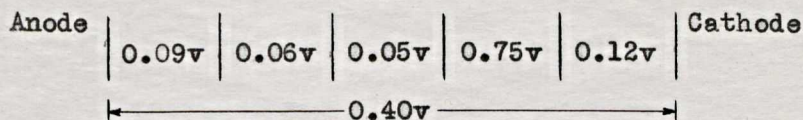
A comparison of test number 3 with tank number 1 of test number 4 shows the voltage drops of the two tests to be similar. The over-all voltage drop of the second test was lower which could be the result of an increased electrolyte temperature.

The second tank shows a decreased voltage drop which was to be expected with close spacing. However, close spacing does not seem to affect the proportion of the voltage drops between the end and middle electrodes as compared to tank number 1 of this test, and to test number 3. This test did not reveal any method of reducing the differences between the voltage drops of the end and middle electrodes.

As the cathodes could not again be stripped, the electrodes' weights before and after the run are not particularly significant. Cathode current efficiencies were 99.2 per cent for tank number 1, and 99.3 per cent for tank number 2.
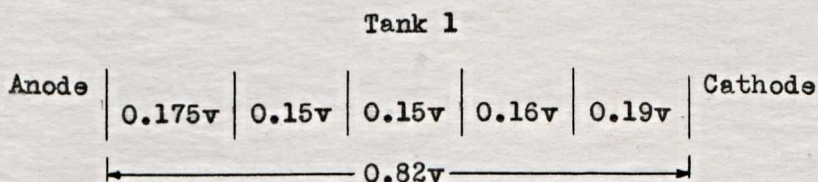
Test 5

Mr. Carl Howald found that larger electrodes were giving him better corrosion and deposition on the bipolar electrodes. However, he was not able to determine to what extent the bipolar electrodes were being affected.

In the light of Mr. Howald's work, it seemed desirable to use the $4\frac{1}{4}$-by $4\frac{1}{2}$-in. copper-sheet electrodes. The idea behind such an electrode was to create a condition for greater over-all electrolyte circulation, and at the same time, eliminate any large unrestricted volumes of electrolyte. This latter case resulted from the use of 3- by $3\frac{1}{2}$-in. electrodes in a tank of a cross-sectional area of 4 3/4 by 4 3/4 in. The larger size anodes were suspended in a $7\frac{1}{4}$- by 4 3/4- by 4 3/4-in. tank and treated with vasoline as in the previous tests.

The decision was made at this time to feed the electrolyte to the center of the tank, and withdraw from both ends. Two tanks were readied. The tanks were identical except that the feed in number 1 tank was brought through a restricted orfice to the lower edge of the electrodes, while the feed in number 2 tank was discharged through a restricted orfice at a point one-half the submerged depth of the electrodes.

A current density of 18 amp per sq ft was used for this seven-hour test. The feed to the tank was maintained at 9 ml per minute. Glue and goulac were added at the start of the test.

This test resulted in a cathode current efficiency of 98.8 per cent for both tanks. As previously, the bipolar electrodes could not be stripped and no way was available to determine the true current efficiency of the cells. However, the observed voltage drops across electrodes had greatly improved as shown.

Tank 1

Anode						Cathode
	0.175v	0.15v	0.15v	0.16v	0.19v	

$\leftarrow$————— 0.82v —————$\rightarrow$

Tank 2

Anode	0.175v	0.16v	0.16v	0.16v	0.18v	Cathode

|←——————————— 0.82v ———————————→|
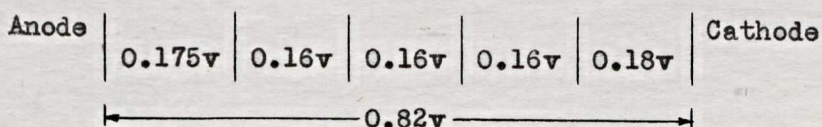
With the improved leveling off of the voltages, it was
thought the current efficiencies of the bipolar electrodes
had greatly improved, although as yet unmeasurable. From the
observed voltage drops, greater current efficiency was ap-
parently effected by bringing the electrolyte feed to a point
one-half the submerged area of the anode.

Test 6

After many discouragements in casting, Mr. Kupfer was,
however, able to gather together five anodes which were used
in the final test. The anodes were not smoothed off except
for the edges which were cut and ground to bring all anodes
to an approximate size of $3\frac{1}{2}$ by $3\frac{1}{4}$ inches at a submerged area
of 3 by $3\frac{1}{4}$ inches, or 9.75 sq in. Each anode was cleaned in
dilute nitric acid, washed with water, dried, and weighed on
the pulp balance. The top edge of each anode had been previ-
ously nicked with a file to indicate its position in the tank.
All cathode faces of the electrodes were lightly brushed with
quenching oil.

