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THE ELECTROLYTIC SEPARATION OF COPPER NICKEL, AND PRECIOUS METALS FROM COPPER-NICKEL MATTE

BY

ODEN CASS GARST

- - -

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

Chemical Engineer

Rolla, Mo.

1941

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Approved by W T Schrenk

Professor of Chemical Engineering

PREFACE

This Thesis is submitted to the Faculty of the Graduate School of the University of Missouri, Missouri School of Mines, in partial fulfillment of the requirements for the degree of Chemical Engineer. The work reported herein was accomplished while employed by the United States Department of the Interior, Bureau of Mines, as a part of the author's regular duties. This work has been published by the Bureau of Mines in Report of Investigations No. 3483, "Recovery of Nickel, Copper, and Precious Metals from Domestic Ores by a Combined Electrothermal and Electrolytic Method", by J. Koster, R. G. Knickerbocker, O. C. Garst, T. E. Evans and W. E. Cody. The Bureau publication covers in great detail the ore dressing and smelting procedure which has been practically omitted from this thesis.

ACKNOWLEDGMENTS

The author desires to express his appreciation to Dr. J. Koster, Supervising Engineer, Electrometallurgical Section, Metallurgical Division, Bureau of Mines, and Mr. R. G. Knickerbocker, Engineer in Charge, Boulder Unit, Electrometallurgical Section, Metallurgical Division, Bureau of Mines, for the many valuable suggestions they offered during the course of the work.

Acknowledgment is also due to Mr. P. R. Perry and Mr. P. E. Churchward who performed the necessary analyses during this investigation, and to Dr. A. C. Rice and Mr. C. E. Arrington for making spectographic examinations of the electrolytic products.

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INTRODUCTION

During the last few years considerable interest has been shown in domestic reserves of strategic metals. Broadly speaking, the strategic materials of any nation are those materials of commerce essential to the country both in time of war and peace, which are not produced within the boundaries of that country in sufficient quantities to supply even peace-time requirements. The United States is far more fortunate than other countries inasmuch as there are only eight metals which may be classified as being strategic metals; namely, aluminum, antimony, chromium, manganese, nickel, mercury, tin, and tungsten. The work on nickel covered herein was inaugurated because nickel is included on the list of these strategic metals. An outcrop of copper-nickel-iron sulfides occurs in the Bunkerville district, Clark County, Nevada. The geology of this district has been reported [1][2][3][4][5][6] by various authorities. Figure 1 is a photograph of diamond drill exploration on the Great Eastern claims in this district during June, 1939.

1/ Schrader, F.C., Stone, R.W., and Sanford, S., "Useful Minerals of the United States," U.S. Geol. Survey Bull. 624, 1917, p. 412.

2/ Lincoln, F.C., "Mining Districts and Mineral Resources of Nevada," Reno, Nevada Newsletter Publishing Company, 1923, p. 295.

3/ Lindgren, Waldemar, and Davy, W.M., "Nickel Ores from the Key West Mine, Nevada," Econ. Geol., 19, 1924, p. 309-319.

4/ Longwell, C.R., "Geology of the Muddy Mountains, Nevada, With a Section Through the Virgin Range to the Grand Wash Cliffs, Arizona," U.S. Geol. Survey Bull. 798, 1928, p. 152.

5/ Carpenter, J.A., "Mineral Resources of Southern Nevada," Nevada State Bureau of Mines, 1 (1929).

6/ Bancroft, Howland, "Platinum in Southeastern Nevada," U.S. Geol. Survey Bull. 430, Pt. 1, 1910, p. 192-199.

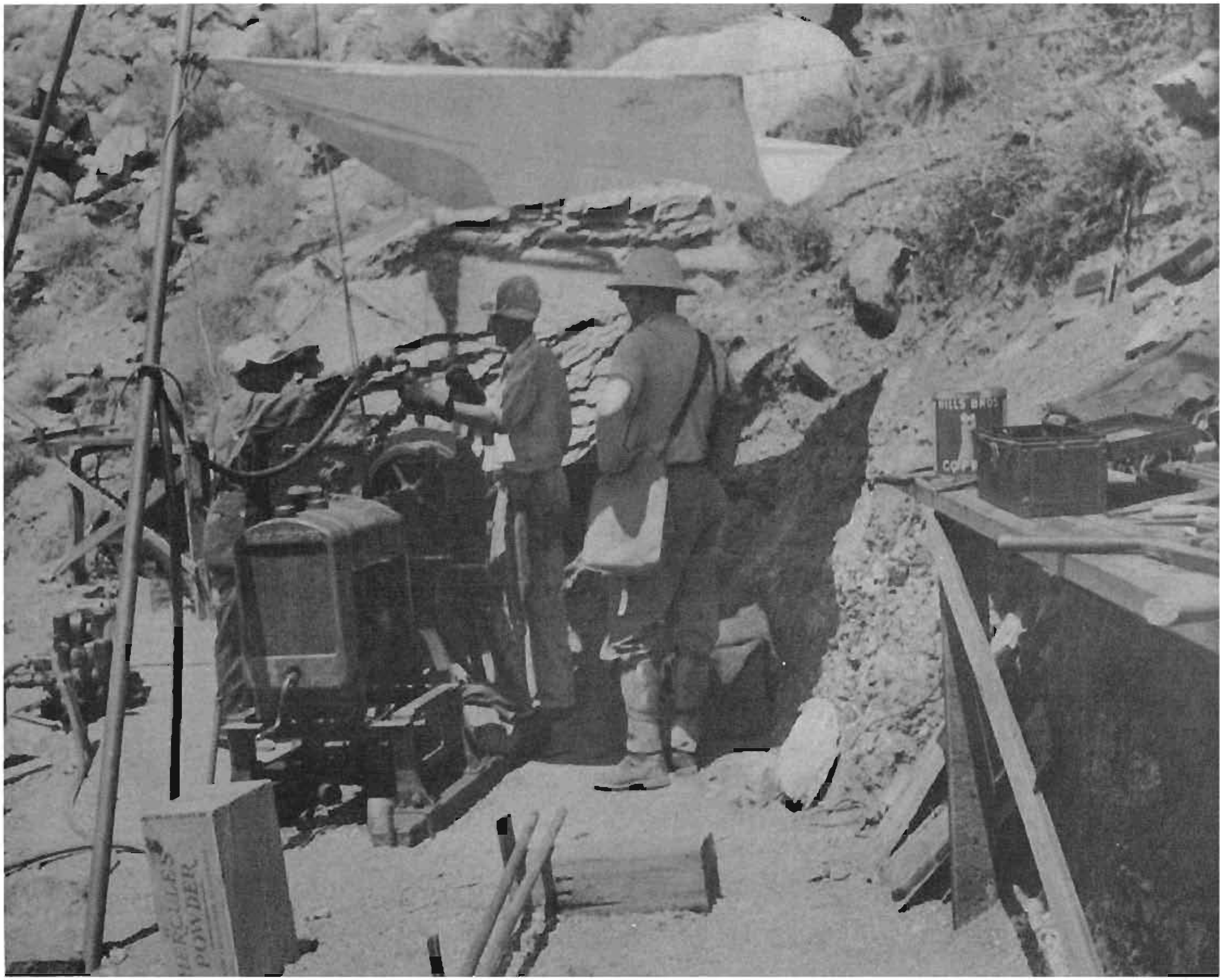

Figure 1.- Diamond drilling at Great Eastern claims.

ORE DRESSING

The ore dressing of these sulfide ores was comparatively simple as routine bulk sulfide flotation methods produced a satisfactory concentrate with a minimum loss of values in the tails. Selective flotation of the copper and nickel sulfides throwing the pyrite into the tails was not satisfactory as a considerable portion of the precious metal content is associated with the iron. The reagents used were pine oil, barrett No. 4, aerofloat, xanthate, and copper sulfate.

The concentrate produced assayed as tabulated in Table No. 1. Table No. 2 is a log of the concentration plant's daily run for a four-day period. The various steps and the sequence of operations of the concentration plant is presented graphically in figure No. 2, flow sheet No. 1.

Table No. 1 - Analysis of Concentrates

Reported		Percent
Nickel		4.60
Copper		6.00
Iron		25.88
Sulfur		16.9
Silica		21.2
Lime		1.4
Magnesia		13.0
Alumina		2.9
Silver (ounces per short ton)		0.29
Gold	do	0.001
Platinum	do	0.135
Palladium	do	0.192

Several charges of this concentrate were sintered on the machine shown in Figure 3.

Table 2. - Flotation Pilot Plant Daily Run, March 1938

Date	Pounds Ore Treated	Analysis, percent Cu and Ni						Ore Feed lb/hr.	Reagents, grams per minute					pH
		Heads		Tails		Concentrates			Pine Oil	Barrett No.4	Aero-float	Xan-thate	Copper Sulfate	
		Cu	Ni	Cu	Ni	Cu	Ni							
23	3,000	0.51	.49	0.14	0.14	1.80	1.60	1,000	2.25	1.25	0.45	0.83	1.5	8.7
24	3,500	.60	.68	.05	.06	7.91	5.80	1,000	*	*	*	*	*	8.8
25	4,000	.50	.51	.05	.07	2.67	2.75	1,000	1.03	.31	.24	.87	3.0	8.9
28	3,500	.50	.45	.04	.08	7.28	5.70	1,000	.65	.40	.10	1.7	1.5	8.9

* Reagent feeders off. Surplus from run of March 23rd in circuit.

All runs were on 65-mesh rod-mill grinding in closed circuit with classifier.

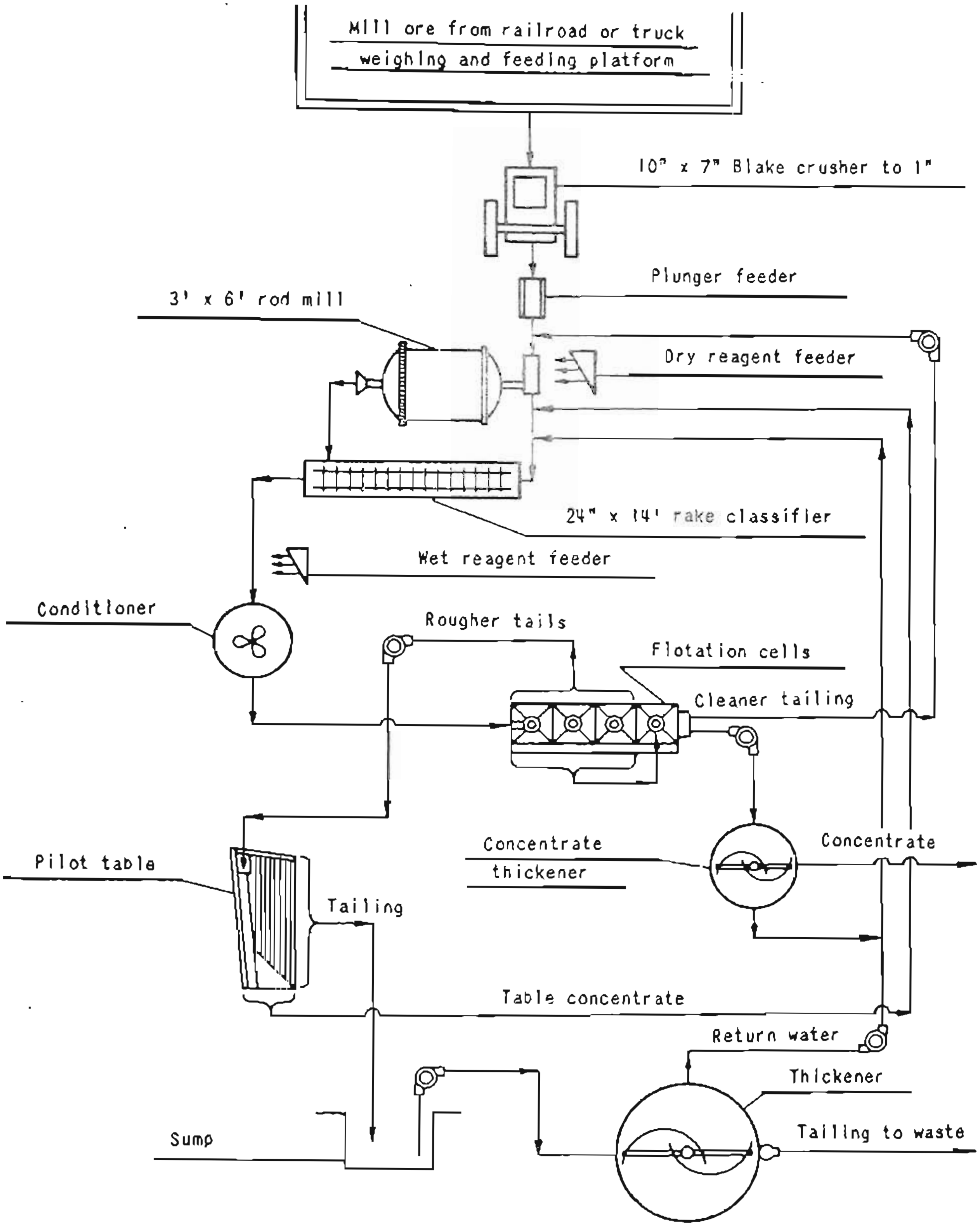

Figure 2.- Flow sheet 1.

