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INVESTIGATIONS IN THE HYDROMETALLURGY
OF COPPER SULPHIDES

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BY:

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GOLDEN, COLORADO

MAY 3, 1933.

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INTRODUCTION

During the past few years the application of hydrometallurgical methods for recovering metals from their ores has expanded rapidly. This has been activated by the fact that pyrometallurgical methods have not been economical on low grade complex ores, and further, that most of the products obtained from pyrometallurgical plants must be refined before marketing. Also the close competition with foreign production has increased the desire to improve present day metallurgical methods, so as to lower unit production costs. New and more efficient equipment has greatly aided in the development of these processes.

The hydrometallurgy of copper is by no means new, but up to the present time has been confined mainly to the recovery of copper from oxidized ores, and the refining of blister copper by electrolysis. In Arizona, (1) gratifying results have been obtained by leaching mixed oxide and sulphide ores using sulphuric acid and ferric sulphate as leaching agents.

Since the advent of flotation and the increased production of high-grade copper concentrates increased interest has been directed toward and numerous methods

(1) Aldrich and Scott: E. & M. J. 128 16, 612 1929

outlined for the hydrometallurgical treatment of these products. Greenawalt (2) in his latest article, advocates a sulfatizing roast with a split leach on high and low grade calcines to control impurities. Floe and Drucker (3) have outlined a process whereby about 50 per cent of the contained copper is converted to water-soluble copper, ~~X~~ leaching with sulphuric acid, with subsequent purification and electrolysis.

The method worked out at the Bagdad Pilot Plant (Hillside, Arizona) (4) utilizes a three-stage roast; in the final stage the temperature is high enough to decompose water-soluble salts. A single-step leach was advocated, with impurity control by "bleed off" and stripping.

The chief disadvantages of the above mentioned processes are: First, the relatively small tonnage of concentrates that may be roasted in a given furnace per day; second, the control of sulphuric acid generated in the electrolytic division.

SULPHURIC ACID---FERRIC SULPHATE LEACH

The object of this work is an attempt to overcome the two disadvantages mentioned: First, by increasing the tonnage roasted per unit of time for a given

-
- (2) The Mines Magazine 23 - 1 - 1933.
(3) Bulletins 35 & 38: Washington State College, 1932.
(4) E. & M. J. 130, 10, 522, 1930.

roaster. This may only be done by the elimination of a "sweet roast", which will leave a certain quantity of the copper in the calcine as sulphides, for which a solvent must be found. Ferric sulphate was the solvent chosen for this purpose. Second, to produce a calcine containing a small amount of water-soluble copper, by finishing the roast at or near 700° C. This will automatically control the excess sulphuric acid generated by electrolysis.

In order for a process of this nature to be commercial it will be necessary to regenerate the solvents used. During the electrolysis of aqueous copper sulphate solution, approximately 1½ pounds of sulphuric acid are regenerated for every pound of copper deposited.



A certain amount of iron must be present in the solution entering the electrolytic division in order for ferric sulphate to be regenerated. It is, however, common knowledge that the presence of iron in a copper electrolytic decreases the current efficiency. The presence of iron also lowers the cell potential thus tending to offset this lowering of current efficiency. Therefore, the concentration of iron to carry in the solution will be that quantity which will compensate

for the decrease in electrical efficiency. A slight excess over this amount may be necessary to insure an efficient leach of the copper sulphides that remain in the calcine.

Since copper is soluble in ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3 + \text{Cu} \rightarrow 2 \text{FeSO}_4 + \text{CuSO}_4$) it is imperative for the iron in the incoming solution to be in the ferrous state. This ferrous iron will be oxidized during electrolysis to ferric iron by the following reaction:



The ferric iron thus produced is to be utilized in leaching, the sulphide copper remaining in the calcine.

The work performed to date has been: First, to determine the nature of calcine produced from various concentrates when roasted as outlined above; second, to determine the solubility of the sulphide copper present in these calcines, in a solution containing sulphuric acid and ferric sulphate; third, to obtain data from the electrolysis of solutions containing various concentrations of iron, copper and free sulphuric acid, relative to current efficiency, power consumption per ton of copper deposited and the iron oxidation efficiency.

All the chemical reactions illustrated in this report have been known to chemistry for many years. Therefore, no originality is claimed in this connection.

Figure 1 illustrates the general flow sheet followed in this investigation.

ORES TESTED

Two different chalcopyrite concentrates were used for these tests; one from Lake City, Colorado, and the other from Utah Copper, Garfield, Utah. The first named is relatively low grade, containing various amounts of impurities, while the latter is fairly clean. The following tables give the analysis of these concentrates:

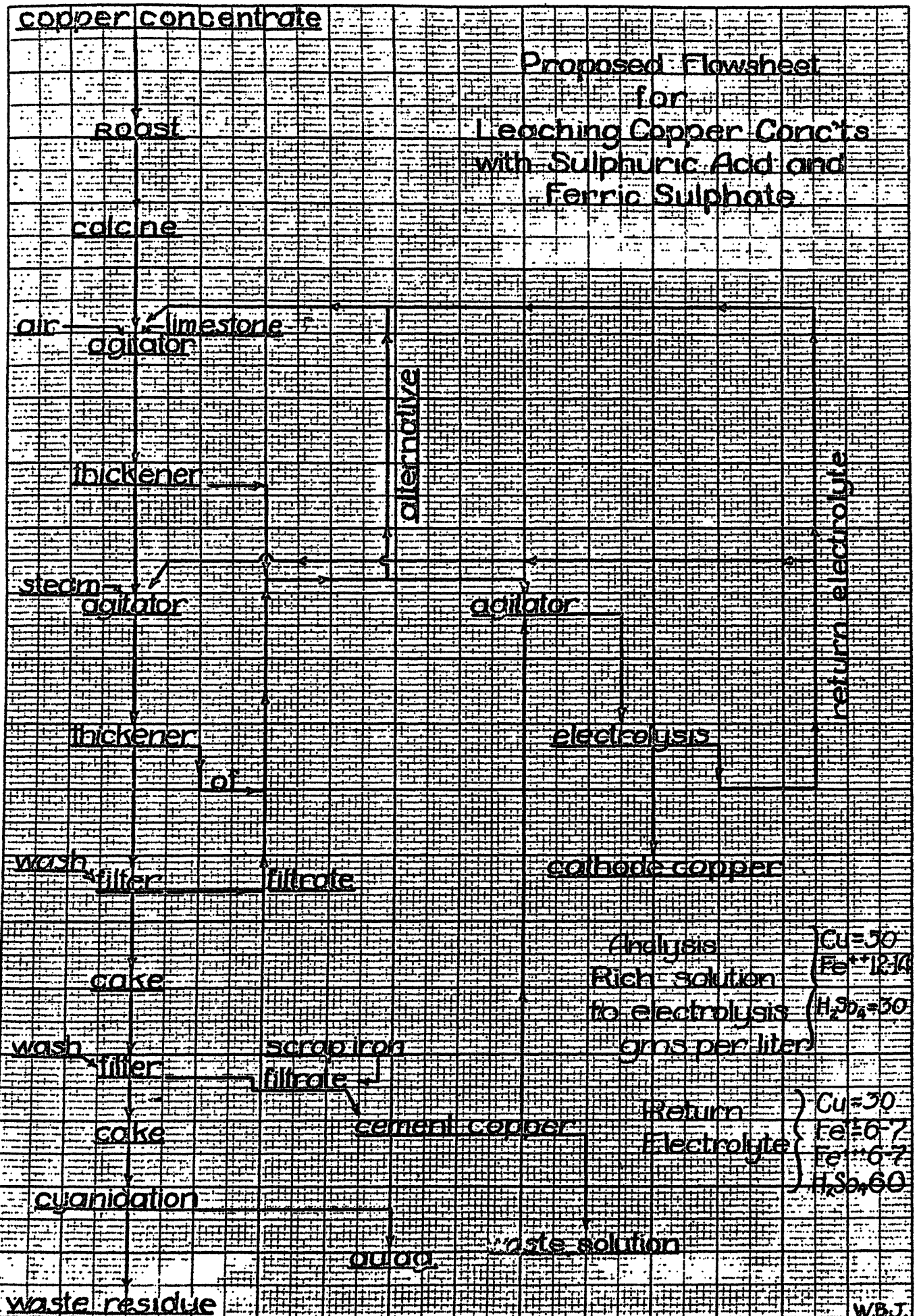
Table I Screen Analysis:

	<u>Lake City</u>	<u>Utah Copper</u>
- 35	2.0 %	0.0 %
- 35 - 48	3.0 %	2.0 %
- 48 - 65	2.0 %	7.5 %
- 65 - 100	4.0 %	10.5 %
- 100 - 150	8.3 %	11.0 %
- 150 - 200	15.4 %	11.5 %
- 200	76.2 %	57.5 %

Table II Quantitative Analysis:

	<u>Lake City</u>	<u>Utah Copper</u>
Copper	15.1 %	30.74 %
Zinc	4.1 %	
Lead	3.9 %	trace
Iron	24.1 %	25.40 %
Sulphur	34.1 %	29.30 %
Insol	11.6 %	8.30 %
Gold	0.04 oz	0.23 oz
Silver	11.60 oz	2.22 oz

FIG I



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ROASTING TESTS

Preliminary roasting was accomplished by means of a 25-volt, 170-ampere electric furnace. One thousand gram samples were roasted in a nichrome dish. Intermittent rabbling was performed by hand. Openings at both ends of the muffle permitted air circulation, which was kept as nearly constant as possible. Temperature was measured with a Wilson-Mauielen pyrometer, which was placed inside the nichrome dish just above the bed. The temperature of the muffle was controlled by means of an American transformer No. 31818. Samples were taken by hand at one-hour intervals and analyzed for copper and sulphur. Fifty-gram samples were then leached with water and 7 per cent sulphuric acid to determine the water-and acid-soluble copper, also to determine the progress of the roast. No record was kept on the water-soluble iron made in the roast, because the finishing temperature was sufficiently high to decompose any of these salts formed.

The major roasting tests were accomplished in an Nichols-Herreshoff laboratory roaster No. H-2728, containing a single hearth 13 inches in diameter. Rabbling was done by rabble arms, driven by suitable gears and an electric motor. These arms moved at a rate of two

revolutions per minute. Heating was accomplished by a nichrome electrical heating-element fastened to the top of the hearth.

The same procedure as outlined above was followed in making these tests. Samples were taken at shorter intervals, however, owing to increased rate of roasting. These samples were taken by placing a pan under the discharge opening during one complete revolution of the rabble arm.