A new size tank was used in this test. The tank was $7\frac{1}{2}$ in.
long, $3\frac{1}{2}$ in. wide, and 3 3/4 in. deep (inside dimensions).
With this tank, there was only about 1/8 in. between the sides
of the tank and the electrodes, and $\frac{1}{4}$ in. between the bottom
of the tank and the electrodes. The cell feed was brought

through a restricted orfice to a point about two-thirds the
depth of the submerged area of electrodes at the center of
the tank. The electrolyte, a quantity of ten liters necessary
for the long run, was fed into the tank from the constant-head
feed bottle through a calibrated orfice at the rate of 9.2 ml
per minute. Discharge was made from the two ends of the tank
with the automatic siphons. A current density of 18 amp per sq
ft was used for a total of 92 hours and 52 minutes. At the end
of the test the cathode deposit, which followed the contours
of the original electrode, was stripped from the electrodes
and weighed. Slight treeing had occurred near the bottom of
the cathodes. Stripping was not too difficult, although a
sodium resinate solution on the cathode face may have made
stripping easier.

In general, the corrosion was fairly constant over the
anode and seemed to follow the contour of the surface. Within
the area 3/8 in. below the electrolyte surface, corrosion was
greater. This was probably due to a higher acid content of the
electrolyte at this point.

The results of this test are most interesting, as the
following data and calculations show.

DATA (Grams):

		Before Test	After Test	Differ- ence	Stripped Electrodes	Recover- ed Cu	Corrod- ed Cu
Anode	1.	397.4	262.4	-135.0	262.4	---	135.0
	2.	374.5	368.7	-5.8	302.9	65.8	71.6
Bipolar	3.	470.3	467.6	-2.7	408.7	58.9	61.6
	4.	443.7	441.4	-2.3	376.4	65.0	67.3
	5.	499.1	495.9	-3.2	438.1	57.8	61.0
Cathode	6.	36.5	164.3	+127.8	36.5	127.8	----
						375.3	396.5

CALCULATIONS:

Theoretical Deposit

$$m = \frac{Zit}{96,500} \text{ grams}$$

$$= \frac{63.57}{2} \text{ x } \frac{1.22 \text{ amp x } 5572 \text{ min x } 60 \text{ sec/min}}{96,500}$$

$$m = 134.4 \text{g/cathode}$$

Total $m = 5 \text{ x } 134.4 = 672.0 \text{g/5 cathodes}$

Apparent Current Efficiency

$$\frac{127.8 \text{g}}{134.4 \text{g}} = 95.0\%$$

Actual Current Efficiency

$$\frac{375.3 \text{g}}{672.0 \text{g}} = 55.9\%$$

Metal Recovered

$$\frac{375.3 \text{g (recovered)}}{396.5 \text{g (corroded)}} = 94.7\%$$

Pounds Deposited per kwhr

Average voltage drop across cell = 1.29

$$\text{kwhr} = \frac{IE \text{ hr}}{1000}$$

$$= \frac{1.22 \text{ amp x } 1.29 \text{ volts x } 92.867 \text{ hr}}{1000}$$

$$= 0.1462 \text{ kwhr}$$

$$\frac{375.3 \text{g (recovered)}}{453.6 \text{g/lb}} \text{ x } \frac{1}{0.1462} = 5.66 \text{ lb/kwhr}$$

The current efficiency based on the cathode alone is 95.0 per cent. The low over-all current efficiency of 55.9 per cent is probably due to copper ions which by-passed the bipolar electrodes. Of the total amount of copper that was corroded from the anodes, 94.7 per cent was recovered as refined copper. No doubt the greatest percentage of the copper not recovered was due to a physical breakdown at the anodes which dropped to the bottom of the tank. Also, the anodes may have contained considerable copper oxide which would go into solution. Insufficient time was available to check the copper content of the electrolyte after the test. The pounds of copper recovered per kilowatthour appears to be rather small at 5.66 lb, as compared to some operations where 14 lb of copper are recovered. However, this low recovery is the result of high voltage drops across the cells, in addition to low current efficiencies. Heating the electrolyte would have greatly increased the pounds of copper recovered per kilowatthour.