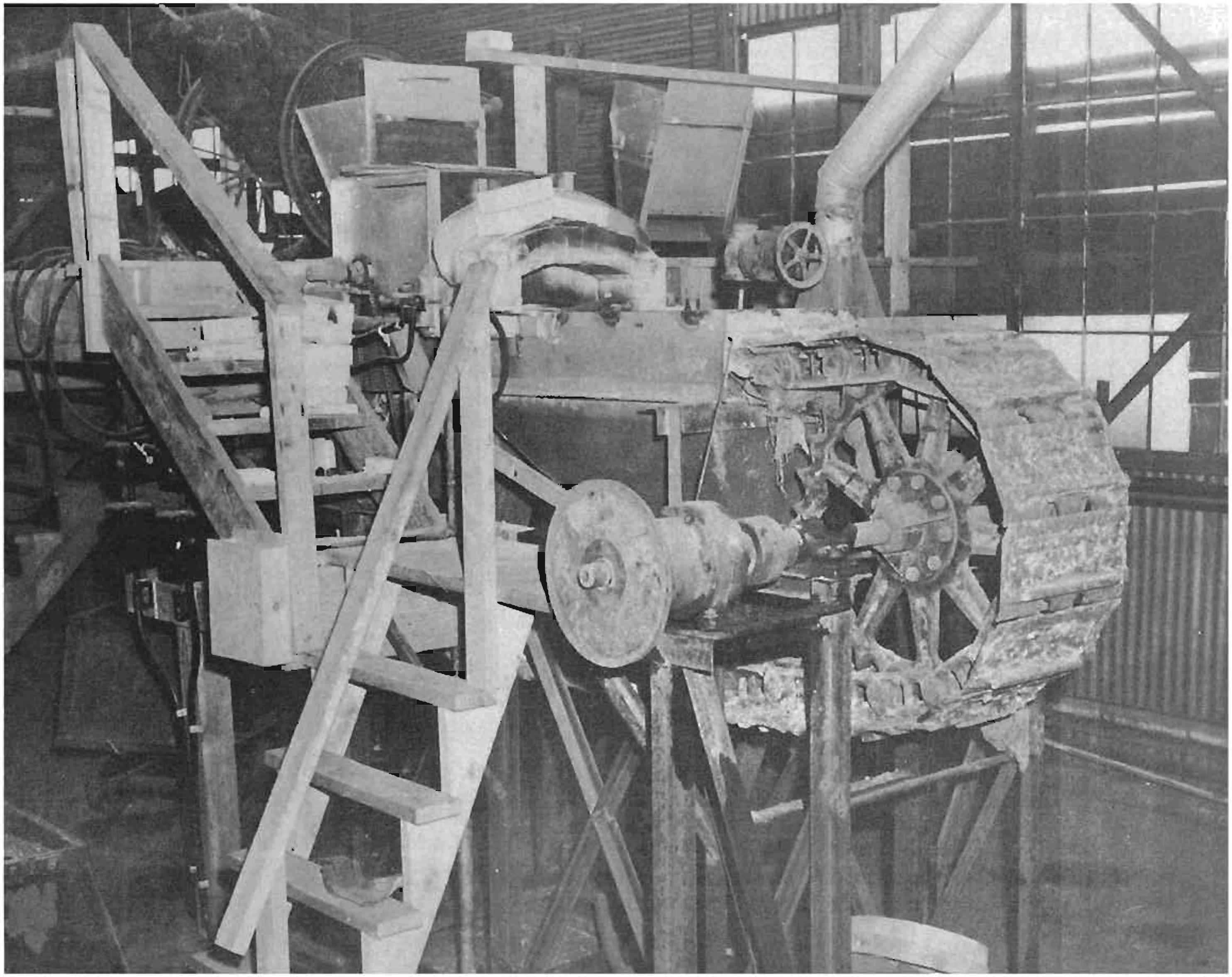

Figure 3.- Sintering machine constructed at Boulder City laboratory.

SMELTING

The concentrates were smelted with gold-bearing quartz flux in an electric furnace, and matte produced. A portion of the concentrates were sintered on the machine shown in Figure No. 3 before smelting. This practice, however, was abandoned as the slag losses of copper and nickel were too high when sinter was used instead of raw concentrates. The ore was smelted and the waste slag poured from the bath as illustrated in Figure No. 4, quartz placed on the bath and the furnace tipped back into converting position and blown with an air-oxygen mixture. The oxygen-enriched air was used instead of normal air because the bath was small and difficulty was encountered in maintaining bath temperature sufficiently high with air alone using the equipment at hand. The converted matte was cast into anode molds either with or without copper lugs, depending on whether the matte was to be used as anode metal or was to be ground, sintered, and leached to provide electrolyte for the copper refining cells. Table No. 3 gives typical analytical data on the various products encountered in the ore dressing and smelting operations.

TABLE No. 3 - Analyses of Materials Involved in Electric Thermal Treatment of Nickel-Copper Ores

Analysis, percent	Low Grade Ore	Float Concentrates	Float Tails	Matte Furnace Waste Slag	Matte	Converter Matte
Ni	0.51	4.66	0.07	0.10	9.15	28.42
Cu	.52	6.12	.04	.15	11.61	44.01
Fe	9.63	25.85	-	18.35	47.4	2.95
S	-	17.63	-	.30	32.4	21.75
CaO	7.20	1.40	-	.23	-	Nil
Al_2O_3	5.80	2.90	-	3.44	-	Nil
MgO	22.0	13.00	-	22.44	-	Nil
SiO_2	39.0	21.2	-	46.60	-	.21
Oz./2,000 lb.						
Ag	-	.29	-	-	-	3.93
Au	-	.001	-	-	-	1.12
Pt	-	.135	-	-	-	.65
Pd	-	.192	-	-	-	1.32

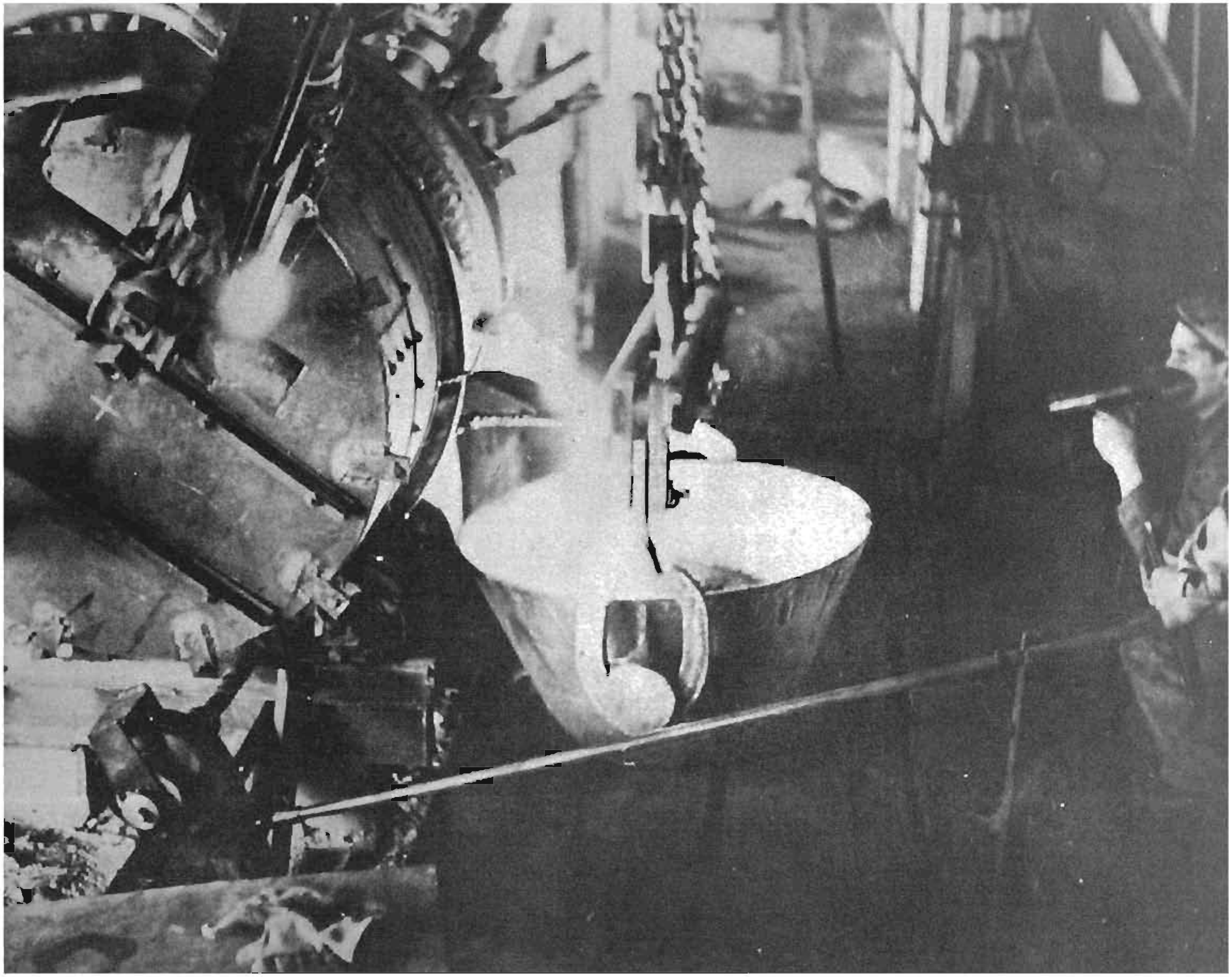

Figure 4.- Pouring slag from combination smelting and converting furnace.

ELECTROLYTIC PRODUCTION OF NICKEL AND COPPER

REVIEW OF NICKEL-COPPER ELECTROMETALLURGICAL INDUSTRY

There are two industrial processes by which electrolytic copper and nickel are recovered from copper-nickel sulfide ores, namely, the Stanley and the Hybinette processes. Briefly, the Stanley[7] process consists of sulfidizing completely the converter metal to Ni_3S_2 and Cu_2S, fusing with sodium sulfide, and allowing the melt to solidify in pots. The melt is allowed to freeze, whereupon it seperates into two layers, the top rich in copper and the bottom rich in nickel. The tops are blown to blister in a series of converters, and the copper is cast into anodes, which are refined electrolytically. A portion of the precious-metal slime is recovered here.[8] The bottoms are re-treated with sodium sulfide in the above-described manner. In the second treatment the tops are not rich enough in copper to be converted directly, so they are returned to the first-treatment pots and combined with the raw converter metal. The

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[7] Peek, R.L., "Refining Nickel-Copper Matte at Port Colborne", Eng. and Min. Journal, 130, 482, 488 (1930).