No effort was made to make conditions in the laboratory too ideal. The concentrates were taken from their respective containers and placed directly in the roaster. In all these tests a bed of one inch or greater was maintained.

ASSAYS

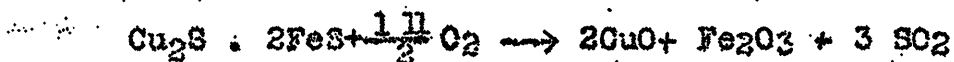
Analyses were made by the standard methods, copper being determined by the iodide method, and iron by the permanganate method. The methods for free acid, ferrous iron and total iron determinations of solutions may be found in Keffer's "Methods in Non-Ferrous Metallurgical Analysis". The copper content of the solutions was sometimes determined by a special fluoride method. The procedure was short and accurate. Duplicate

samples were run by this method, which was checked by the standard iodide method to determine its accuracy before it was adopted for general use.

Most of the analytical results check quite accurately. Every effort was made to make them do so, but slight discrepancies do occur in some instances, owing mainly to errors in solution volumes caused by evaporation and leakage.

RESULTS OF ROASTING TESTS

On roasting, chalcopyrite (CuFeS_2 or $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$) first loses one atom of sulphur, leaving $\text{Cu}_2\text{S} \cdot 2\text{FeS}$. This then roasts further:



Therefore, the copper remaining in the calcine as sulphide, is considered to be combined as $\text{Cu}_2\text{S} \cdot 2\text{FeS}$, rather than Cu_2S . Figuring on this basis each per cent of sulphide sulphur in the calcine will "tie up" 1.33 per cent of copper and 1.16 per cent of iron.

Following the first sulphur elimination, the roast proceeds as indicated by the above reaction. The concentrate gradually changes from a brassy yellow color to black (similar to the color of cupric oxide) (5). Upon continuous roasting it takes on a reddish tint, but after

(5) The color of copper oxide seems to dominate in this type of roast.

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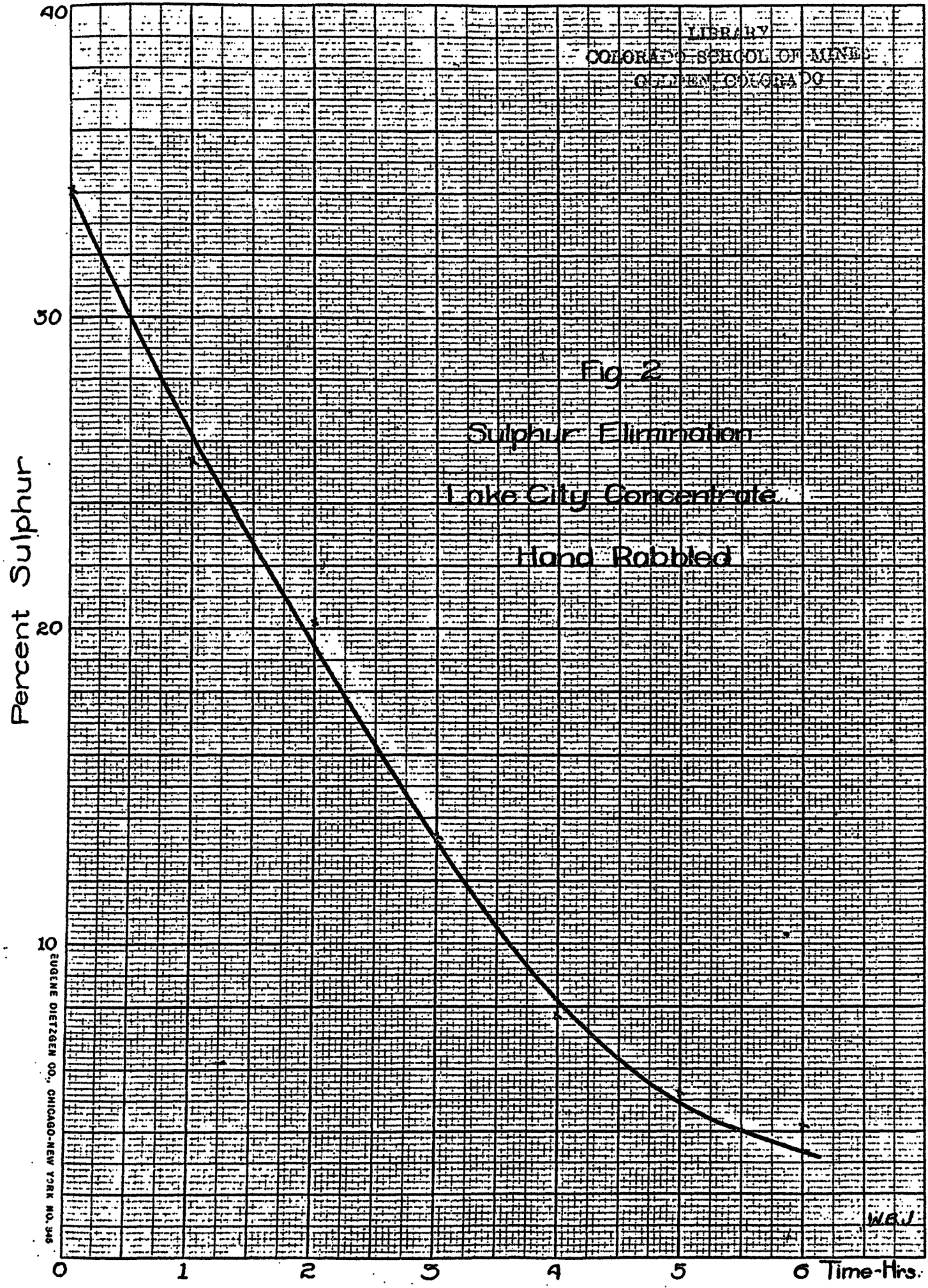
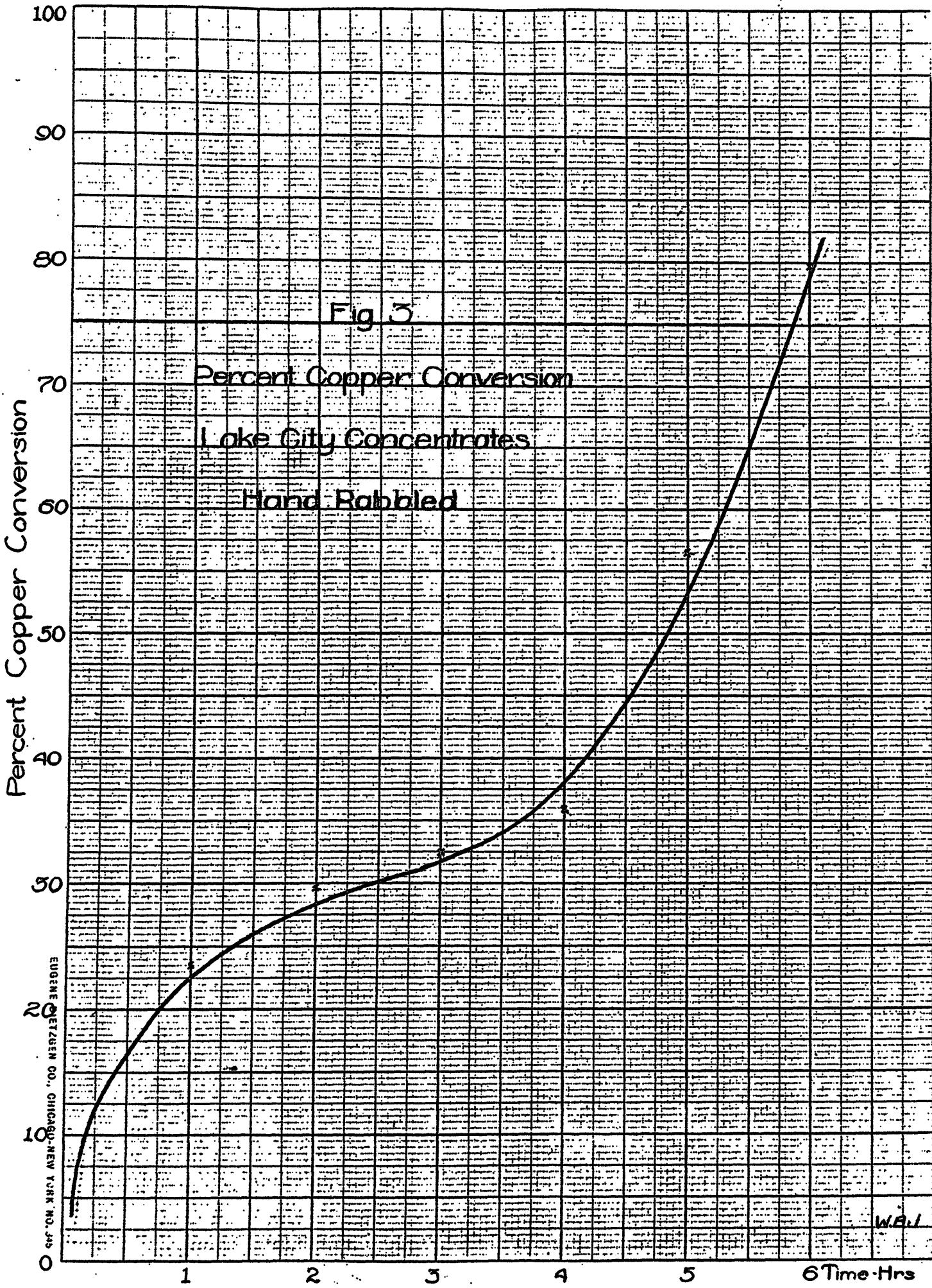


Fig. 2
Sulphur Elimination
Lake City Concentrate
Hand Robbled

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EUGENE GETZGEN CO., CHICAGO-NEW YORK NO. 445