In this test, it was observed that when the current was shut off for a few minutes, the voltage drops across the individual cells was an almost constant 0.21v immediately after resuming operation. Fifteen minutes later the voltage drops varied 0.05v between the bipolar cells and the two end cells. Typical voltage drop readings are shown below.

Anode						Cathode
	0.30v	0.23v	0.23v	0.23v	0.30v	

←————————— 1.29v —————————→
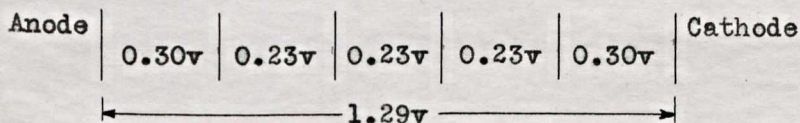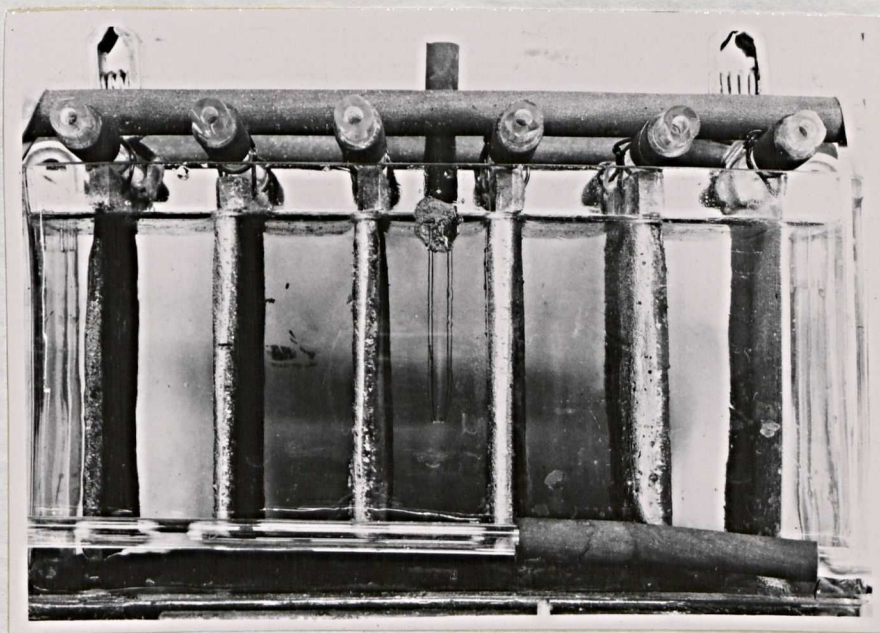
Close-up of cast anodes
in cell during test 6.

Anode

Cathode

Close-up of the anode and the
cathode side of a bipolar electrode
after test 6. Note slight treeing.

SUMMARY OF TESTS

The results of the six tests made may be grouped together
into four divisions. These divisions are: current densities,
anode spacing, relation of anode and tank sizes, and circu-
lation.

Current Densities

Very little of the experimental work was based upon
current densities, and no systematic tests were made to deter-
mine the effects of different current densities. The test at
26 amp per sq ft gave a coarse, beady, and non-adherent deposit.
Because the greatest concentration of the copper ions was near
the bottom of the tank, the cathode deposit was much heavier
near the bottom edge. This effect probably resulted in a
greater current density than 26 amp per sq ft near the bottom
of the cathodes and to lesser current densities near the top.
The actual current density which caused the beady and non-
adherent cathode deposit is not known.

The second test used a current density of 14 amp per sq ft,
while the balance of the tests were made at 18 amp per sq ft.
The deposit at both current densities was fine grained and ad-
herent.

In all tests, the copper deposited on both sides of the
cathode. Such an effect results because a copper ion can be-
come a copper atom upon receiving two electrons, regardless of
the side of the cathode the ion happens to be. Because of the
circulation and proximity of the inside face of the cathode to
the anode, the greatest copper deposit will occur on the inside

face of the cathode.

The anode corrodes the most on the inside face. Some corrosion occurs on the outside face of the anode depending upon copper ion concentration at any one time, which in turn is largely dependent upon circulation and proximity to a cathode. The greater the copper ion concentration at some point, the more resistant will be that point to corrosion, and the more likely will corrosion occur at a point of lesser copper ion concentration.

Anode Spacing

Electrode spacing, face to face, varied from $1\frac{1}{4}$ in. to 7/16 in. The width of spacing did not seem to have any effect upon the ratio of the differences in voltage drops between the end and bipolar cells. The voltage drops in the end cells were always greater, and at times were twice as great as the voltage drops of the bipolar cells. The cause of this voltage difference is explained under circulation. Individual cell and tank voltage drops were less when electrodes were more closely spaced.