[8] Aldrich, C.H., and Bryan, J.K., "The British Empire's Largest Copper Refinery," Eng. and Min. Journal, 130, 489-492 (1930).

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bottoms, however, are comparatively pure nickel sulfide contaminated with only a small percentage of copper sulfide and some sodium sulfide. The sodium sulfide is removed by leaching with hot water. The copper sulfide is removed by chlorinating with salt at a high temperature and releaching with hot water. This product is then calcined with soda ash and releached to obtain black nickel oxide contaminated by only 0.1 percent copper. The oxide is smelted with carbonaceous fuel and coal as a reducing agent in an open-hearth furnace, and the nickel oxide is reduced to metallic nickel. The metallic nickel is cast into anodes and refined electrolytically in a neutral boric acid-nickel sulfate electrolyte. A portion of the precious-metal slimes is recovered here.

In the Hybinette[9] process the Bessemerized matte is first used to remove traces of copper from the nickel electrolyte by replacement and precipitation of cement copper, after which it is roasted to a very low sulfur content. The roasted matte is then leached with sulfuric acid to provide electrolyte for

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[9] Gowland, W., and Bannister, C.O., "The Metallurgy of Nonferrous Metals," London, Griffin, 1930, p. 551.

the insoluble-anode, copper-electrowinning cells. This electrolyte is electrolyzed with lead anodes; electrolytic copper, sulfuric acid, and nickel sulfate being the products of the electrolysis. The solution is evaporated, the nickel sulfate crystallized out, and the sulfuric acid returned to the copper leach tanks. The leach residue, which is much lower in copper than the original converter matte, is smelted with coke and suitable fluxes and soluble high nickel-low copper anodes cast from the resultant metal. These anodes are refined electrolytically in a compartment cell; the neutral nickel sulfate-boric acid electrolyte is kept free of copper dissolved from the anodes by contact with raw converted matte and anode scrap in cementation tanks. Electrolytic nickel and precious-metal slimes are the end products of this electrolysis.

R. G. Knickerbocker[10] has reported the use of a coke blast-furnace, matte anodes for copper electrolysis at the plant of the Missouri Cobalt Company in Fredericktown, Missouri. These anodes were far more complex than those used in the present

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[10] Knickerbocker, R. G., "Electrolytic Separation of Copper from a Copper-Cobalt-Nickel Matte", Mining Sci. Press, 121, 45-50 (1920).

work, but were used in a manner similar to that reported in this paper. However, the Missouri Cobalt Company did not recover the nickel in the spent copper electrolyte by electrolysis because of the high cobalt content, but separated it from the cobalt and iron by a complex series of precipitations and purifications. Nickel oxide was precipitated and either reduced in an oil-fired reverbatory furnace or sold as an oxide. Cobalt oxide was marketed as such.

PRESENT WORK ON ELECTROLYSIS OF MATTE ANODES FROM BUNKERVILLE ORES

A portion of the copper-nickel converter anode metal was ground through 28-mesh, mixed with suitable agglomerate, and sintered to oxides on the laboratory sintering machine, and reground. The sinter was then leached with 10-percent sulfuric acid to provide electrolyte for the copper-electrowinning cells. In plant practice, the leach residue would be charged into the electric converter. These nickel-copper sulfide anodes were used in the copper cells. The copper electrowinning cells were conventional multiple-system tanks as used by the majority of commercial copper refineries. Cathodes were the regular copper starting sheets. The experimental copper-refining cells were made of maple. All joints at corners were half-lapped and screwed in place as tightly as possible. After the cells were assembled they were lined with a thin coating of soft rubber. The electrolyte was fed by glass tubing, which passed through rubber stoppers cemented to the cell walls. Spent

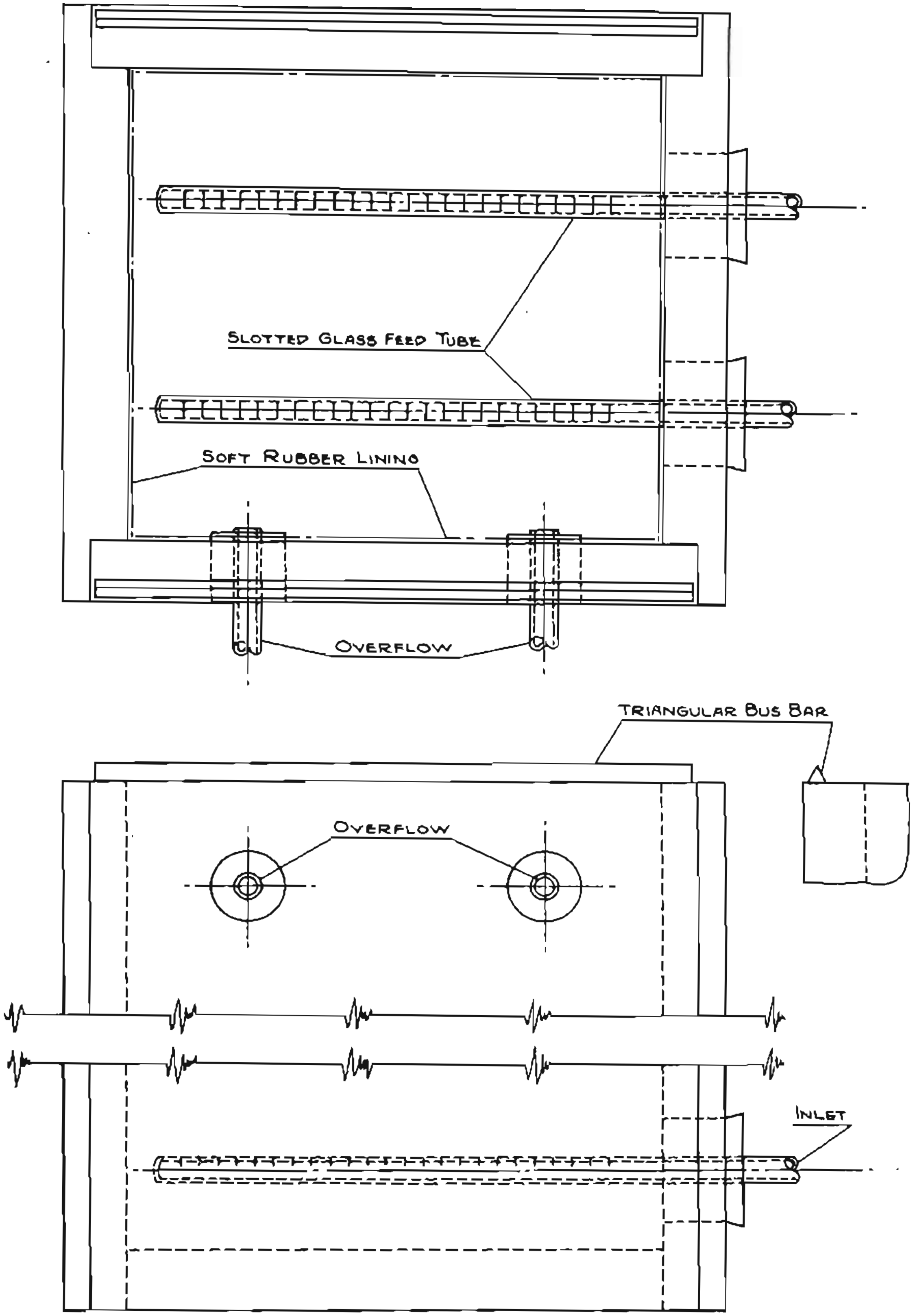

Figure 5.- Copper refining cell.

electrolyte was conducted from the cell by a similar set of pipes. The main busbars and the anode cross bars were triangular sections of copper. Cathode cross bars were rectangular in cross section and were soldered to the starting sheets. Figure 5 is a drawing of one of the cells.

During electrolysis copper sulfate, nickel sulfate, elemental sulfur, and sulfuric acid formed at the anodes. Inasmuch as the rate of copper dissolution from the anode was considerable slower than the rate of copper deposition at the cathode, the solution was constantly being depleted of copper and at the same time was being built up in nickel sulfate and sulfuric acid. When the solution had reached a copper concentration so low that the cathode deposit would not adhere, a portion of the electrolyte was returned to the copper leach tanks and again built up in copper. By this method of alternate leaching and electrolysis, the nickel and the copper concentration was reduced to below 5 grams per liter. The low copper solution was then electrolyzed with lead anodes in a separate series of cells to free the solution of copper. The copper produced in the cells in which the soluble anodes were used formed firm adherent cathodes, but that formed in the cells with lead anodes dropped to the bottom as "soft copper."

After the lead anode electrolysis, the solution contained less than 0.05 gram copper per liter. The solution was treated hot with anode scrap from the first series of copper refining cells or with metallic nickel powder, which cemented out the small amount of copper remaining in solution. The free sulfuric acid was neutralized with calcium carbonate, and the precipitate of calcium sulfate was filtered off and washed free of nickel sulfate. The washings were combined with the filtrate, the solution was heated and held at about 90°C, while being agitated and blown with air. At all times during this blowing process the solution was in contact with precipitated nickel carbonate, which was added to the tanks. During the course of this treatment the ferrous iron was oxidized to the ferric state and precipitated as oxide or basic sulfate. A portion of the nickel carbonate chemically equivalent to the iron precipitated went into solution. The iron precipitate was filtered off, and the nickel was precipitated from part of the filtrate as basic nickel carbonates by treatment with a saturated solution of sodium carbonate. The nickel carbonate was filtered off and washed free of soluble salts with hot water. The washings were combined with the filtrate, and sodium sulfate was crystallized therefrom. The precipitated nickel carbonate was of the composition given in Table 4.

TABLE 4 - Analysis of Nickel Carbonate Precipitate

	Percent
$NiCO_3$	73
$NiSO_4$	7.7
H_2O	19.3

That portion of the iron-free solution that was not treated with sodium carbonate was made up into pure nickel catholyte by the addition of boric acid and sodium fluoride and adjustment of the nickel concentration to 30 grams per liter. Nickel was recovered from this solution as electrolytic nickel by electrolysis in a compartment cell.

The cathode was placed in a slotted diaphragm frame covered with light canvas. The anodes of soft lead were separated from the cathode by these canvas diaphragms. The purified nickel electrolyte was introduced into the top of the cathode compartment through flow tubes drilled in the frame, passed down the face of the cathode, out through a like system of flow tubes drilled in the bottom of the frame, and into the anode compartment. The anolyte flowed past the face of the anodes and out into the anolyte sump. The acid anolyte was then treated to neutrality with the precipitated nickel carbonate, filtered, and returned to the purified-nickel catholyte tank. Figure 6 is a diagrammatic flow sheet showing the sequence of the processes.