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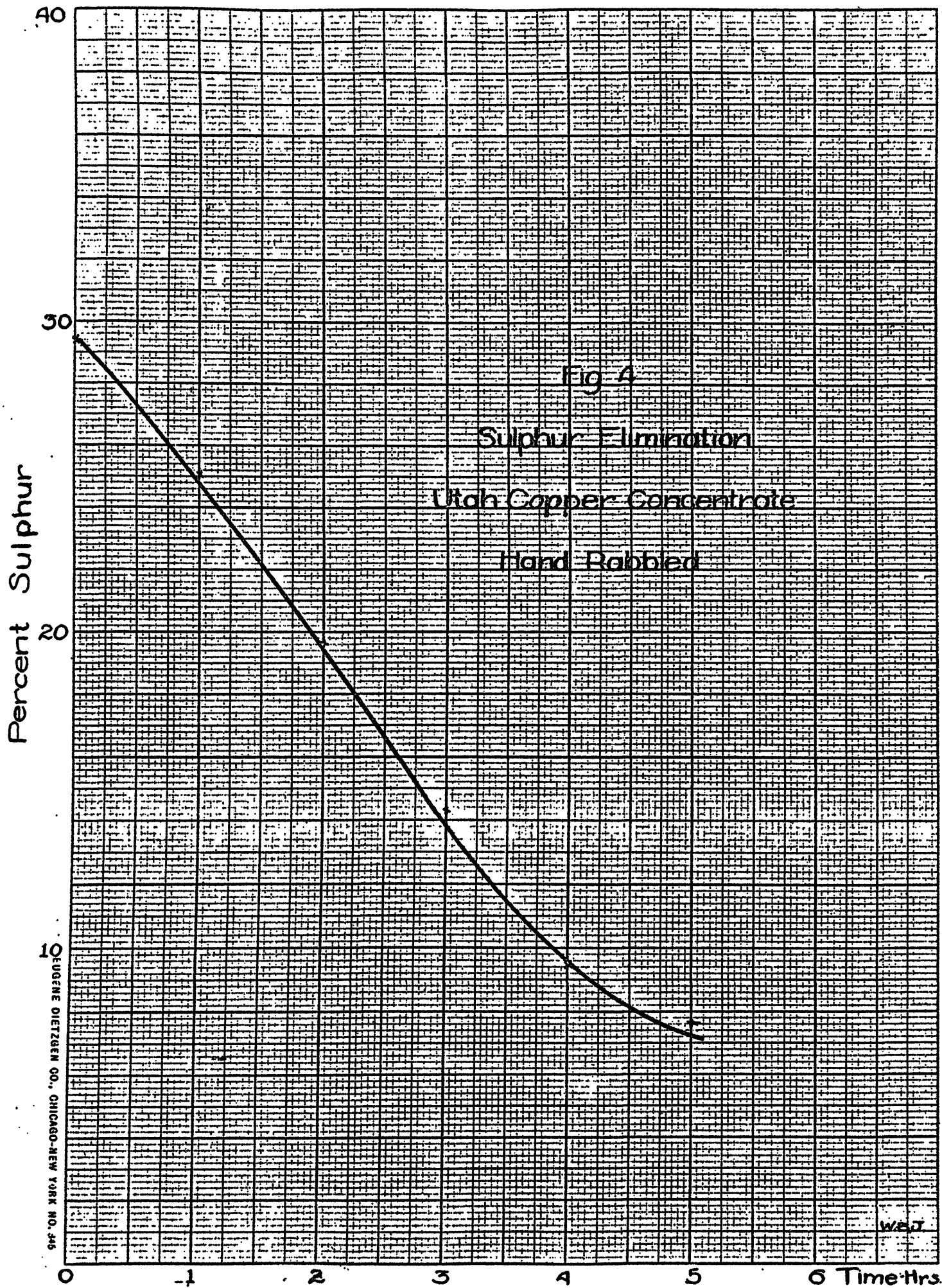


Fig 4

Sulphur Elimination

Utah Copper Concentrate

Hand Rabbled

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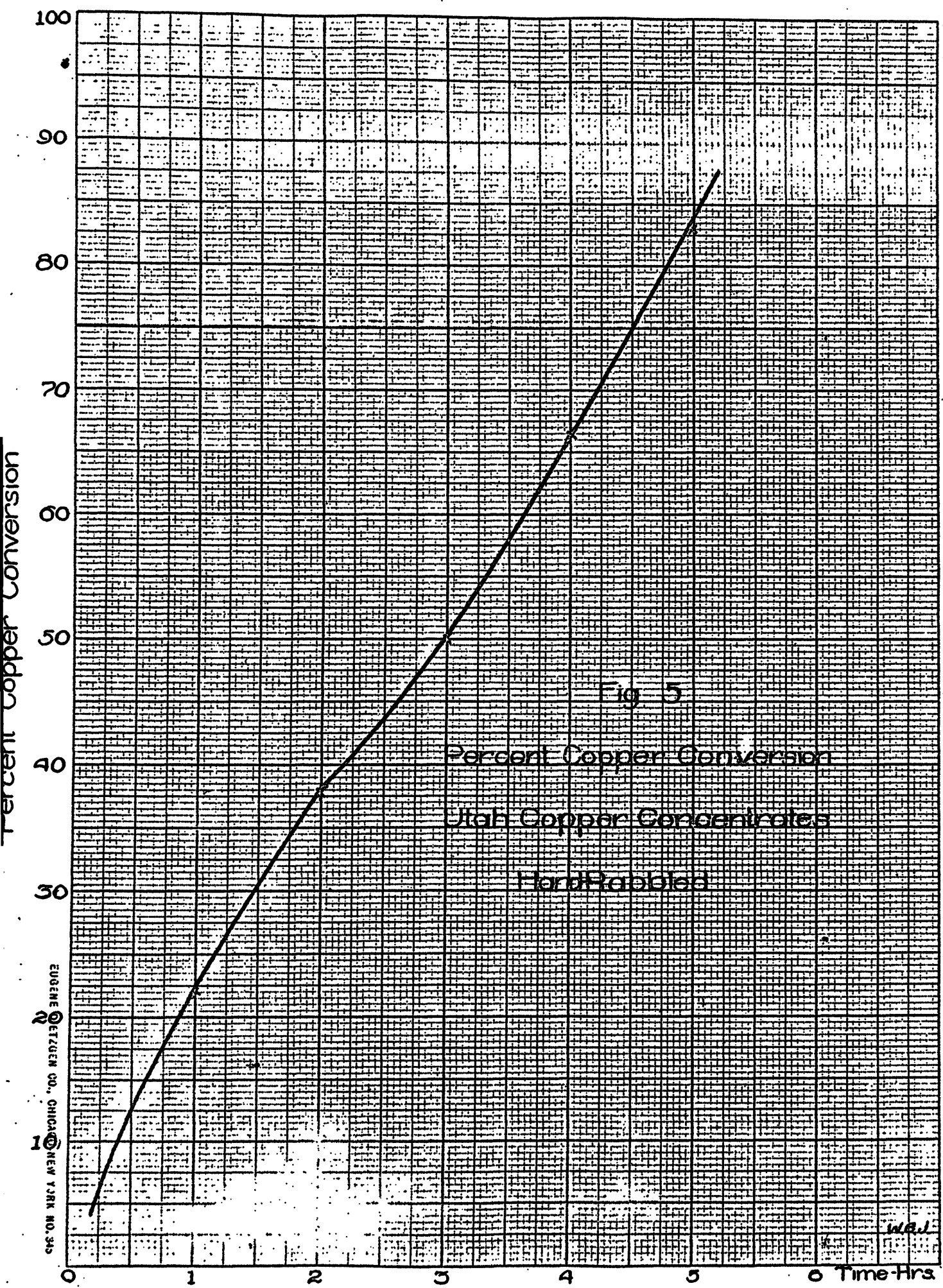


Fig 5

Percent Copper Conversion
Utah Copper Concentrates
Hard Rabbled

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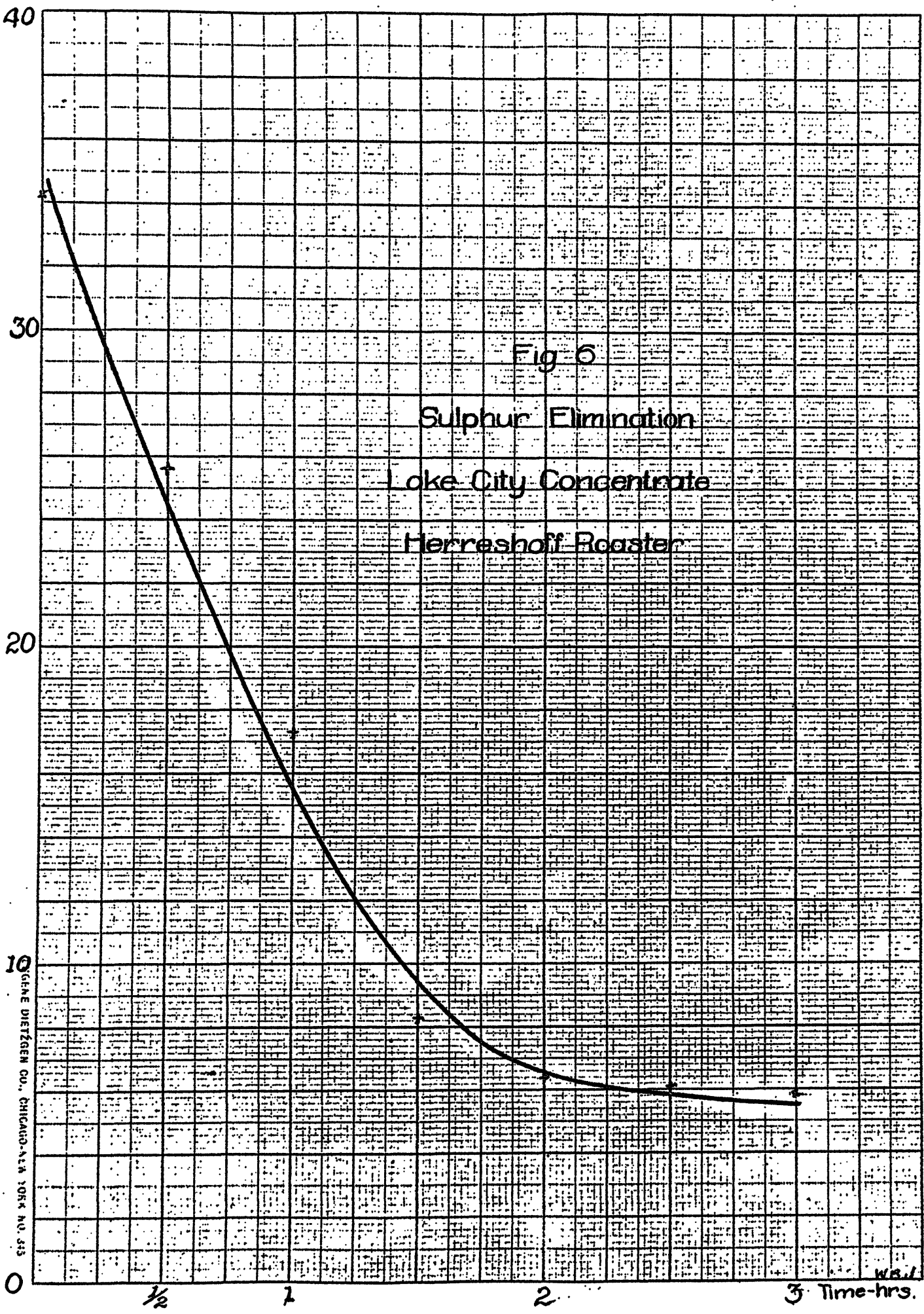


Fig 6

Sulphur Elimination

Lake City Concentrate

Herrshoff Roaster

Percent of Sulphur

GENE DIETZEN CO., CHICAGO-ALM YORK NO. 333

W.B.L.