Relation of Anode and Tank Sizes

When this research was first started, we believed that the copper ions would travel in an ideal behavior from an anode to the closest cathode. This supposition proved false. Instead of following the shortest path between two electrodes, the ions apparently wandered from place to place dependent for the most part upon circulation. This supposition leads one to believe that there must be a definite relation between the size of the

electrode to the cross-sectional area of the tank. As the
copper ions will by-pass the bipolar electrodes rather
easily, the size of the electrode should rather closely approx-
imate the size of the tank. However, electrodes that are too
large will limit circulation. Increasing the rate of circu-
lation to give a more uniform electrolyte concentration, would
not allow the anode mud to settle. This particular problem
becomes one of determining what electrode size and arrangement
in the tank will give the greatest current efficiency of the
bipolar electrodes and still maintain a desired rate of circu-
lation. The Nichols[13] system used five anodes on each suspension
bar, spaced one-half inch apart. Perhaps a similar arrangement
is necessary for a laboratory tank.

Circulation

Perhaps the most critical problem in the series electro-
lytic refining of copper is the rate and method of circulation.
This problem is tied in rather closely to the relations between
the sizes of the anodes and tank.

One of the more significant facts observed occurred in
Mr. Howalds' and my electrolytic tanks. At the first part of
the tests we both brought our electrolytes into the bottom of
one end of the tank and discharged from the top at the opposite
end. However, we had our anodes and cathodes in the opposite
positions in relation to the point of electrolyte intake and
discharge. Sketches of our tanks appear on the following page.

[13] Ibid., p. 398.

Howald

O'Donnell
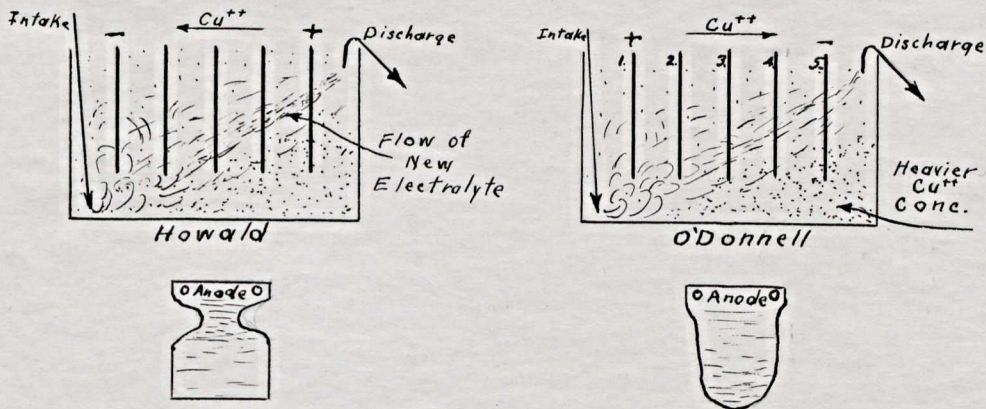
From the sketches it can be seen that the anode corrosion
was taking place where the new acid-rich electrolyte was circu-
lating. At this time the electrolyte in our tanks was circulated
at the low rate of 3.2 ml per min and little agitation was effect-
ed. The low rate of circulation probably caused a difference
in electrolyte concentration to occur through the tank. This
effect was noticeable in several of the tests made, shown by
the corrosion of the bipolar anodes. Sketches below illustrate
the point. Referring to the previous tank diagram, the anode
corrosion occurred as follows:
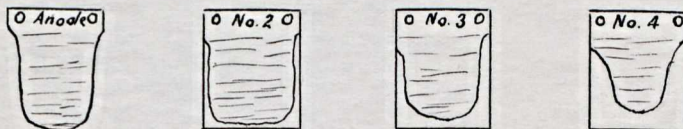
The anode side of the bipolar electrodes sketched above
corroded the most in the shaded area. Apparently the acid-
rich new electrolyte caused the anode corrosion of the bipolar
electrodes to take place through the center portion of the tank,
and to become more and more restricted in cross-sectional area
as the discharge end of the tank was approached. No doubt the

heavier copper ions upon settling to the bottom of the tank,
also helped to restrict the volume of the lighter acid solution.
This latter effect was noticeable as a heavier copper deposit
on the lower portions of the cathode side of the bipolar electro-
des, caused by the greater concentration of copper ions.