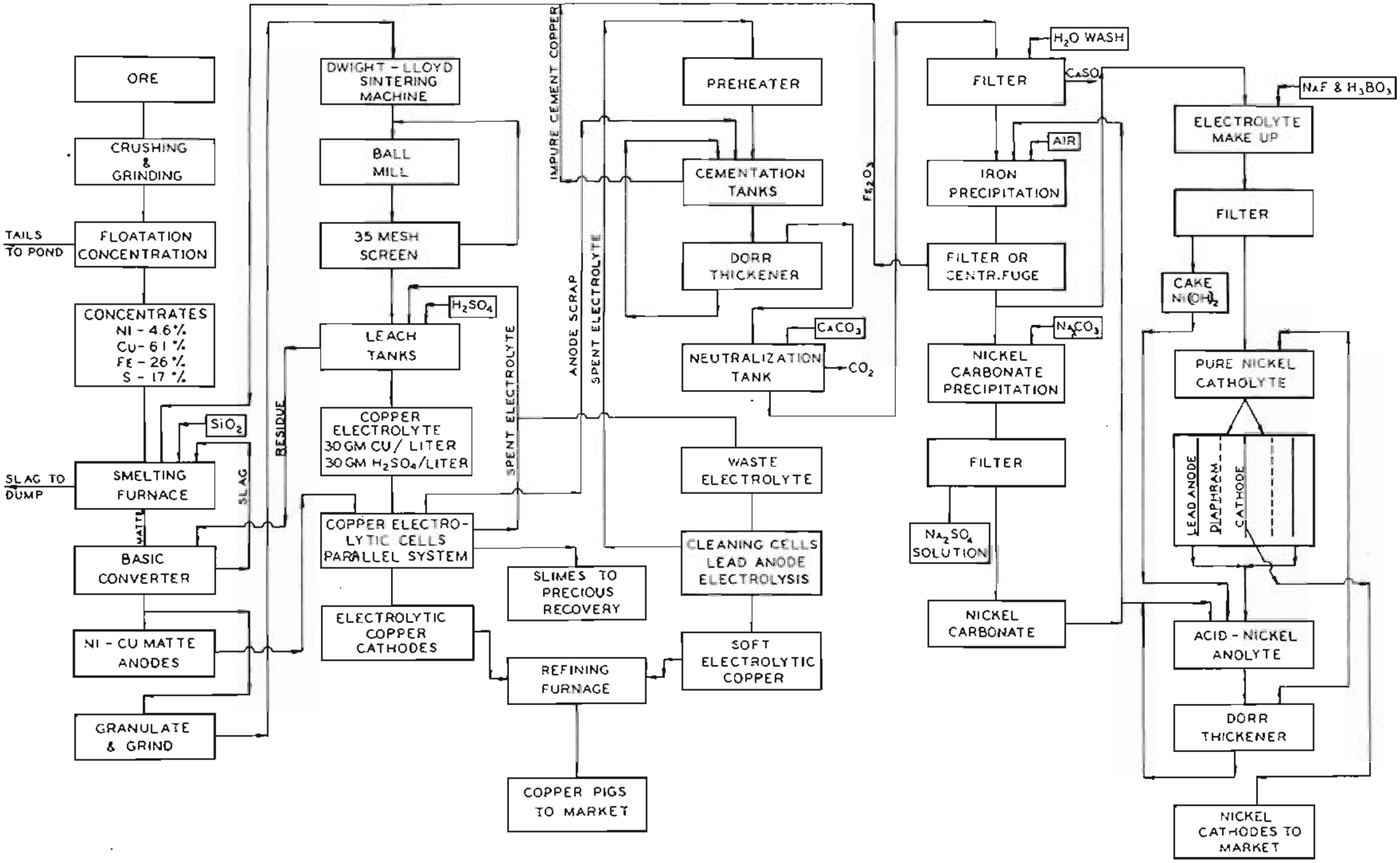

Figure 6.- Diagrammatic flow sheet.

DISCUSSION OF RESULTS ON ELECTROLYSIS OF NICKEL COPPER ANODES

Copper Electrolysis

Three different anode compositions were used in the copper-refining cells. These compositions were as shown in Table 5.

TABLE 5 - Converter Anode Compositions, Percent

Anode No.	Cu	Ni	Fe	S	Cu/Ni
1	44.01	28.42	2.95	21.75	1.55
2	44.40	28.08	.34	25.82	1.58
3	44.42	39.48	.30	13.21	1.12

The precious metals content of the anodes was:

	Ounces per ton of 2,000 lbs.
Ag	3.93
Au	1.12
Pt	.65
Pd	1.32

Anode composition 2 is more than completely saturated with sulfur and would not be made in normal converter practice unless the pyritic sulfur content of the ore increased. To prepare this anode, metal of anode composition No. 1 was crushed and fused with niter to remove the iron, the slag being discarded. This sulfide was fused with a large excess of sulfur and cast into anodes. This anode metal was prepared for strictly theoretical reasons, as it was desired to study the effect of variation in sulfur content upon anode electrolytic characteristics. Voltage across the copper-refining cell varied with anode composition as shown in Table 6. Copper concentration of electrolyte was 30 grams per liter, and temperature of electrolyte was 55° to 60°C.

For the purpose of this discussion, the percentage of sulfur saturation was caldulated on the assumption that all of the sulfides present were in solid solution as Ni_3S_2, Cu_2S, and FeS.

TABLE 6. - Relation of Cell Voltages to the Sulfur Content of the Anodes

Anode Composition	Sulfur Satura- tion percent	Total Voltage Through Cell	E Drop at Anode	E Drop at Cathode	E Drop Through Solution
Conductivity					
Copper	0	0.43	0.13	0.10	0.20
No. 3	51.4	.45	.15	.10	.20
No. 1	93.4	.50	.20	.10	.20
No. 2	120.0	1.65	1.20	.25	.20

Complete saturation of the anode metal with sulfur caused excessive anode polarization and high power costs per pound of copper plated. The voltage across the cell was so high when anode No. 2 was used that the copper plated did not form firm adherent cathodes, such as were produced when the other anode compositions were used. Reduction of sulfur content gave an anode that approached the voltage drop of conductivity copper anodes.

The anodes being composed of a solid solution of copper and nickel sulfides, the ratio between copper and nickel in the anode greatly affects the anode reactions. The effect of variation of the copper-nickel ratio on anode dissolution characteristics is summarized in Table 7. In those instances where the listed anode dissolution efficiency is less than one hundred percent other reactions occurred, such as the oxidation of divalent sulfur to hexavalent sulfur and the evolution of oxygen.

TABLE 7 - Relation of Anode Cu-Ni Ratio to Anode Dissolution Characteristics

Anode Composition	Cu/Ni	Anode Dissolution Efficiency, per cent				Cu/Ni from Anode
		Cu	Ni	Fe	Total	
Conductivity						
Copper	00	100	-	-	100	00
No. 1	1.55	52.7	13.2	3.4	69.3	4.01
No. 2	1.12	42.9	48.5	1.5	92.9	.388

The effect of anode composition on over-all copper-refining-cell characteristics is presented graphically in Figures 7 and 8.

Table 8 presents typical operating data for the copper cells.

According to the results tabulated under anode composition No. 3, 94.3 percent of the copper produced will be in the form of adherent cathodes and 5.7 percent in the form of soft copper. It is interesting to note that all of the nickel in the soft copper is as nickel-sulfate, which can be water-leached and returned to the electrolyte.

TABLE 8 - Typical Operating Data for Copper-Refining Cells

	Anode	
	No. 1	No. 3
Current Density	10 amp/sq.ft.	10 amp/sq.ft.
Ampere Efficiency	95% +	95% +
Solution Assay (gm/liter):		
Cu	33 to 19	45 to 4.5
Ni	16 to 20	0 to 30
Fe	5 to 6	0 to 0.5
H_2SO_4	32 to 58	20 to 25
Voltage across cell . . .	0.50	0.51
Cu per kw.-hr., lb. . . .	5.247	5.115
Kw.-hr. per lb. Cu	.190	.196
Cathode assay (percent):		
Cu	99.77	
Ni	.008	
Fe	.0014	
Ag	.00076, or 0.22 oz./T	
"Soft" Copper Assay (percent on unwashed basis):		
Water insoluble	92.65	
Water soluble	7.35	
Water-insoluble portion:		
Cu	99.10	
Ni	.0032	
Fe	.0043	
Total	99.1075	
Water-soluble portion:		
$CuSO_4 \cdot 5H_2O$	42.0	
$NiSO_4 \cdot 6H_2O$	37.8	
$Fe_2(SO_4)_3 \cdot 9H_2O$	8.9	
H_2SO_4	2.5	
H_2O	8.8	
Total	100.0	

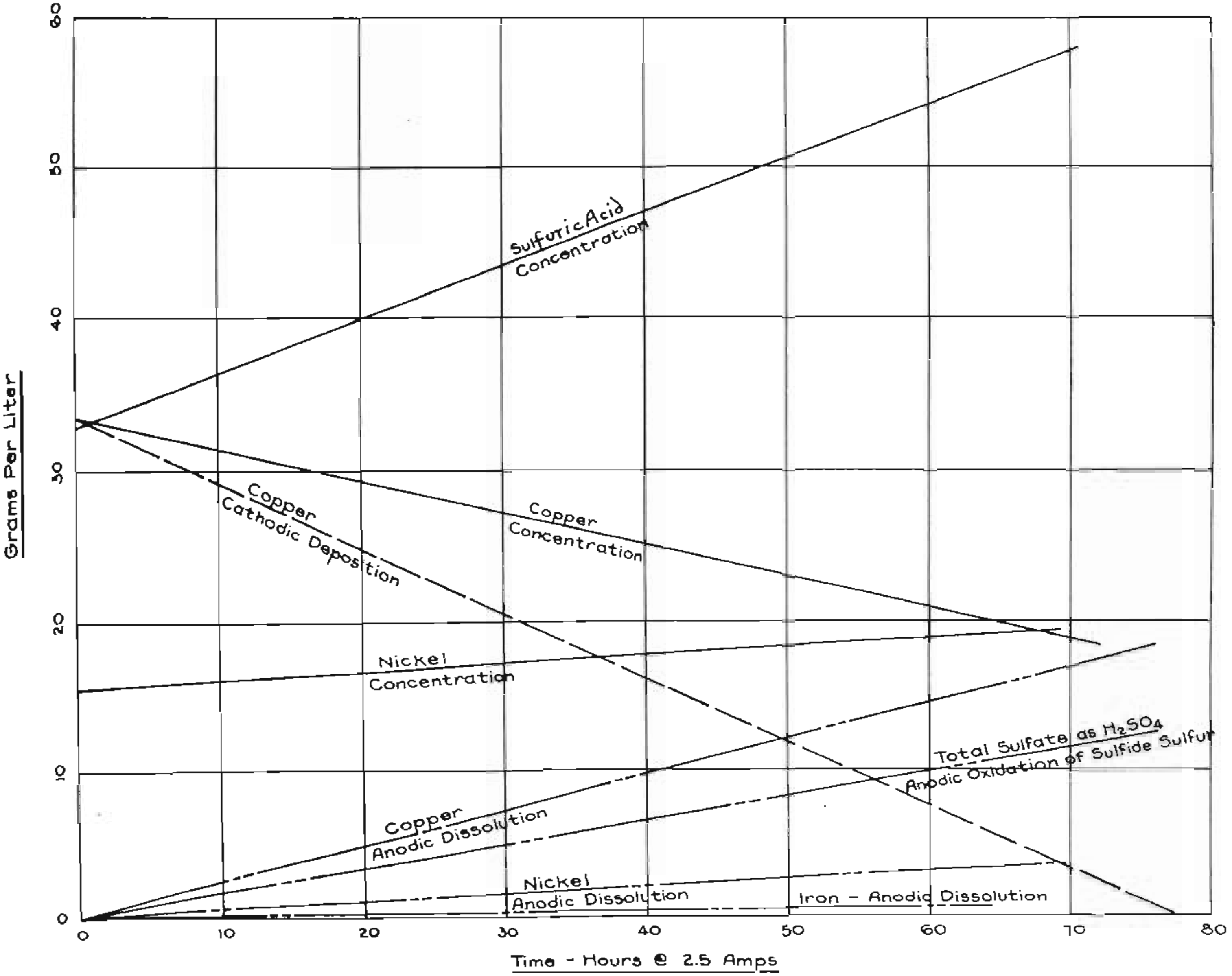

Figure 7.- Characteristics of copper refining cells with anode No. 1.