Time-hrs.

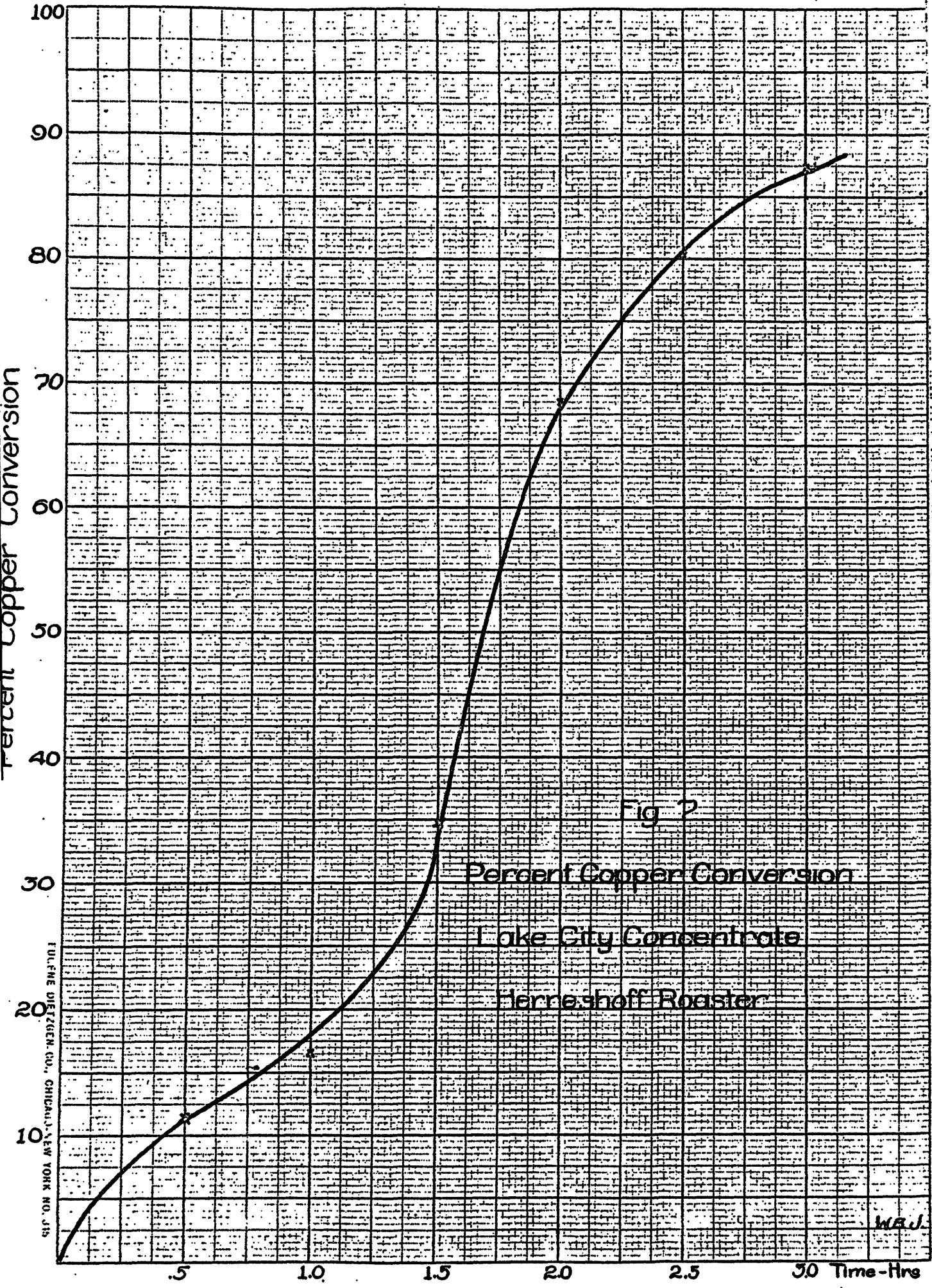


Fig 2

Percent Copper Conversion
Lake City Concentrate
Herreshoff Roaster

FULFIRE DIEZGEN CO., CHICAGO, NEW YORK NO. 315

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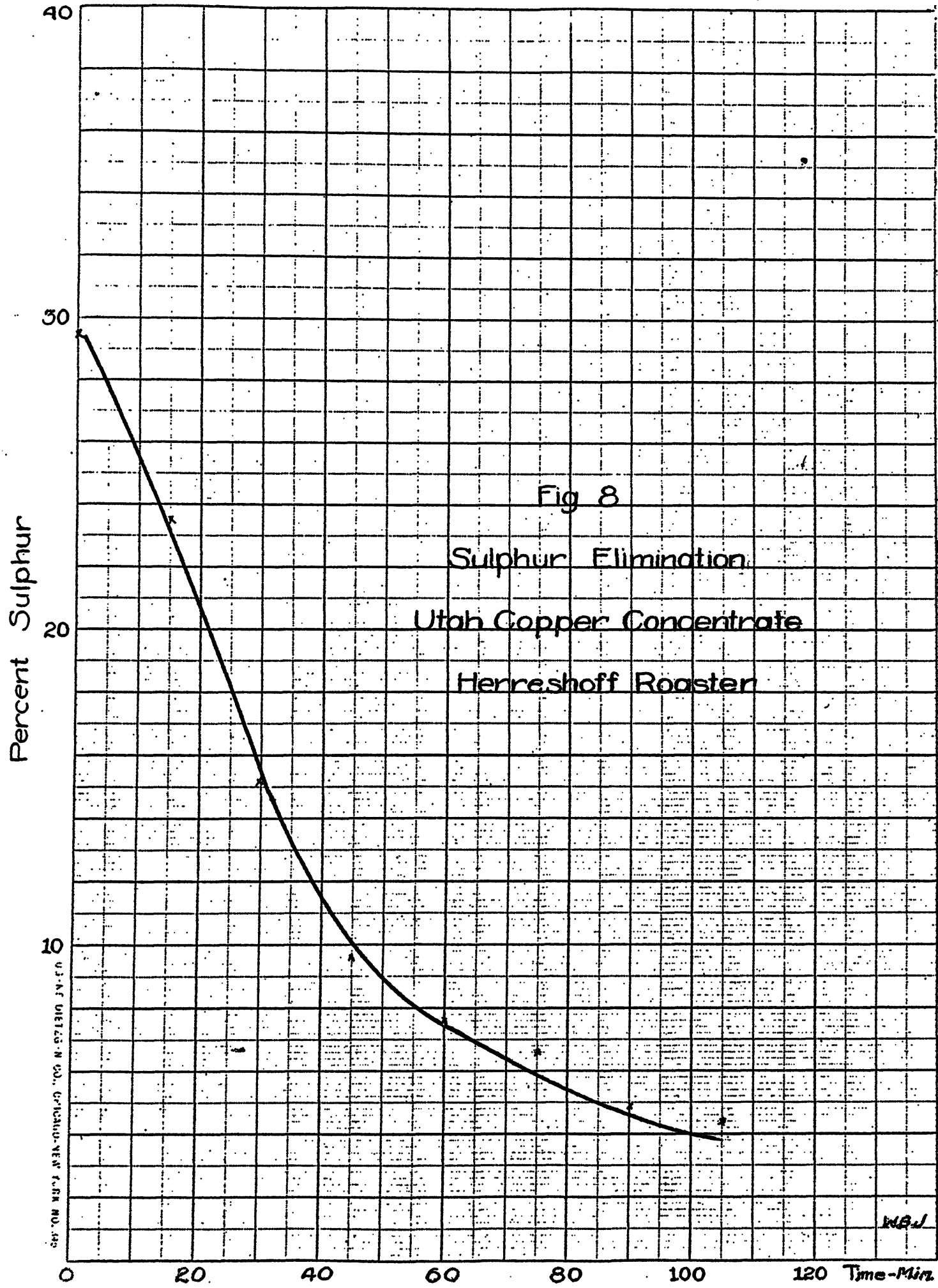


Fig 8

Sulphur Elimination

Utah Copper Concentrate

Herreshoff Roaster

U.S. PAT. OFFICE, WASHINGTON, D.C. 20540

W.B.J.