As mentioned previously, when a tank is operated without
circulation, there is a concentration of the heavier copper ions
near the bottom of the tank. Such a result is possibly effected
as shown in the sketch below.
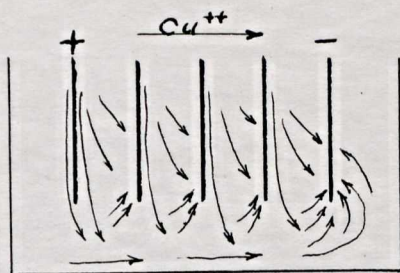
The arrows show the probable paths of the copper ions.
As the copper ions go into solution, they tend to settle to
the bottom with a few being deposited on the next cathode. If
sufficient volume is allowed below the electrodes, a large
percentage of the copper ions will by-pass the bipolar electrodes
and not become neutralized until the cathode is reached. This
would cause greater voltage drops across the end cells, as
these cells are maintaining a greater current density in con-
junction with the electrolyte at the bottom of the cells. The
voltage drops read across the top of the electrodes are not
necessarily the same as the voltage drops across the bottoms
of the electrodes. A difference in potential probably exists
between the tops and the bottoms of the same electrodes. This

difference in potential is shown by the differences in the amount of copper deposited at the top and bottom of the cathodes. Circulation is therefore necessary to the proper operation of a series electrolytic tank.

There is much work that can be done to determine the true flow of copper ions in a series electrolytic tank. Mr. G. G. Harmon, Assistant Professor of Physics, suggested that all points of equal potentials for a given cell be found and plotted. Then lines at right angles to the lines of equal potential would show the flow of the copper ions. No time was available to conduct this work.

As mentioned previously, when test six was conducted the current was shut off several times for periods of four minutes. Upon resuming operations, the voltage drops across the electrodes were found to be practically the same, as equilibrium of the electrolyte had apparently resulted. However, after fifteen minutes the voltage drops across the end cells had again increased over the middle cells. Such an effect shows the need for proper circulation.

In test 4 agitation was used with small anodes without decreasing the differences in voltage drops across the cells. It is believed that the larger sized anode would have given better results.

CONCLUSIONS

The apparent conclusion to be deduced from this problem is the need for extensive research into the causes and effects of various variables, such as anode spacing, anode sizes and shapes, current densities, circulation, etc. It is very probable that much time and effort will be expended before definite conclusions can be made.

It was found that circulation is a very important factor in the successful operation of a series system, and that the size of the anode to the size of the tank is critical, but it is not known to what extent and in what manner procedures of operation will be found and used to make this system of refining more general.

Without a doubt much research has been made and will continue to be made by the electrolytic refineries, but up to the present time they haven't revealed any new information on the series process. Undoubtedly some, or all of the answers sought at the start of this research will be found by those who continue on in this interesting problem.

ACKNOWLEDGMENT

The writer wishes to express his appreciation to Professor John P. Spielman for his advice and criticism, to George G. Harmon, Doctor Kenneth N. McLeod and Ralph I. Smith for their valuable assistance, and to other members of the faculty who made this work possible.

BIBLIOGRAPHY

Addicks, Lawrence Copper Refining. New York and London:
McGraw-Hill Book Co., Inc., 1921.

Bray, John L. Non-Ferrous Production Metallurgy. New
York: John Wiley and Sons, Inc., 1947.

Creighton and Koehler Electrochemistry, Volume I, Princi-
ples. New York: John Wiley and Sons, Inc., 1947.

Creighton and Koehler Electrochemistry, Volume II, Appli-
cations. New York: John Wiley and Sons, Inc., 1947.

Encyclopaedia Britannica, Vol. 6, 1944 Edition Chicago,
London, Toronto: The University of Chicago, Encyclopaedia
Britannica, Inc.

Harloff, C. S. and Johnson, H. F. The Nichols Series System
of Electrolytic Copper Refining, A. I. M. E. Transactions,
Vol. 106. New York: 1933.

Minerals Yearbook, 1946 Edition, United States Department
of Interior, Bureau of Mines. United States Government Print-
ing Office, Washington, 1948.

Newton, Joseph and Wilson, Curtis L. Metallurgy of Copper.
New York: John Wiley and Sons, Inc., 1942.

Walker, Arthur L. Learning How to Refine and Cast Copper;
"Choice of Methods in Mining and Metallurgy," A. I. M. E.
New York and London: McGraw-Hill Book Inc., 1932. (Seeley W.
Mudd Series)