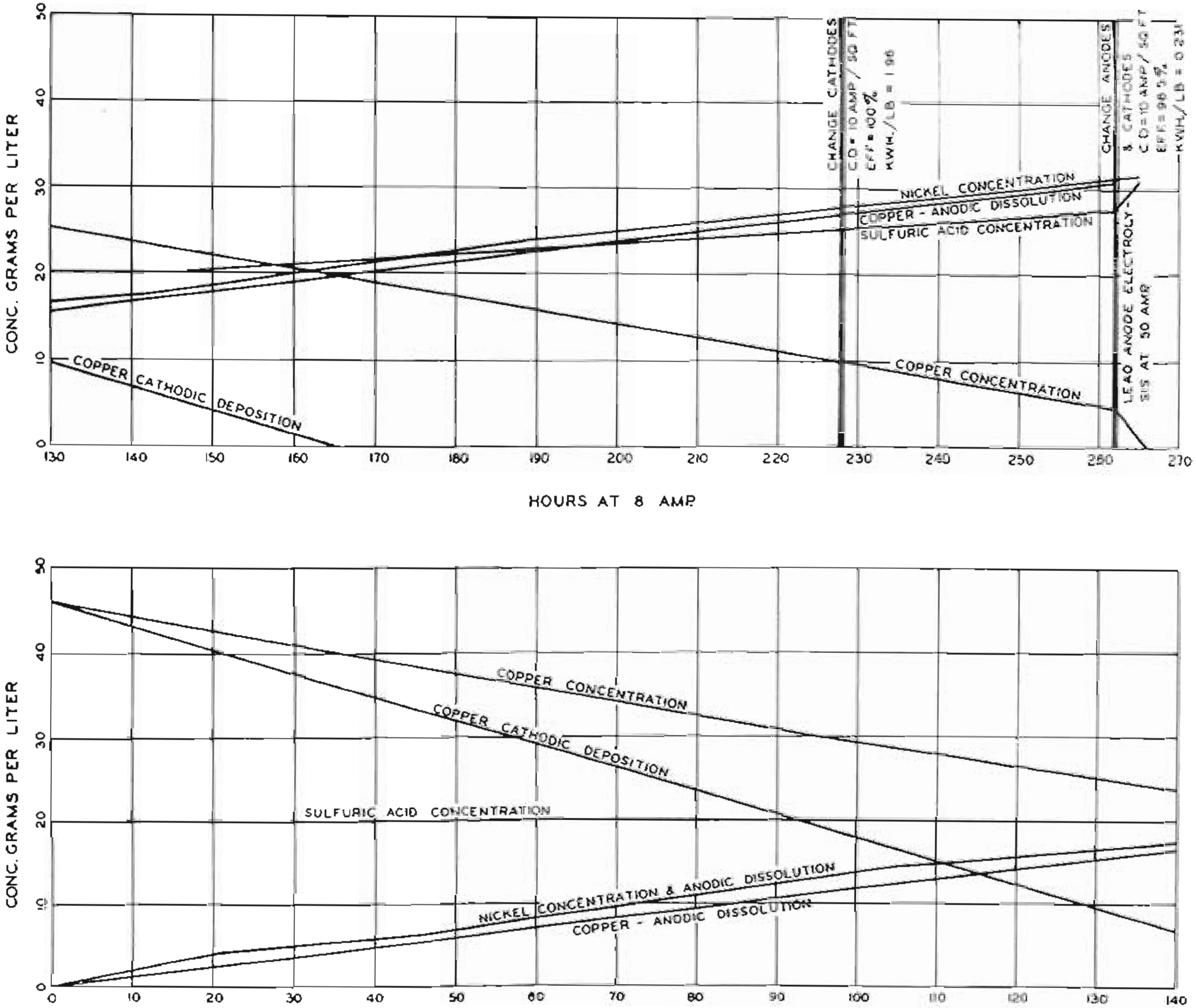

Figure 8.- Characteristics of copper refining cell with anode No. 3.

At the beginning of the electrolysis tabulated above under Anode Composition No. 3, the temperature of the electrolyte was varied over a wide range, and suitable voltage measurements were made. Since these measurements were made at the beginning of the electrolysis, when the copper concentration of the electrolyte was at its highest and before enough slime had collected on the face of the anode to affect the voltage, these measurements do not reflect the average operating condition of the electrolysis but are 0.05 to 0.1 volt lower than the mean voltage for the entire 10-day run. These measurements are given in Table 9.

TABLE 9. Relation of Electrolyte Temperature to Total Cell Voltage

Temperature of Electrolyte, °C.	Voltage Across Cells
24.5	0.71
36	.68
46	.64
53	.58
59	.49
62	.48
64	.47

Suitable starting sheets were produced using the copper-nickel sulfide anodes over a comparatively wide range of operating conditions. Acid concentration at the beginning of electrolysis was 35 to 45 grams sulfuric acid per liter. Current densities of 6 to 10 amperes per square foot were utilized. Copper concentration of 40 to 50 grams per liter at the beginning of the electrolysis produced firmer starting sheets than those produced at lower copper concentration. Starting sheets of 48 hours' deposition time could be stripped easily from the blanks. The starting-sheet blanks were conductivity copper plates 1/4 inch thick, the surfaces being polished so that no scratches were visible.

Before use, the blanks were painted with a coat of graphite paint, compounded especially for this service. The paint was composed of one pound of fine flake graphite per gallon of 3.5-hour-bodied linseed oil. The paint was applied at a temperature of 50°C and, after being painted, the blank was stored in a warm place for a few minutes so that the paint would flow out well and show no brush marks. The surface of the painted blank was then dusted with flake graphite so that no oil was apparent on it. The blanks were used immediately after being dusted with graphite. Electrolyte circulation at the beginning of electrolysis was quite slow so as not to wash the paint from the surface of the blank. After running for approximately two hours, the paint was covered with a film of copper, and at that time the circulation of electrolyte was increased to normal value. Typical operating data for the starting-sheet cells are as shown in Table 10.

TABLE No. 10 - Electrolysis Data for Starting Sheets

Current Density	Amps/sq.ft.	9
Electrolyte Temperature . . .	Degrees C.	57
Electrolyte to Assay:		
Cu	grams/liter	47.0
Ni	do	1.2
H_2SO_4	do	41.6
Cell Voltage	Volts	0.27
Current Efficiency	Percent	100

NICKEL ELECTROLYSIS

The electrowinning of nickel from nickel sulfate solutions by means of insoluble anodes depends mainly on chemical control of the pH of the catholyte. If the catholyte becomes basic enough, a precipitate of nickel hydroxide or basic nickel sulfates will form in the catholyte at pH 7 to 8. On the other hand, if the catholyte becomes acid enough, hydrogen is evolved at the cathode in preference to nickel. The evolution of hydrogen becomes a major difficulty at pH 4 or under. Thompson[11] has correlated the pH of nickel electroplating baths using soluble nickel anodes with the structure and physical characteristic of the deposited nickel and has found that there are definite ranges in which specific common flaws occur in nickel plate. He summarized the results of carefully standardized plating tests in which the bath pH was varied, as follows:

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[11] Thompson, M.R., "The Acidity of Nickel Depositing Solutions," Trans. Am. Electrochem. Soc., 41, 1922, p. 333-362.

1. The cathode efficiency may be increased either by raising the current density or the pH, or by raising both.

2. In the range of pH 6, or above, the current density has little or no effect on cathode efficiency.

3. Below pH 3 and up to 4, gas pits and streaks, which are usually attributed to hydrogen evolution, are very pronounced. Cracking and peeling of the deposits are generally encountered in this range. The nickel deposited is usually rather bright.

4. Between pH 5.5 and 6.5, gas pits and streaks are found only rarely. Above pH 6.3, blistering, cracking, and curling are again likely to occur, also "burning" of the deposit near sharp edges, especially with high-current densities. This is characterized by dark or black bands or patches. The nickel appears grayer in color, verging toward bluish near the upper limit of pH. Above pH 6.3, it seems difficult to get deposits in still solutions. In agitated electrotyping solutions good deposits may be obtained up to nearly pH 7.0.

The presence of borates in the nickel electrolyte improved the characteristics of the nickel deposit and to some extent limited the ionization of free sulfuric acid present originally or formed in the electrolyte.

Several methods were tried in an attempt to control the pH of the catholyte during the course of electrolysis. Some of these were (1) rapid circulation of electrolyte, the catholyte feed to the cell being at all times saturated with and carrying in suspension nickel carbonate; (2) the introduction of alkali ion in the form of sodium sulfate, together with a somewhat slower circulation; and (3) the introduction of ammonium ion as ammonium sulfate. Keeping the catholyte feed saturated with nickel carbonate gave satisfactory nickel deposits, but this scheme was not deemed satisfactory, as the use of such a method would force the precipitation of all the nickel as nickel carbonate before electrolysis. The addition of sodium ion to the electrolyte when at all effective caused too high a pH to be maintained in the catholyte compartment. Addition of ammonium ion, while at first showing indications of desirable effects, was found to be ineffective for extended electrolyses within the solubility range of $Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$.

The characteristics of nickel sulfate-fluoborate baths with soluble nickel anodes have been studied by the Bureau of Standards[12] and reported to be the only nickel baths that were buffered effectively. Electrolyte compositions in line with those baths were tried; it was found that these sulfate-fluoborate electrolytes gave deposits of satisfactory physical characteristics and were effective in the limitation of hydrogen evolution over a wide pH range, and that cell conditions would stay in equilibrium for indefinite periods, thus making possible the deposition of the thick cathode deposits desired in electrorefining or electrowinning of metals. The nickel deposits formed from nickel sulfate-fluoborate electrolytes had less tendency to split, peel, pit, and tree than did those deposits formed in other electrolytes.

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[12] Blum, William, "The Uses of Fluorides in Solutions for Nickel Deposition," Trans. Am. Electrochem. Soc., 39, Brass World, 17, 121 (1921), p. 459-481.

As it is necessary to control the pH of the solution from which the nickel was deposited, a compartment cell was used for all experimental work. The construction of the cathode frame utilized in these experiments has been described by S. M. Shelton and co-workers.[13]

The purified electrolyte was introduced into the top of the cathode compartment, flowed down the face of the cathode, and out of the cathode compartment into the anolyte compartment. The cathode frame was constructed of a single piece of phenol-formaldehyde plastic board, such as is used for switchboard service. The nickel-winning cell, like the copper-winning cell, was made up of hardwood lined with a thin coating of soft rubber. The outlet boot and anodes were made of soft lead.

Inasmuch as the speed of circulation of the electrolyte was found to be a very important variable in relation to the cathode current density and to the nickel concentration of the catholyte feed, a method expressing rate of flow, taking into account these other variables,

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[13] Shelton, S. M., Royer, M.B., and Towne, A. P., "Electrolytic Manganese", U.S. Bureau of Mines Rept. of Investigations 3406, 1938, p. 28.

was evolved. By definition, the "flow number" is equal to the ratio between the nickel in solution actually introduced into the cell in the catholyte feed in a unit time and the amount of nickel that could theoretically be plated from the solution by the current through the cell in the same unit time. This may be expressed mathematically by the equation:

$$\text{Flow number} = \frac{\text{Grams of Nickel Introduced per hour}}{\text{Amperage Through Cell x Electrochemical Equivalent of Nickel.}}$$

Using nickel sulfate-nickel fluoborate electrolyte of the following composition:

	Grams/liter
Ni	30
NaF	4.2
H_3BO_3	20
pH Catholyte Feed	5.8

at a temperature of 30°C., a study was made of the effect of variations in current density. Representative data are reported in Table 11.

TABLE 11 - Effect of Current Density on Cell Voltage and Energy Requirements

Current Density	Flow Number	Volts Across Cell	Kw-hr/Pound Nickel
20.6	6	4.40	1.83
18.5	6	4.20	1.74
9.25	8	3.2	1.34

Cathode ampere efficiency for these tests was 100 percent, as at flow rates as high as flow No. 6 the catholyte pH was maintained at such a point as to prevent the evolution of hydrogen. The deposits formed at higher current densities were finer-grained than those formed at low cathode current densities. Photomicrographs at 150X showing structures typical of this series are given in Figures 9, 10 and 11.