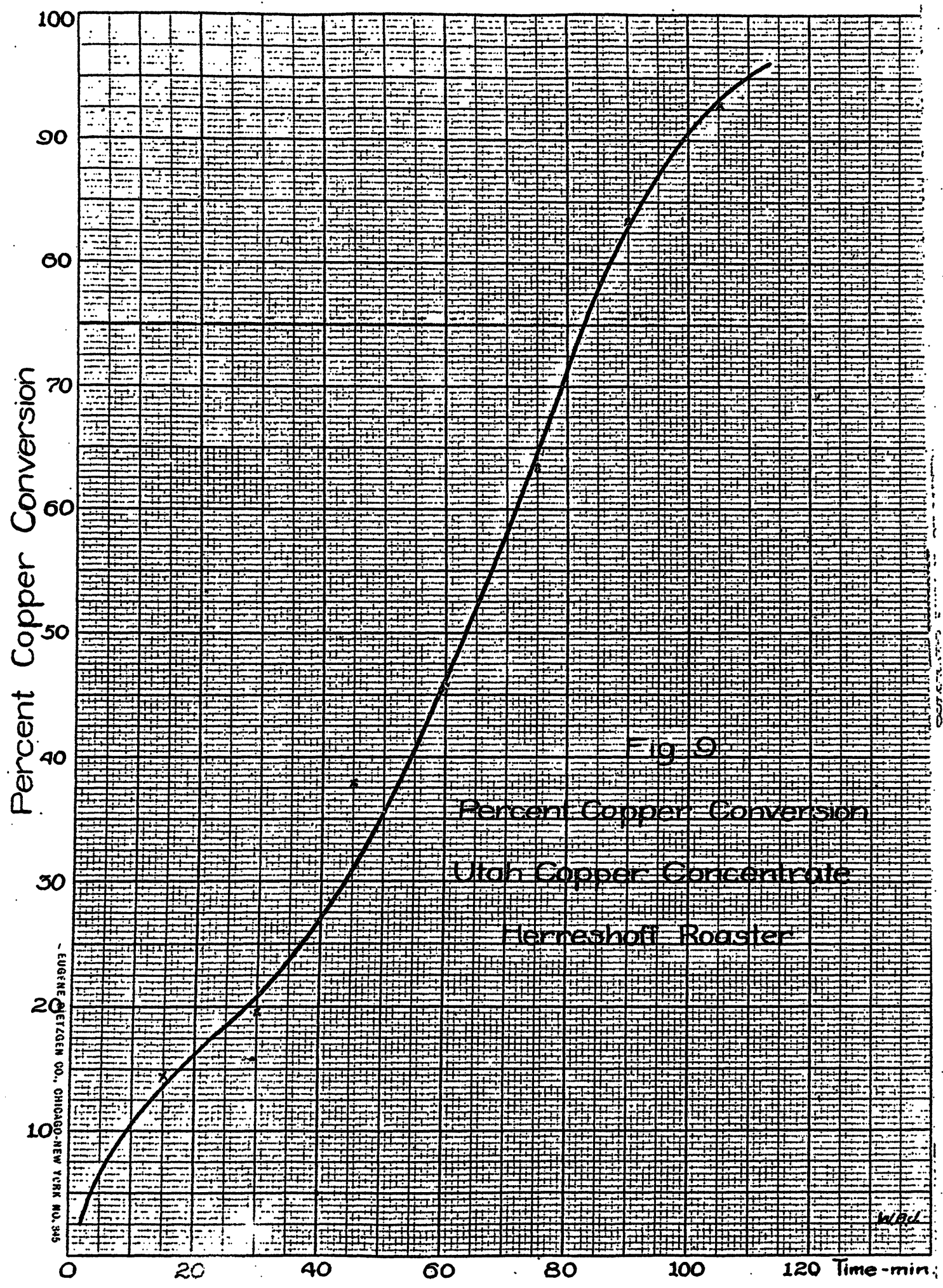


Fig. 9

Percent Copper Conversion
Utah Copper Concentrate
Ferrishoff Roaster

EUGENE GETZGEN CO., CHICAGO-NEW YORK NO. 345

Wibel

completion the dark color still predominates. If, however, the calcine is examined closely red iron oxide, (Fe_2O_3) may be seen. Leach tailings are composed mainly of this oxide and are distinctly red in color.

No direct evidence of the formation of copper ferrates was noted during these tests. Since the copper and the iron are combined in the concentrate, some ferrates are likely to be formed. No difficulty, however, has been met in leaching them.

The results prove that the water-soluble copper ($CuSO_4$) content of the calcine may be controlled by finishing the roast at or near $700^{\circ} C.$, and may be regulated by limiting the time the calcine is exposed to that temperature.

The chemistry of roasting will not be discussed in this report. It may be reviewed in any suitable textbook on Metallurgy. Thermodynamic calculations made on the reactions taking place show that this roast is practically self-sustaining. Temperature limitations make it necessary, however, to add some external fuel.

Figures 2 to 9 inclusive show the results of the roasting tests completed. The general trend of each individual curve is practically the same when the concentrate is hand rabbled as when it is roasted in the

mechanical roaster. The slope is, however, changed considerably and the time of roasting cut tremendously by mechanical roasting.

The sulphur elimination is very rapid at first and is nearly a straight-line function for both types of concentrate until about 65 per cent of the sulphur has been eliminated. At this point the slope changes materially and approaches the horizontal axis slowly.

The copper-conversion curves, however, show wide variations between the two different concentrates. The per cent conversion from the Utah copper concentrate is nearly a straight-line function until about 80 per cent of the copper has been converted, at which time the rate decreases, owing to the decreased rate of sulphur elimination. The irregularity in the rate of conversion of the copper in the Lake City concentrate is due primarily to the roasting of impurities (galena, sphalerite and pyrite).

When roasting concentrates for leaching purposes an effort was made to produce a calcine containing about 5 per cent of sulphide sulphur, which is near the point where the rate of sulphur elimination decreases materially. A large roaster tonnage per unit of time may then be obtained.

The concentrates decreased in weight when roasted with a corresponding increase in copper content. A slight dust loss was also suffered, but with adequate draft-control will not exceed 2 per cent. The decrease in weight during roasting depends upon the percentage of sulphur eliminated and the amount of sulphate copper remaining in the calcine. In general this loss of weight will be between 4 and 5 per cent of the total weight of concentrate charged.

The following tables show the results obtained from the roasting tests performed:

TABULATED RESULTS OF ROASTING TESTS

Table III. - Hand Rabbled:

<u>Time in hours.</u>	<u>Temperature degrees C.</u>	<u>Lake City</u>			<u>Utah Corner</u>		
		<u>%Cu</u>	<u>%S</u>	<u>%Cu conversion</u>	<u>%Cu</u>	<u>%S</u>	<u>%Cu con.</u>
0	275--325	15.1	34.1	0.0	30.74	29.3	0
1	325--450	16.2	25.4	23.5	31.8	25.3	22.0
2	450--525	17.0	20.3	29.5	32.5	19.6	37.5
3	525--575	17.8	13.4	32.5	33.4	14.3	50.0
4	575--650	18.2	7.7	36.0	34.5	9.4	66.5
5	650--700	18.7	5.3	57.5	32.8	7.8	83.0
6	650--700	17.6	3.5	79.5			

Table IV:

Lake City
Herreshoff Roaster.

<u>Time--hours</u>	<u>Temperature</u> <u>degrees C.</u>	<u>%Cu</u>	<u>%S</u>	<u>%Cu conversion</u>
0	300--375	15.1	34.1	0
.5	375--445	15.6	25.6	11.45
1.0	445--490	15.8	17.3	17.50
1.5	490--525	17.8	8.6	34.5
2.0	525--575	16.5	6.4	68.5
2.50	575--635	16.6	6.1	80.5
3.0	635--700	16.9	5.9	87.1

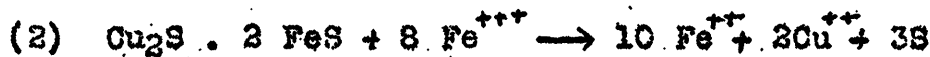
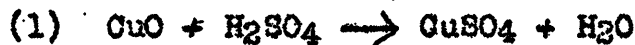
Table V:

Utah Copper
Herreshoff Roaster.

<u>Time--minutes</u>	<u>Temperature</u> <u>degrees C.</u>	<u>%Cu</u>	<u>%S</u>	<u>%Cu conversion</u>
0	300--350	30.74	29.6	0.0
15	350--400	32.70	23.5	14.5
30	400--450	34.10	13.1	19.5
45	450--500	33.60	9.6	37.9
60	500--550	33.10	7.6	45.5
75	550--600	32.60	6.6	63.4
90	600--650	32.50	4.8	83.5
105	650--700	31.90	4.4	92.6

LEACHING TESTS

The type of leach used in this investigation revolves around two fundamental reactions:



The first will proceed from left to right readily at the working temperature proposed for this work

(70- 80°C.). The latter will go as shown, but very little is known of the rate of this reaction.

Laboratory tests have shown that the acid concentration need not be high. In fact, highly concentrated acid dissolves large amounts of impurities, which probably would not dissolve if the acid concentration were kept fairly low. For this reason, plus the problem of neutralization in the "neutral leach", the strong solution used contained approximately 8 per cent of free acid.

The leach solution (return electrolyte) used in these tests had approximately the following analysis:

$\frac{Cu}{30}$	$\frac{Fe}{14}$	$\frac{H_2SO_4}{60}$	grams per liter
-----------------	-----------------	----------------------	-----------------

About 1.5 liters per 100 grams of calcine was used. This ratio was not constant, varying somewhat as the calcine analysis changed. Calculations based on Reaction given above, show that roughly 18 per cent of the solution would have to go to the "neutral leach" and the iron would have to be completely precipitated in order to insure iron control in the solution. (6)

As indicated by the general flow sheet (Figure 1) the calcine was leached in two steps, a "neutral leach" and an "acid leach". The object of the neutral leach is for purification of the solution. An attempt was made to precipitate enough iron in the neutral leach to compensate

(6) All the sulphide iron was not taken into solution, but the acid soluble iron just about compensated for this.

for the iron dissolved in the acid leach. Since the precipitated iron ($\text{Fe}(\text{OH})_3$) will also carry down arsenic and antimony (7) and the concentration of iron in the solution going to electrolysis must be limited, no further purification was attempted. The reduction of the ferric iron by cement copper ahead of electrolysis is, of course, very essential. See Figure 1.

The first tests were run in beakers, using compressed-air agitation in the "neutral leach" and intermittent hand-stirring in the "acid leach". Both were run hot ($65 - 85^\circ \text{C}$.) The leach solution was the return electrolyte from electrolytic tests, previously performed. The "neutral leach" was not very successful because the proportion of calcine used was not sufficient to bring about complete neutralization of electrolyte. The addition of a large excess of calcine did not solve this problem for the solution still contained 2 -- 3 grams of free acid per liter. Sufficient limestone (CaCO_3) was then added to complete neutralization. Some iron was precipitated, but not enough to insure that the iron in the solution could be controlled in this manner.

No trouble was encountered in the "acid leach". The recovery, however, was quite low (75 - 78 per cent). The lack of proper agitation in both cases no doubt lowered the overall efficiency of these tests. Sufficient

(7) Principles of Hydro-Metallurgy and Electro-deposition of metals. Thomas P. Campbell.

information, however, was obtained to continue on a somewhat larger scale.

The large scale leaching tests were made in small Dorr agitators (Figure 10). This leaching equipment was mounted on a table which was placed beside the electrolytic cell. An electrically heated boiler furnished steam under pressure for heating the solution. The complete installation was very flexible in that the flow of solids or liquids could be changed by simple hose connections.

Before continuing further it might be well to illustrate the composition of the calcines leached. Table VI gives an average composition of calcines resulting from roasting both types of concentrate.

Table VI:

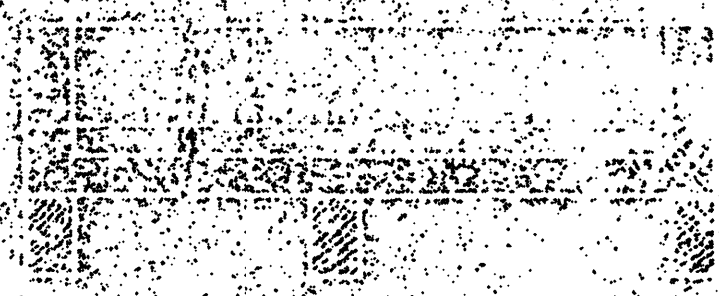
	<u>Lake City</u>	<u>Utah Copper</u>
Total copper:	18.5 per cent	32.5 per cent
Water-soluble copper:	3.0 per cent	4.0 per cent
Acid-soluble copper:	9.5 per cent	21.9 per cent
Total sulphur:	6.0 per cent	7.0 per cent
Sulphide sulphur:	4.5 per cent	5.0 per cent

RESULTS OF LEACHING TESTS

The results obtained from the large scale leaching tests were somewhat similar to those obtained from the beaker tests. They, however, did bring to light

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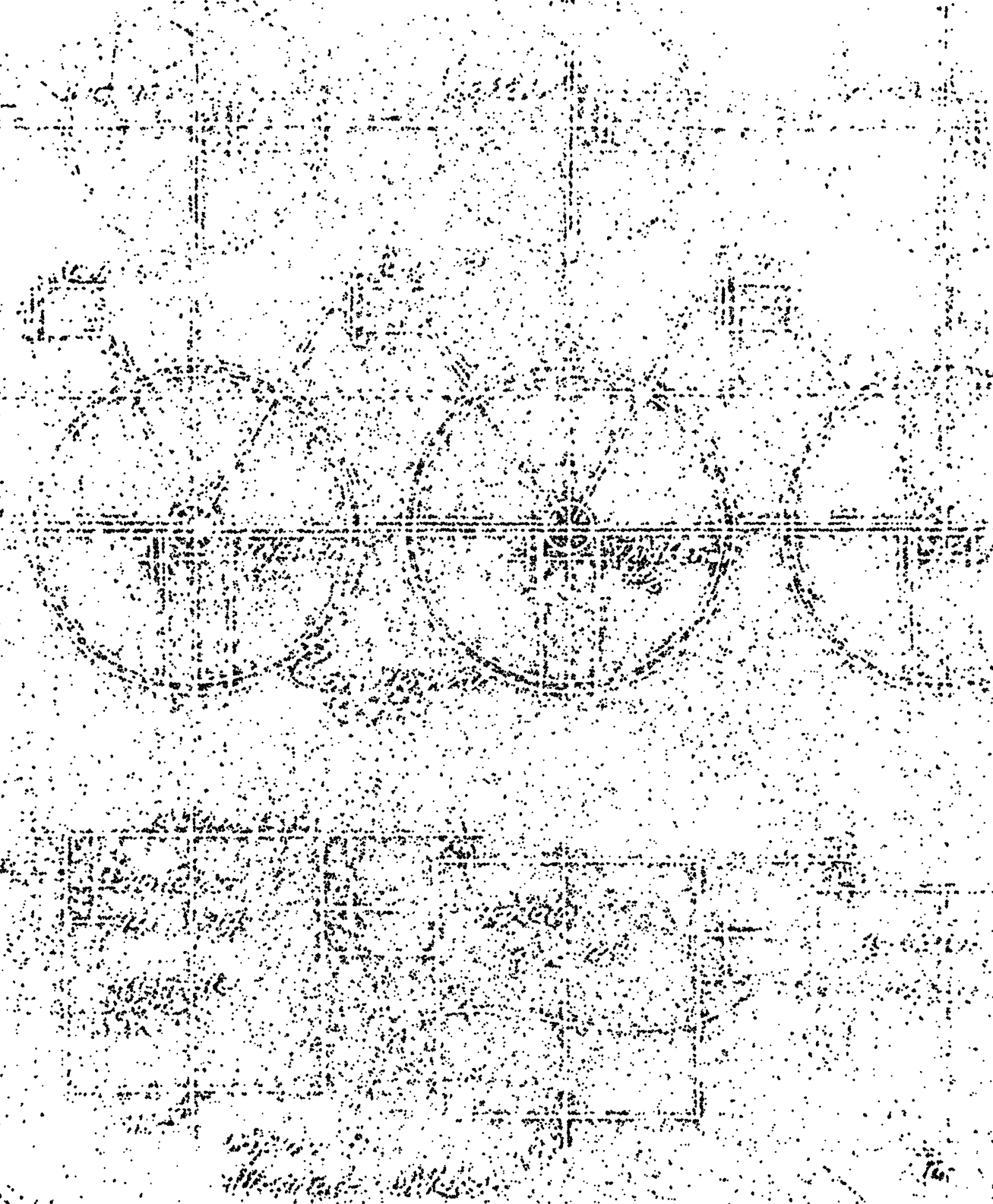
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16

three important facts. First, they proved conclusively that the electrolyte could be neutralized by a proper proportion of calcine but neutralization was not always certain (8). Second, the neutralized solution still contained iron, but the concentration was always less than that of the leach solution. Third, the remaining iron in the neutral solution was in the ferrous state.

Tests were then run to determine the acidity and general character of the calcines. The results of these tests showed the calcines were distinctly acid, and that from 25 to 120 pounds of lime (CaO) per ton of calcine was necessary to neutralize this primary acidity. This no doubt is an explanation for the troubles encountered in the "neutral leach". The Utah copper concentrates contained chlorides that caused considerable trouble in the electrolytic tests. The chlorides were completely eliminated in the basic wash.

Investigations as to the cause of only partial iron precipitation in the "neutral leach" show that a portion of the ferric iron in the leach solution was reduced by the action of sulphides, the resulting ferrous iron failing to precipitate. The following figures will illustrate this point: 30 liters of solution containing 27.5 grams of copper per liter, 14 grams of ferric iron.

(8) Neutralization was obtained at times, but the addition of limestone was necessary in a large percentage of tests run.

and 55.2 grams of free sulphuric acid, was neutralized with calcoine and limestone. The neutral solution contained, in grams per liter:

<u>copper</u>	<u>Fe⁺⁺</u>	<u>Fe⁺⁺⁺</u>	<u>H₂SO₄</u>
59.6	6.5	nil	nil

No actual data for recovery calculations were obtained from these tests, for the following reasons:

- (1) A large percentage of the solids were inadequately leached owing to the formation of a working bed at the bottom of the agitators.
- (2) The small agitators acted somewhat like thickeners, thereby preventing a uniform discharge.
- (3) Small, but continuous leaks prevented accurate volume measurements.

An attempt was made to make a continuous run of 24 hours or more in order to overcome the above mentioned difficulties. This was never accomplished, however, owing mainly to mechanical failures; that is, the small pumps would not handle the solids, and therefore continuous operation was impossible.

The failure to produce a pure solution in the "neutral leach" made certain changes in the flow sheet necessary. Since only a portion of the iron could be precipitated the percentage of solution going to the neutral leach had to be increased from 10 per cent to

50 per cent. Also it was necessary to neutralize the primary acid salts contained in the calcines ahead of the "neutral leach". With this information available, tests were run in lead pachuca tanks, from which a balance of all products could be obtained.

TABULATED RESULTS OF LEACHING TESTS

Table VII:

Utah Copper Calcine

	I	II
Analysis of calcine, copper	32.5 %	32.5 %
iron	27.1 %	27.1 %
Total copper soluble in H ₂ O	4.8 %	4.8 %
Total sulphur	7.6 %	7.6 %
Sulphide sulphur	5.3 %	5.3 %
Grams of calcine, leached	4000	2000
Weight of "tails" --grams	1985	965
Analysis of "tails" --copper	10.9 %	11.5 %
Iron	32.0 %	31.0
Gold	0.28 oz	0.25oz./T
Silver	5.05 oz	4.00oz./T
Extraction of copper (total)	83.4 %	83.00%
Extraction of acid sol. copper	75.3	75.4 %
Extraction Sulphide copper	8.1	7.7

Table VIII:

Utah Copper

Solution Analysis. Grams per liter

Test # I.

	<u>Volume</u>	<u>Copper</u>	<u>Iron</u> (total)	<u>Fe⁺⁺</u>	<u>Fe⁺⁺⁺</u>	<u>H₂SO₄</u>
"neutral leach"	15lit.	25.6	11.85	6.5	5.35	56.4
"acid leach"	15lit.					
From neut.leach	16.0	58.8	8.48	8.3	nil	nil
Combined acid and neutral	33.0	56.2	11.02	9.8	1.23	23.4
Cement Cu from filtrate		5grams				
Extraction		84.1%				

Table IX:

Utah Copper

Test # II.

	<u>Volume</u>	<u>Copper</u>	<u>Iron</u> (total)	<u>Fe⁺⁺</u>	<u>Fe⁺⁺⁺</u>	<u>H₂SO₄</u>
"neutral leach"	15lit.)	33.1	13.65	7.4	6.25	47.3
"acid leach"	15lit.)					
From neut.leach	15.8	52.1	9.7	9.4	tr.	nil
Combined acid and neutral	34.0	45.3	13.1	12.4	0.70	11.4
Cement Cu from filtrate		nil				
Extraction		84. %				

Table X:

Lake City Calcine

Analysis of Calcine, copper	18.5 per cent
Total Copper soluble in H ₂ O	3.5 per cent
Total sulphur	6.7 per cent
Sulphide sulphur	5.0 per cent
Grams of calcine leached	3000 grams
Weight of "tails"	1520
Analysis of "tails" copper	8.9 per cent
Extraction of copper	73.8 per cent
Extraction of acid soluble copper	64.0 per cent
Extraction of Sulphide copper	9.8 per cent

Table XI:

Lake CitySolution Analysis. Grams per liter.

	<u>Volume</u>	<u>Copper</u>	<u>Iron</u> (total)	<u>Fe</u>	<u>Fe</u>	<u>H₂SO₄</u>
"neutral leach"	12	20.3	12.1	5.1	7.0	43.2
"acid leach"	12	20.3	12.1	5.1	7.0	43.2
From neut. leach	13.5	32.7	8.7	8.6	tr.	nil
Combined acid and neutral	26.0		12.72	12.5	.82	10.6
Cement from filtrate		nil				
Extraction		nil				

The "neutral leach" required about 90 minutes; while the "acid leach" was run for three hours. The pulp was agitated by air in the "neutral leach" and by steam in the "acid leach". The temperature of the leach solution at the start of the neutral leach was approximately 65° C. while a temperature of about 85° C. was maintained

in the "acid leach".