Inasmuch as it was desired to precipitate the smallest possible proportion of the nickel as carbonate, an extended study was made of the effect of variation of the flow number on the various characteristics of the nickel electrowinning cells. The catholyte feed for these experiments was the nickel sulfate fluoborate electrolyte, which had given the best results of any electrolyte used in the course of the experimental work. The electrolyte composition was:

	Grams/liter	
Ni	30	
NaF	4.2	
H_3BO_3	20	
pH		5.85
Electrolyte Temperature		35°C.

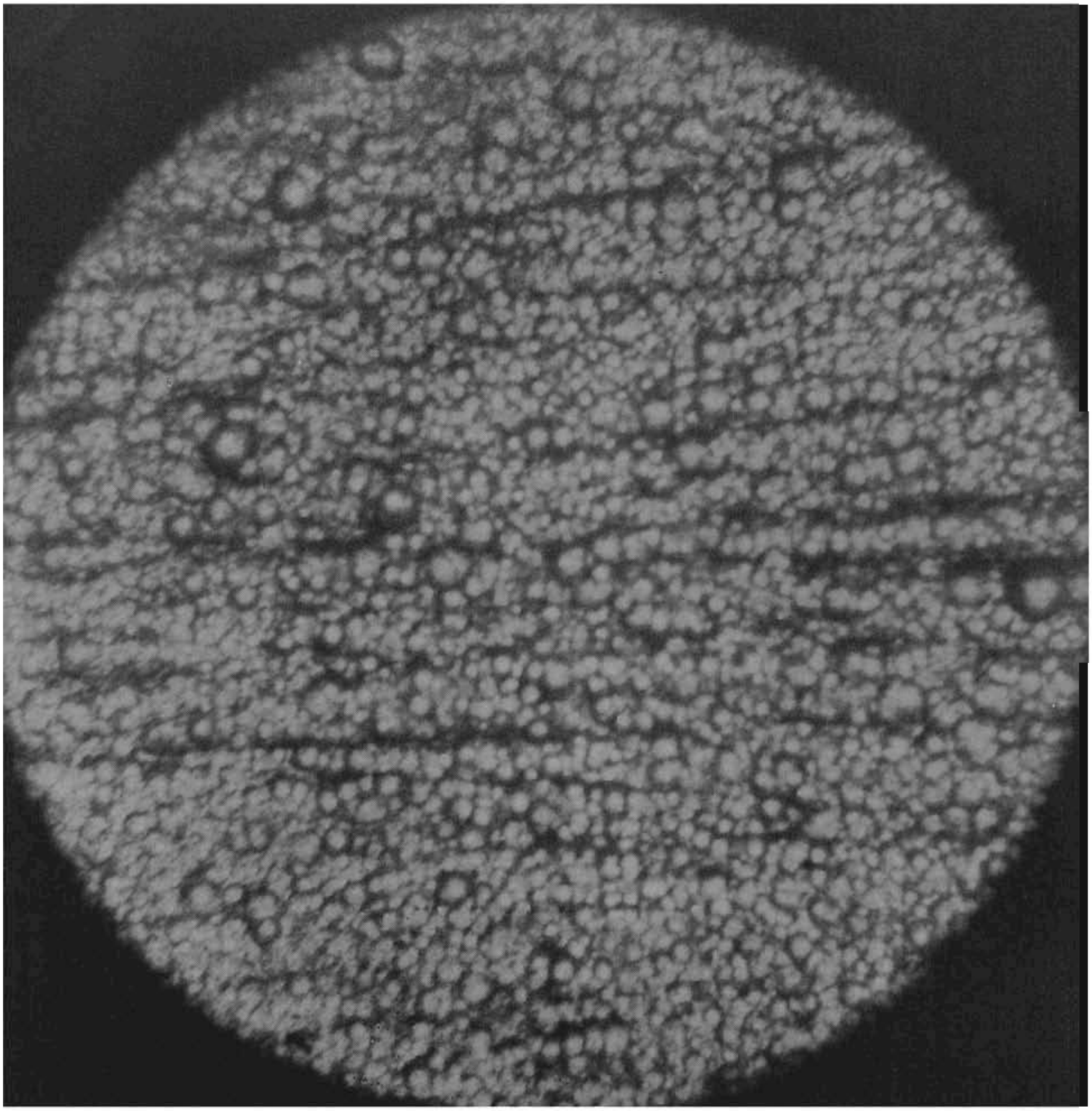

Figure 9.- Nickel deposit at 150X; current density, 9.25 amperes per square foot.

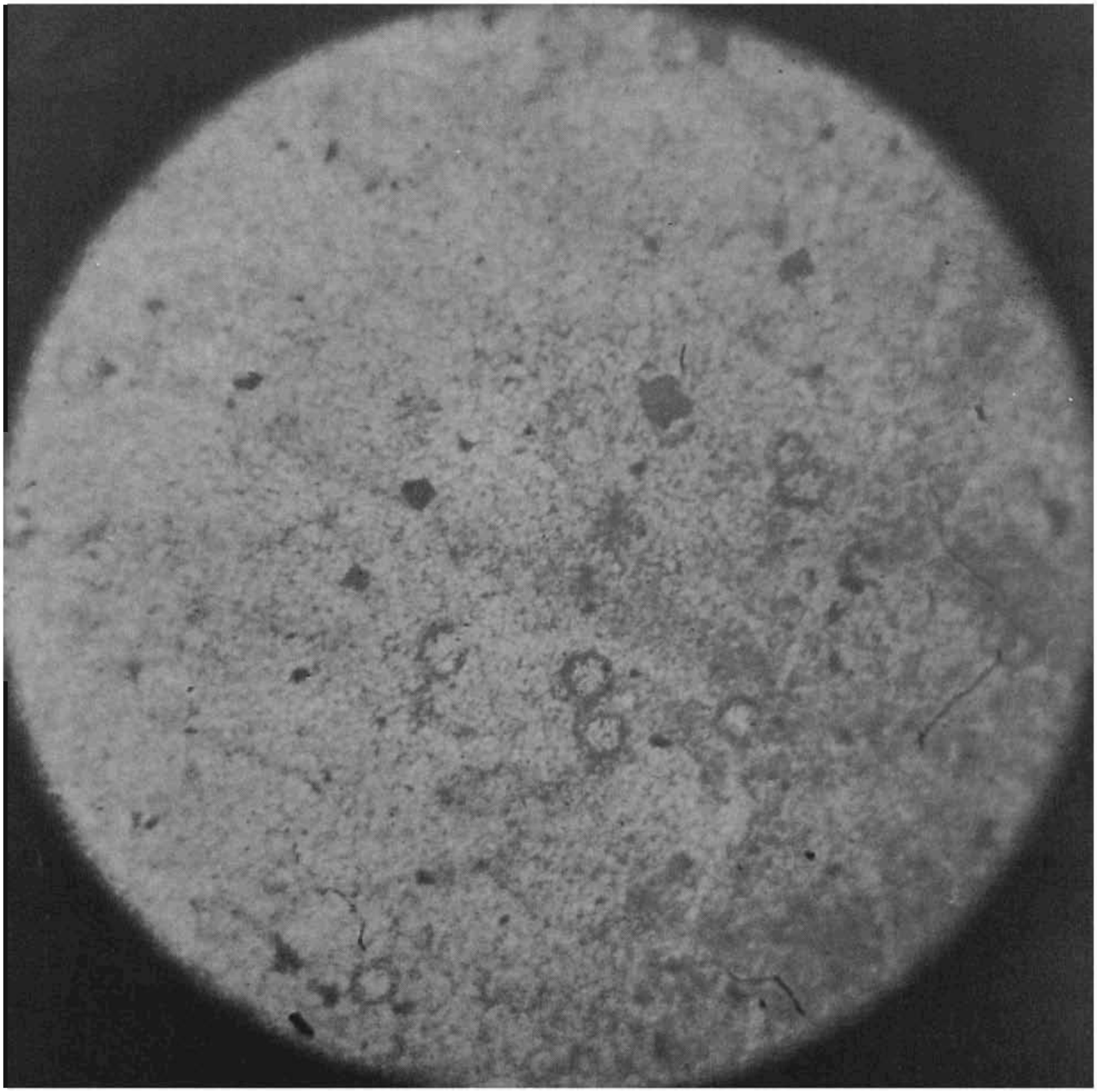

Figure 10.- Nickel deposit at 150X; current density, 18.5 amperes per square foot.

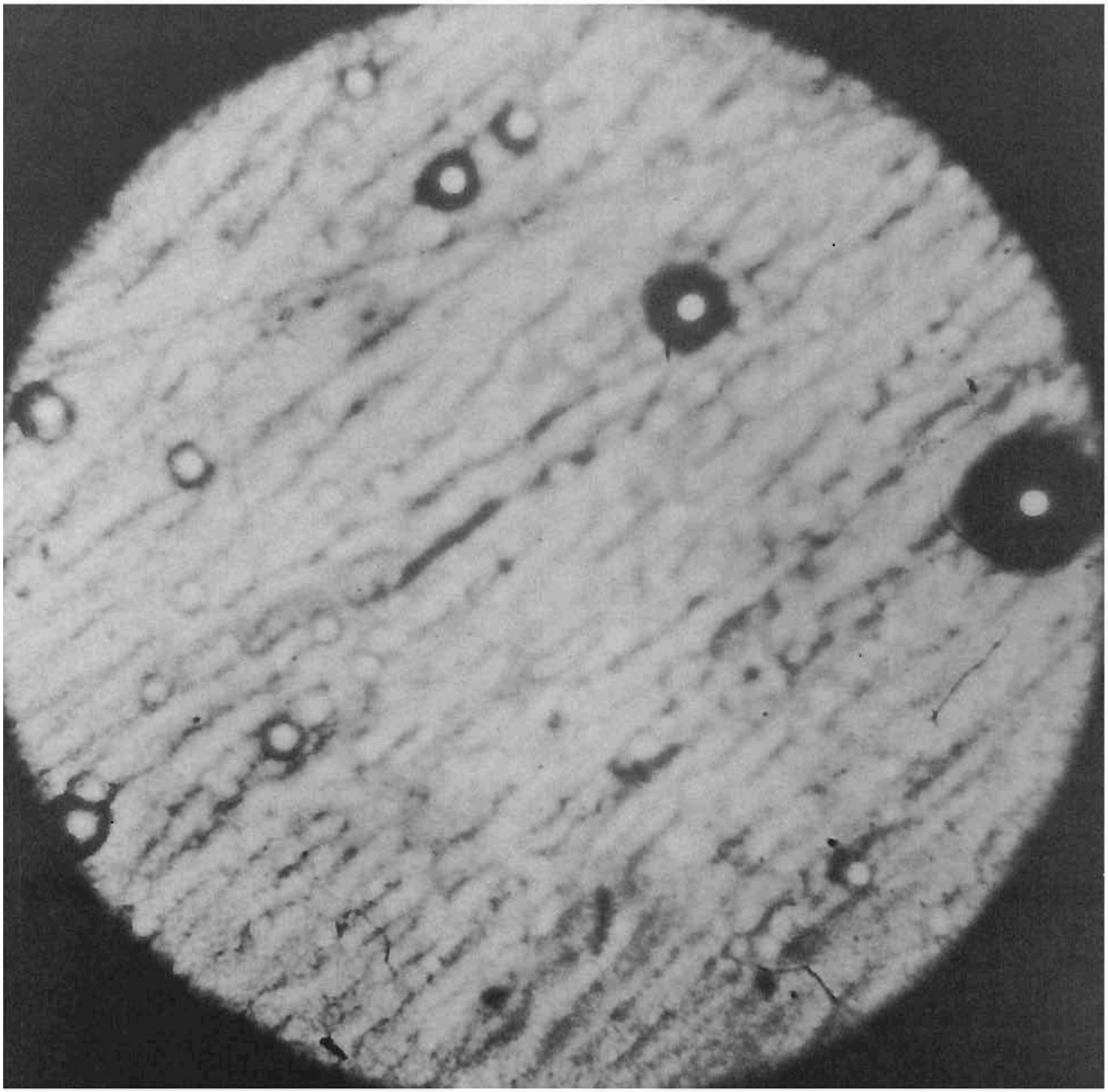

Figure 11.- Nickel deposit at 150X; current density, 20.5 amperes per square foot.