The overall extraction of copper is rather low. This is due primarily to the low sulphide extraction, which could probably be increased by increasing the time of leach. Also continuous operation would no doubt increase the extraction. One other method that suggests itself is to recover the sulphides in the leach residue by flotation and return them to the roaster department. Time has not permitted experimental work in this connection, but it will be tried in the near future.

Approximately 40 per cent of the gold in the concentrate went into solution. This gold loss caused considerable alarm until it was finally traced to the solution. Allowing the solution to circulate through a bed of cement copper was sufficient to precipitate the gold. This method of gold recovery would probably be uneconomical; therefore, recovery of the gold and silver by cyanidation ahead of roasting has been suggested. Tests of this nature are being run at the present time, but so far no data are available.

ELECTROLYSIS

"The principle of the electrolytic deposition of copper may be illustrated by the following reaction":
$$\text{CuSO}_4 + \text{H}_2\text{O} + (\text{current}) \longrightarrow \text{Cu (cathode)} + \text{O (anode)} + \text{H}_2\text{SO}_4$$

Therefore for every pound of copper deposited, an equivalent amount of acid will be regenerated.

As mentioned previously in this report, the presence of iron in a copper electrolyte will lower the current efficiency. If ferrous iron is present it will be oxidized at the anode by the following reaction:



The resulting ferric iron will then react with the copper already deposited on the cathode, thereby lowering the current efficiency.



The preliminary work on electrolysis was done in solutions made from pure salts of copper and iron. Solutions containing approximately 50 grams of copper per liter, with varying amounts of iron and free sulphuric acid were electrolyzed in battery jars having a capacity of 3.5 liters. Insoluble lead anodes (1 1/2" x 7 1/2" x 1/4") and aluminum cathodes (2 1/4" x 8" x 1/8") were used. Three battery jars and the necessary electrodes were supported in a wooden frame. (Figure 11). The electrodes were held tightly in place by the framework and were spaced equally (one inch) so that the R I drop would represent chiefly solution resistance.

The current was furnished by a small motor

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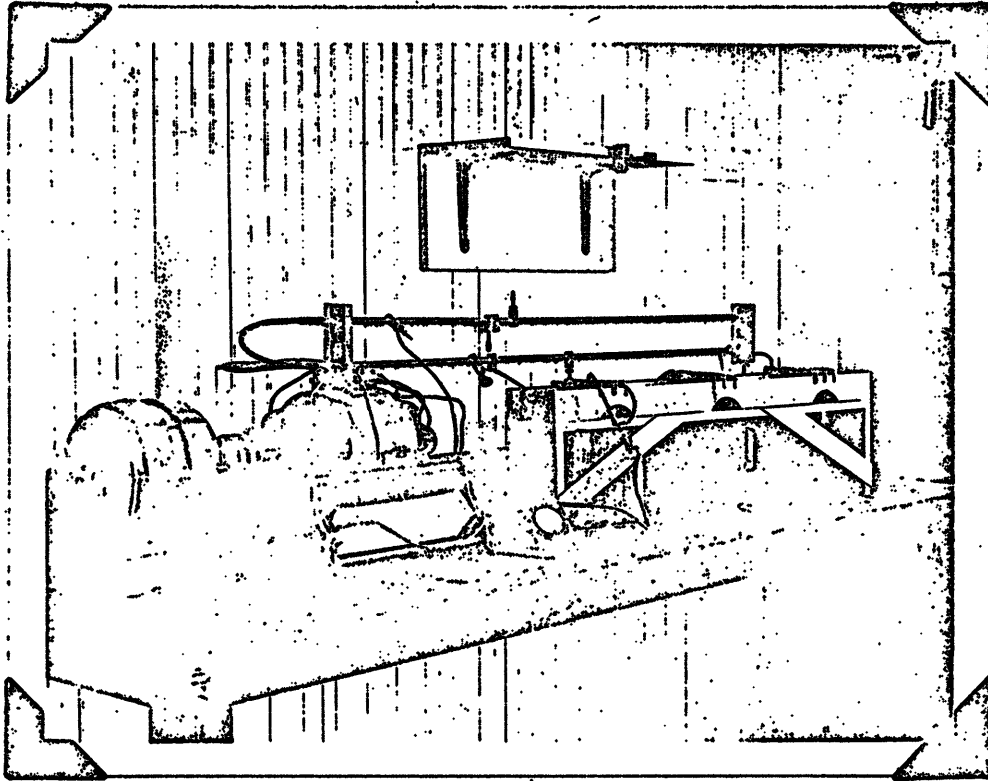


Figure 11: Layout of apparatus
for small scale laboratory elec-
trolysis.

generator set. The electrodes were connected in series to insure constant current conditions in all three cells. The current was measured by a Western Electric D.C. ammeter placed in the circuit. The voltage drop between electrodes was measured by a Western Electric D.C. voltmeter. The current density was approximately 15 amperes per square foot of cathode surface.

RESULTS OF ELECTROLYSIS

The results of the preliminary electrolytic tests are summarized in the following tables:

Table XII:

<u>Time</u>	<u>Line I</u>	<u>Cell Volts</u>		
		<u>1</u>	<u>2</u>	<u>3</u>
1:00 P.M.	3.0	1.92	1.95	1.90
1:30 P.M.	3.2	1.95	1.95	1.91
2:00 P.M.	3.0	1.93	1.97	1.93
2:30 P.M.	3.0	1.94	1.94	1.93
3:00 P.M.	2.8	1.93	1.95	1.95
3:30 P.M.	2.6	1.96	2.00	1.95
4:00 P.M.	2.7	1.96	2.00	1.95
4:30 P.M.	2.6	1.90	1.97	1.90
6:30 P.M.	3.0	1.90	2.02	1.88
10:00 P.M.	2.8	1.97	1.94	1.88
8:30 A.M.	3.0	1.95	2.02	1.88
9:00 A.M.	3.1	1.94	2.04	1.90
9:30 A.M.	3.1	1.94	2.03	1.92
10:00 A.M.	3.1	1.96	2.06	1.92
10:30 A.M.	3.0	1.97	2.06	1.87
11:00 A.M.	3.2	1.95	2.02	1.87
11:30 A.M.	3.2	2.00	2.00	1.88
12:00 A.M.	3.2	1.95	2.04	1.92
12:30 A.M.	3.2	2.00	2.02	1.93
1:00 P.M.	3.2	1.96	2.02	1.90
24 hours	3.0	1.95	2.00	1.90

	<u>Cells</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
Weight of cathodes at end	278.7	273.8	273.7
Weight of cathodes at start	<u>202.1</u>	<u>198.2</u>	<u>198.8</u>
Weight of copper deposited (grams)	76.6	75.6	73.9

Ampere-hours consumed = 72.0

Weight of copper theoretically deposited = 85.40

	<u>1</u>	<u>2</u>	<u>3</u>
Current efficiency, each cell	89.7 %	88.5	86.6
Kilowatt hours per ton copper deposited	1672	1730	1682

	<u>1</u>		<u>2</u>		<u>3</u>	
	<u>Cu</u>	<u>Fe</u>	<u>Cu</u>	<u>Fe</u>	<u>Cu</u>	<u>Fe</u>
Analysis of solutions at start	51.0	8.2	49.6	9.9	49.8	11.9
Analysis of solutions at end	29.2	8.2	26.1	10.1	28.6	12.1
Grams of iron oxidized		7.0		9.0		10.5
Sulphuric acid, start	101.2		98.6		97.8	
Sulphuric acid, end	133.8		131.2		129.3	

The copper deposit during the first few hours was firm and smooth, but later became rough, owing to depletion of copper and lack of circulation. All three cells gassed freely at the anodes.

Table XIII:

Time	Line I	Cell Volts			Temperature ° C.		
		1	2	3	1	2	3
10:00 A.M.	2.6	2.15	2.2	2.16	19	19	19
10:30 A.M.	3.0	1.99	1.97	1.95			
11:00 A.M.	2.9	1.98	1.95	1.92	19	19.5	20
11:30 A.M.	2.9	1.97	1.93	1.90			
12:00 A.M.	2.9	1.98	1.90	1.87	20.5	21	22
12:30 P.M.	3.0	1.96	1.94	1.92			
1:00 P.M.	3.2	1.99	1.94	1.94	20.5	21	23
2:00 P.M.	3.0	1.97	1.93	1.91			
3:00 P.M.	3.1	2.00	1.95	1.94	21.0	22	23.5
4:00 P.M.	3.0	1.95	1.96	1.97			
5:00 P.M.	3.2	1.96	1.94	1.94	22	22	24.0
6:00 P.M.	3.0	2.00	1.96	1.92			
8:00 P.M.	3.0	1.97	2.00	2.00	18.7	18.7	23
9:00 P.M.	3.0	1.97	1.97	1.94	20.0	20.0	23.0
10:00 A.M.	2.9	1.95	2.00	2.00	21.5	21.5	23.0
24 hours	3.06	1.988	1.957	1.93			

Weight of cathodes at end	275.7	271.5	270.8
Weight of cathodes at start	202.5	198.7	199.8
Weight of copper deposited	73.2	72.8	71.0

Ampere-hours consumed = 73.44

Copper theoretically deposited = 87.10 grams

Current efficiency each cell	84.0%	83.7%	81.5%
Kilowatt hours per ton Cu deposited	1810	1795	1815

	1		2		3	
	Cu	Fe	Cu	Fe	Cu	Fe
analysis of solutions, start	34.5	10.7	34.2	12.7	35.0	14.3
analysis of solutions, end	15.5	10.9	15.5	12.8	16.10	14.4
grams of iron oxidized		9.4		10.7		12.3
sulphuric acid(grams/liter, start		73.4		74.6		73.9
sulphuric acid(grams/liter, end		105.4		104.7		104.2

The copper deposit was smooth and uniform for a few hours, then became quite rough, owing to the low copper concentration in the solutions, and lack of circulation.