Carefully standardized, floating siphons were used to feed the pure nickel catholyte into the cathode compartment at a constant rate. As considerable time was needed for the cell to reach equilibrium operating conditions, all tests were conducted so that plating conditions were maintained for at least 6 hours. In some instances plating conditions were maintained for 24 hours or longer, so that any discrepancies between long and short-time cell operation would be disclosed. The results of these studies are summarized and presented graphically in the curves of Figure 12. It can be readily seen that at fairly high values of flow number, a catholyte pH of 6.3 was maintained; in consequence, the ampere efficiency was 100 percent, with a corresponding minimum value for the energy requirements per pound of nickel of 1.74 kw.-hr. per pound of nickel plated.

As the flow through the cell was reduced, the pH of the catholyte solution was lowered. The results of this were reduced ampere efficiency due to hydrogen evolution, reduction of voltage across the cell owing to

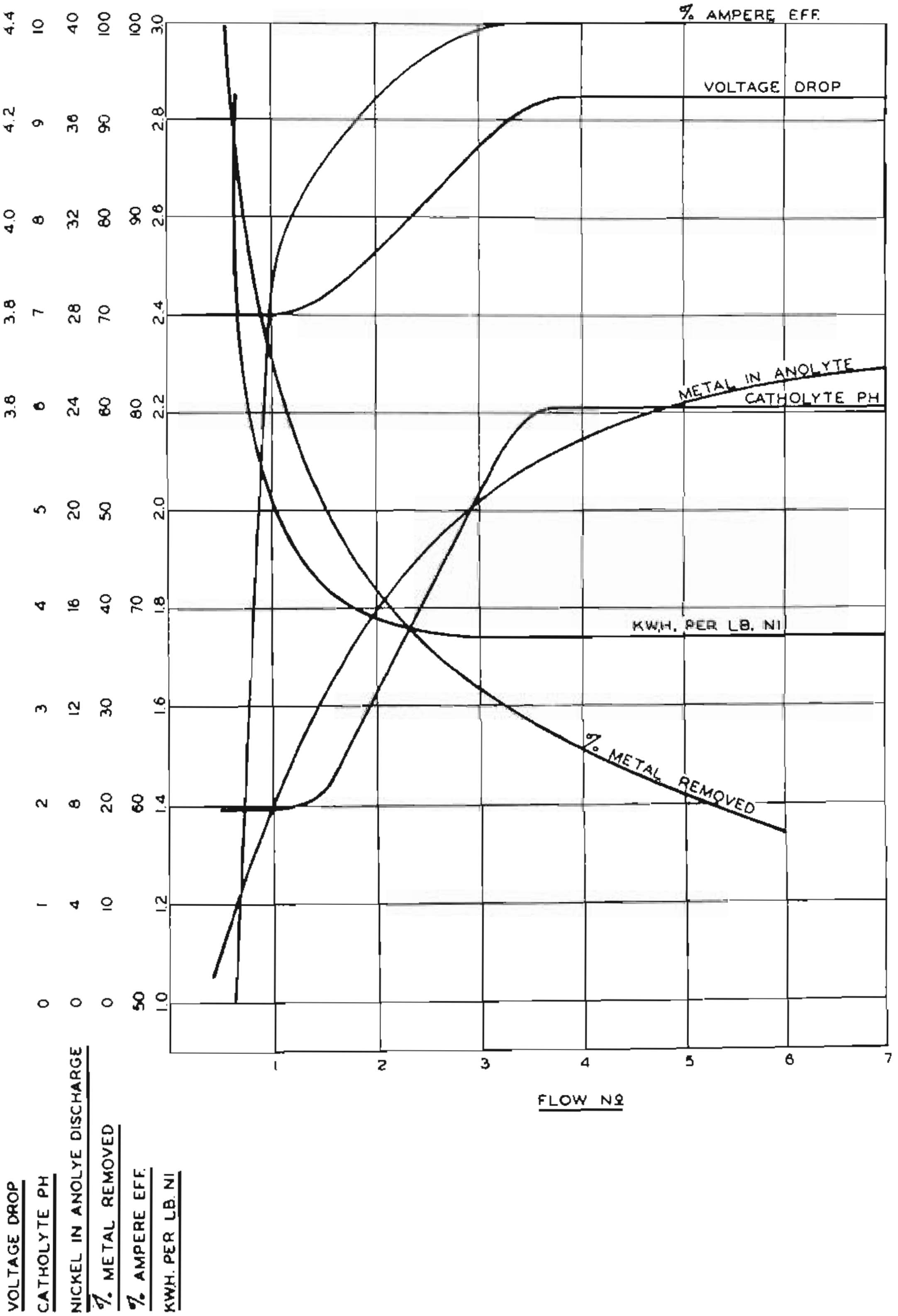

Figure 12.- Effect of flow rate on characteristics of nickel cell.

lowered resistance of the catholyte, and higher energy requirements per pound of nickel deposited. However, in spite of the seeming technical disadvantage of operating at a low flow number, there are economic advantages in so doing. At high flow numbers only a small percentage of the nickel introduced into the cell in the catholyte feed is deposited on the cathode, but at low flow numbers virtually all of the nickel introduced is plated. When operated at a low flow number of approximately 0.75, the anolyte discharge from the nickel electrowinning cell would contain 5 grams nickel per liter out of the 30 grams per liter contained in the pure nickel catholyte fed to the cell; the 25 grams per liter extracted electrolytically from the catholyte and deposited on the cathode would have been replaced with a chemical equivalent of sulfuric acid, making the acid concentration of the cell discharge 4.2 percent sulfuric acid. This dilute sulfuric acid solution then could be returned to the copper leach tanks after having been made up to the 100 grams per liter sulfuric acid required in the leaching operation.

Photomicrographs at 150X showing the variance in structure of the nickel deposited during these tests under different pH conditions and different flow numbers are illustrated in Figures 13, 14, 15 and 16. The grain size of the nickel produced in the more acid solutions is finer than that of the nickel deposited from the more nearly neutral solutions.

Inasmuch as the purpose of this part of the work was to develop an insoluble-anode, electrowinning-nickel process, it was necessary that the deposition conditions be such that the cell would stay in equilibrium for extended periods. This was necessary as industry demands electrolytic nickel cathode of certain definite minimum thickness. It is also quite expensive to remove and strip the cathodes more often than is absolutely necessary. Consequently, plating conditions were maintained for 120 hours. At the end of a 120-hour deposition period, two plates of nickel were stripped from the cathodes, one from each side. The plates were more than 1/8 inch thick, which is acceptable to industry. There was no technical reason why the time of deposition could not have been extended.

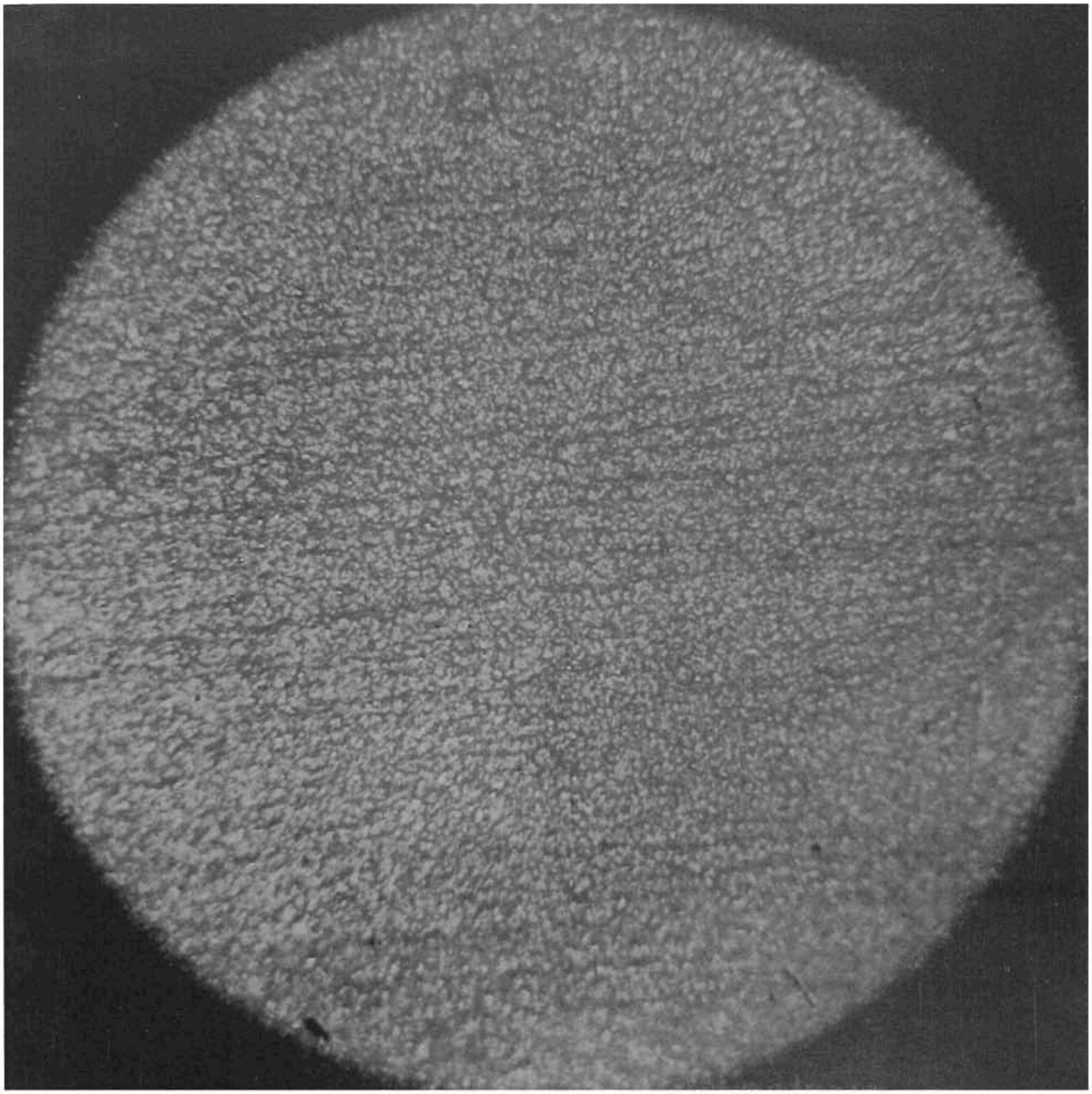

Figure 13.- Nickel deposit at 150X; pH of catholyte, 1.95.