Table XIV:

Time	Line I	<u>Cell Volts</u>		
		<u>1</u>	<u>2</u>	<u>3</u>
11:00 A.M.	3.0	2.00	1.95	1.97
11:30 A.M.	2.5	1.98	1.94	1.95
12:00 A.M.	2.7	2.00	1.97	1.97
1:00 P.M.	2.9	2.01	1.98	1.98
2:00 P.M.	2.7	2.00	1.97	1.97
3:00 P.M.	2.7	2.00	1.98	1.98
4:00 P.M.	2.9	2.00	1.97	1.95
5:00 P.M.	3.0	2.00	1.97	1.95
7:30 P.M.	3.6	2.02	2.00	2.00
9:00 P.M.	3.6	2.02	2.00	2.00
12:00 P.M.	3.2			
6:00 A.M.	3.2			
10:00 A.M.	3.0	2.02	1.97	1.97
11:00 A.M.	2.9	2.00	1.95	1.97
24 hours	3.14	2.02	1.99	1.99

	<u>Cells</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
Weight of cathodes at end	277.0	273.5	272.5
Weight of cathodes at start	202.2	198.4	199.3
	74.8	75.1	73.2

Ampere-hours consumed = 75.35

Copper theoretically deposited = 89.37

Current efficiency, each cell	83.75 %	84.1 %	81.9 %
Kilowatt hours per ton of Cu	1832	1825	1875

	<u>Cu</u> ¹	<u>Fe</u>	<u>Cu</u> ²	<u>Fe</u>	<u>Cu</u> ³	<u>Fe</u>
Analysis of solutions each cell start	3.5	8.2	35.5	10.3	35.6	11.9
Analysis of solutions each cell end	16.1	8.4	16.9	10.5	17.8	12.2
Grams of iron oxidized		7.0		8.6		9.9
Sulphuric acid, start		34.2		35.1		34.7
Sulphuric acid, end		63.8		62.6		61.1

The copper deposit was firm and smooth until a few hours before the current was cut off.

DISCUSSION OF RESULTS OF SMALL SCALE ELECTROLYSIS

The above data would indicate that a good grade of copper may be deposited from solutions containing as high as 14 grams of ferrous iron per liter. With proper circulation and copper concentration the copper deposit will be firm and pure. The copper content of the solution (return electrolyte) should be kept at or near 30 grams per liter.

The high iron concentration (10-14 grams per liter) reduces the current efficiency to between 80 and 83 per cent. The power consumption varies somewhat with the iron concentration, but is not excessive even with 14 grams of iron per liter (9)

(9) The power consumptions given in the above tables will be increased to between 2300 and 2400 kilowatts if the drop in all electrical connections is taken into consideration.

The voltage drop between electrodes is decreased slightly with increased iron concentration and increased temperature. This explains the slight differences in power consumption with different amounts of iron in solution.

All cells gassed freely, but no difference was noticeable between the 3 cells.

The results indicate that about 20 grams of copper per liter will have to be deposited to insure efficient oxidation of the contained iron.

Re-solution of the copper was not noticeable. No corrosion of lead anodes could be noted.

LARGE SCALE LABORATORY ELECTROLYSIS

The large scale tests were run in a concrete tank (7'1 x 13" d x 9"w) lined with 7-pound lead. (Figure 10) The lead lining was painted with acid proof asphalt. The capacity of the tank was about 120 liters with electrodes in place.

The solution used in the first test was prepared as in the small scale tests. This solution contained (grams per liter):

<u>Cu</u>	<u>Fe(total)</u>	<u>Fe</u>	<u>H₂SO₄</u>	<u>Glue</u>
46.6	13.7	nil	38.0	5 m.g.

The electrodes were arranged in three groups containing 8 aluminum cathodes (6" by 13" x 1/8") and

9 lead anodes (5" x 12" x $\frac{1}{4}$ "). These electrodes were connected in multiple. The electrode spacing (anode to cathode) was 1 $\frac{7}{16}$ inches. The current density was approximately 15 amperes per square foot of submerged cathode surface.

The electrolyte was circulated at the rate of about 4 gallons per hour by means of a small diaphragm pump.

A continuous run of 16 hours was made. A very good copper deposit was obtained, being firm, smooth and having a good color. Frequent shorting between the cathodes and tank lining caused the cell voltage to fluctuate so that accurate determinations of current efficiency and power consumption could not be made.

The solution at the end of the run contained (grams per liter):

<u>Cu</u>	<u>Fe(total)</u>	<u>Fe⁺⁺</u>	<u>Fe⁺⁺⁺</u>	<u>H₂SO₄</u>
25.7	13.7	3.4	9.3	36.1

Slight evidence of copper re-solution was noticeable on a number of the cathodes.

The ferric iron in this solution was reduced by circulating it over elemental copper. A portion of the solution was then "bled off" and the copper deficiency made up by adding rich solution obtained from leaching tests. This solution was then electrolyzed. Considerable

difficulty was encountered, however, and the test was discontinued before any data could be collected. The cathodes gassed freely and upon lifting, examination showed that they were being attacked by the solution. A qualitative analysis was then made of the solution, resulting in the finding of chlorides (10) What little copper deposited was red and pulverulent.

This solution was then circulated over cement copper to lower the chloride concentration. The solution was then electrolyzed, using amalgamated copper cathodes. The conditions were the same as given above with one exception: the electrodes were connected in parallel to eliminate shorting with the cell lining. The following data show the results obtained:

Table XV:

<u>Time</u>	<u>Line I</u>	<u>Volts</u>	<u>Temperature ° C.</u>
1:00	370	3.05	19
1:30	370	3.90	22
2:00	370	3.80	24
2:30	390	3.80	25
3:00	360	2.80	26
3:30	360	3.60	28.5
4:00	360	3.60	29.2
4:30	360	2.60	31.0
5:00	360	2.50	32.0
4 hours	388	2.7	

Weight of 25 cathodes (wet) at end	=	40,620 grams
Weight of 25 cathodes (wet) at start	=	39,104 grams
Weight of copper deposited	=	1,516 grams
Weight of copper theoretically depos.	=	1,737 grams

(10) The presence of chlorides and their elimination was mentioned in connection with leaching.

Current efficiency = 87.3 %
 Kilowatt hours per ton of Cu = 2360

Table XVI:

Analysis of solution for the above test (grams per liter):

<u>Time</u>	<u>Cu</u>	<u>Fe(total)</u>	<u>Fe⁺⁺</u>	<u>Fe⁺⁺⁺</u>	<u>H₂SO₄</u>	<u>Glue</u>
1:00 P.M.	35.3	11.9	11.9	nil	26.0	5 m.g.
2:00 P.M.	29.1	11.6	9.8	2.1	34.5	5 m.g.
3:00 P.M.	25.0	11.9	8.5	3.4	38.6	
4:00 P.M.	22.8	11.6	7.2	4.7	42.5	
5:00 P.M.	20.3	11.9	6.8	5.1	46.8	

DISCUSSION OF RESULTS OF LARGE SCALE ELECTROLYTIC TESTS

The results of these tests check rather closely those obtained from the smaller tests. The potential between electrodes averaged 2.3 volts as compared to the line voltage of 2.7. This, plus greater distance between electrodes, accounts for the increased power consumption over that indicated from small tests. Slight evidence of re-solution of the copper was noted in these large scale tests.

TREATMENT OF TAILING

As outlined by the general flow sheet (Figure 1) the contemplated method of gold and silver recovery from the leach tailing is cyanidation. Time has not permitted

* The efficiency shown here seems rather high. An error due to mercury loss in the cell from the freshly amalgamated cathodes seems likely.

work of this nature. The high copper content of the present tailing indicates that the cyanide consumption would be relatively high.

ECONOMIC CONSIDERATIONS

In order to determine whether a process of this kind is economical, a careful investigation of the cost involved must be made, and it compared with the cost of producing electrolytic copper by present methods. This, however, is difficult to do owing to the lack of cost data. If the operating costs of similar processes are taken into consideration a fair estimate may, however, be made. The following figures illustrate this point.

In 1929, after deducting all mining, milling and transportation costs, which include all fixed, general and maintenance charges except federal taxes, the cost of the concentrate produced was about \$31.40 per ton. This amounts to approximately 5.1¢ per pound of contained copper (31 %). Assuming a 100-ton plant and a total cost of leaching and electrolysis (90 % extraction) of 2.5¢ per pound of cathode copper produced, the total cost of electrolytic copper at the plant would then be: 7.6¢ per pound. Then if the copper is credited with the gold and silver values in the concentrate (figuring 90 % extraction at a cost of \$1.50 per ton)

the net cost of copper before taxes would be approximately 7.1¢ per pound, which is considerably lower than the present cost.

The estimated treatment charge of 2.5¢ per pound was figured in the following manner:

Table XVIII:

Cost per ton of cathode copper at 100 tons daily capacity.

Roasting---\$1.50 per ton concentrate	5.38
Labor--- one-man shift per ton of copper	5.00
Superintendency and control	0.10
Maintenance and supplies	0.10
Power (2400 kwh. @ 0.4¢)	9.60
Fixed charges @ 25%	<u>20.50</u>
Total	\$40.50

This is equivalent to 2.034¢ per pound of copper produced. The 2.5¢ per pound, therefore, should be a fair estimate. True enough, 90 per cent extraction of the precious metals and copper have not yet been obtained, but future work will probably make this possible.

CONCLUSIONS AND SUMMARY

From the results obtained the following conclusions are drawn:

1. By means of temperature control in roasting a calcine may be produced in which the amounts of sulphide sulphur and water-soluble copper may be readily controlled. This will permit control of the acid regenerated in the electrolysis.
2. This roast may be done at a cost considerably lower than that required to produce a "sweet roast".
3. The sulphide copper remaining in the calcine may be leached with ferric sulphate, but the rate of extraction is slow.
4. The electrolyte may be purified by means of a "neutral leach", but further work will be necessary in order to make this step more positive.
5. A good copper deposit may be obtained from solutions containing as high as 14 grams of ferrous iron per liter, with a current efficiency of about 80 per cent and a power consumption of 2400 kilowatts per ton of cathode copper produced.
6. About 80 per cent of the contained iron in the electrolyte will be oxidized upon deposition of 20 grams of copper per liter without damage to the cathode.

deposits. However, this ferric iron is reduced during the leach and also by cement copper before returning to the electrolytic tank.

7. During the electrolysis of a solution containing a high percentage of iron the copper content should not be lower than 30 grams per liter.

8. The acid strength of the electrolyte need not be greater than 5--6 per cent.

9. The dissolution of all copper other than sulphide in the calcine is very rapid at a temperature of 200° C.

10. The separation of the solids and liquids following leaching is not difficult.

11. Every copper concentrate will present its own problem, which must be solved before application of the general treatment.

12. The possibility of reclaiming the sulphides in the leach residue is one factor that will probably increase the overall efficiency of this process.

13. The process as outlined in this report has economic possibilities.