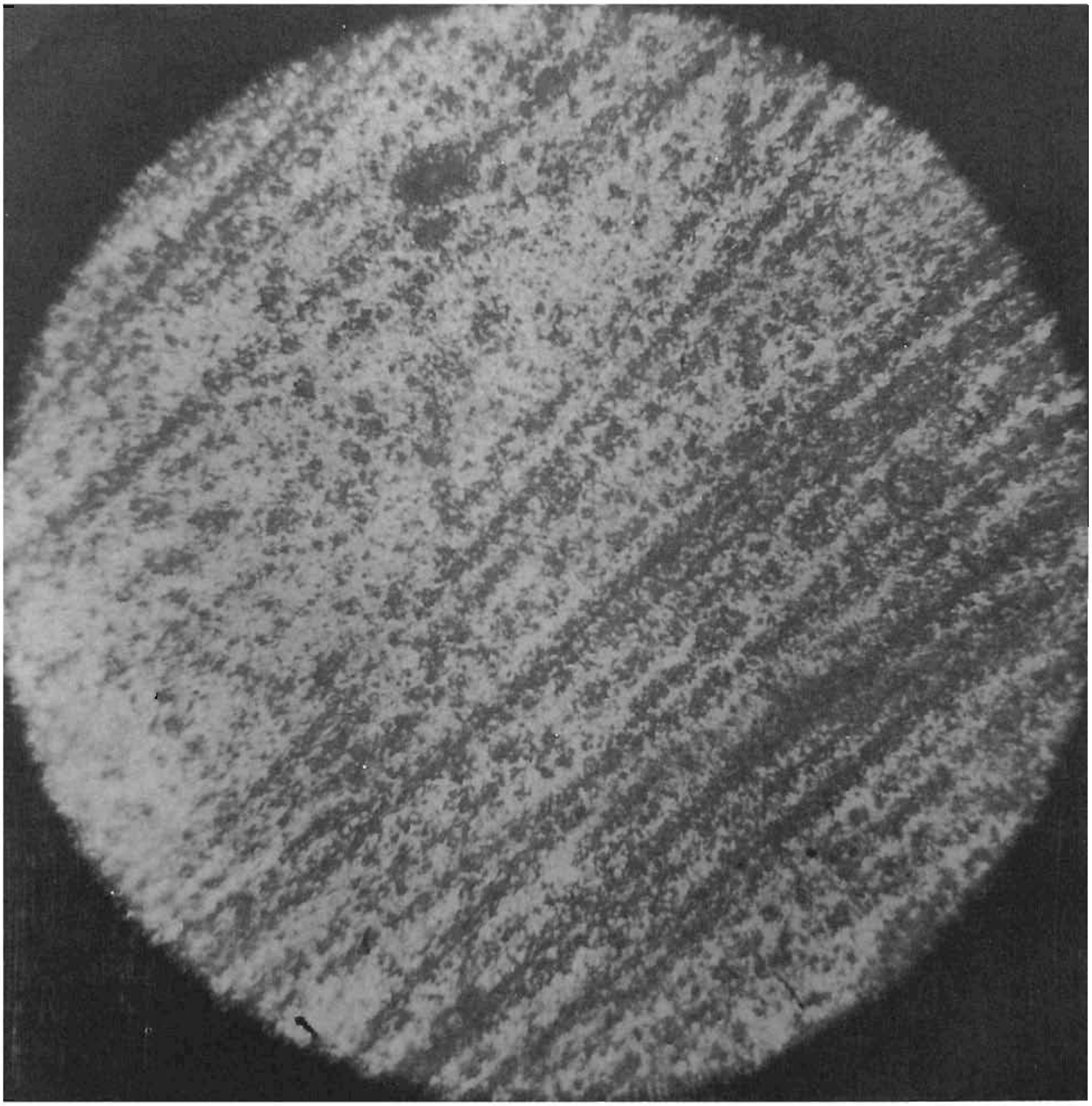

Figure 14.- Nickel deposit at 150X; pH of catholyte, 2.25.

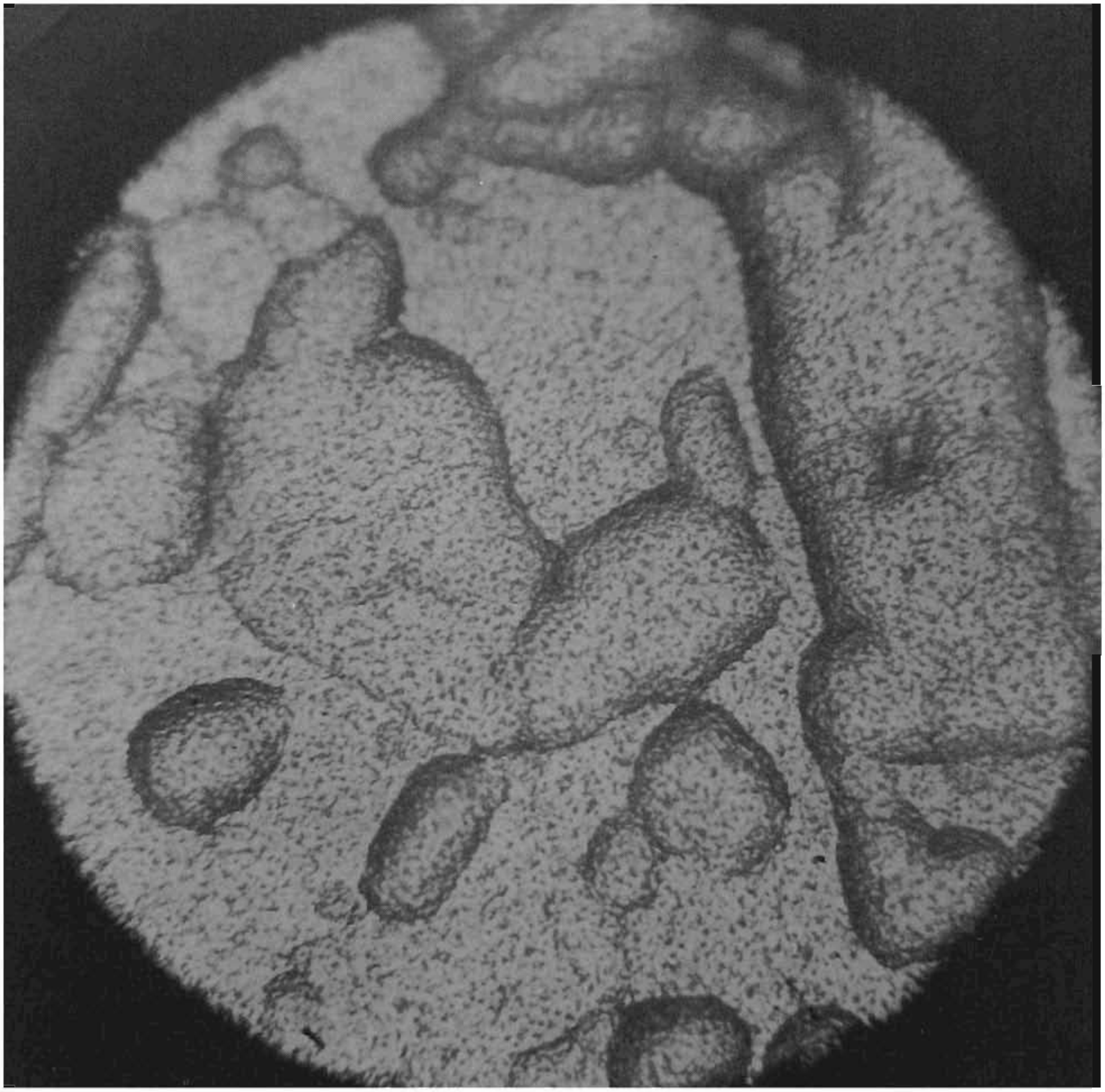

Figure 15.- Nickel deposit at 150X; pH of catholyte, 5.40.

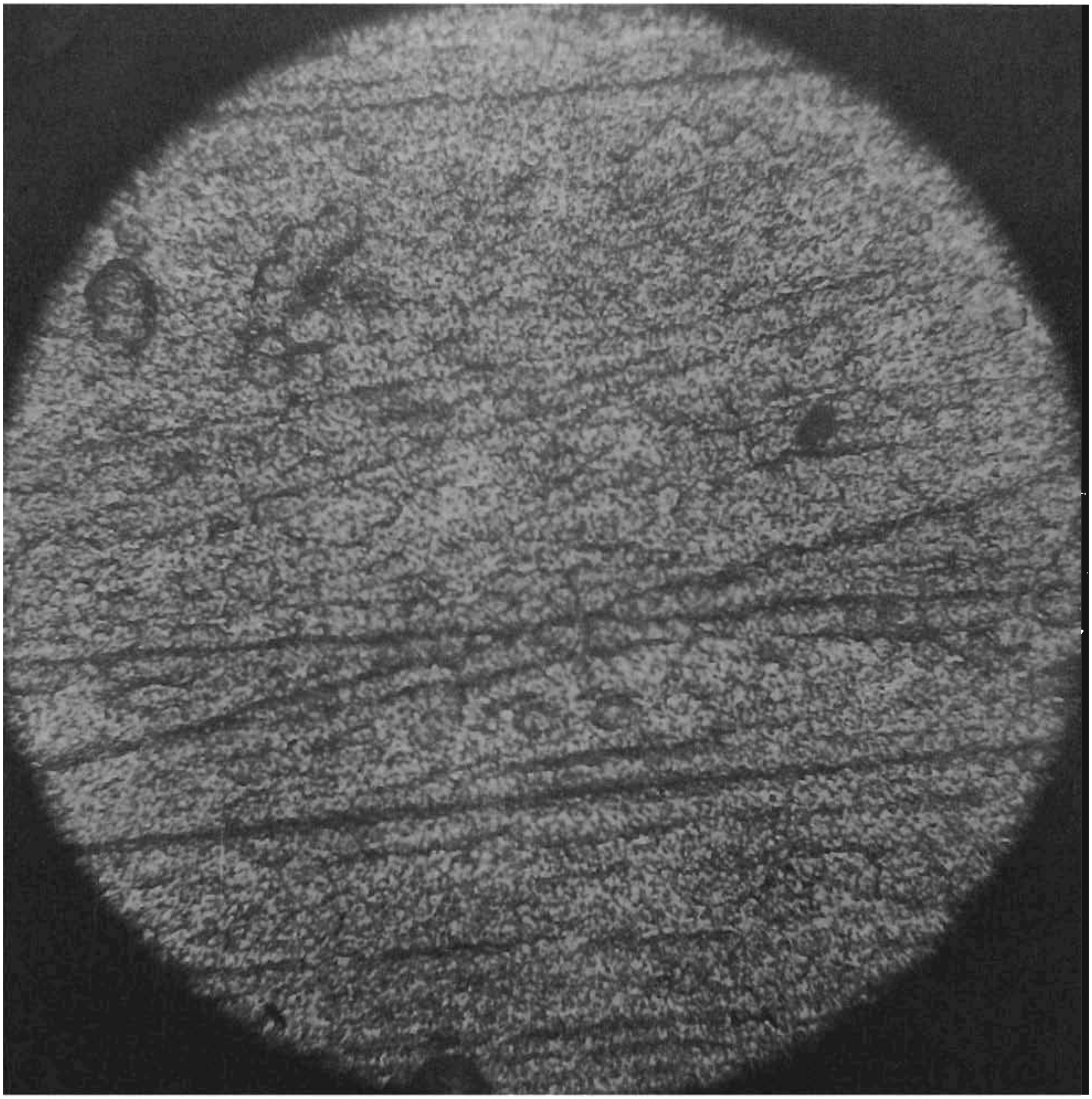

Figure 16.- Nickel deposit at 150X; pH of catholyte, 6.08.

Table 12 gives typical operating data on electrolytic nickel cells.

TABLE 12 - Typical Operating Data on Nickel Cells

Current Density	Amps/sq.ft.	18.5
Voltage Across Cell	Volts	4.2
Ampere Efficiency	Percent	100
Nickel Deposited	Lbs. per kw.-hr.	1.74
Flow Number		.573
Catholyte Feed Assay:		6
Ni	grams/liter	30
NaF	do	4.2
H_3BO_3	do	20
Temperature of Electrolyte	°C	27 to 35
pH Characteristics:		
Catholyte Feed		5.2 to 6.9
Catholyte		5.5 to 6.1
Anolyte		1.4 to 1.6

Analysis of Electrolytic Nickel, Percent

	From Bunkerville ore		From Purified $NiSO_4$ Solution	
Ni	98.69	99.27	99.66	99.71
Co	.59		.05	
Zn	.27		Spectrographic trace	
Mn	.18		- - -	
Cu	.038		.002	
Si	.03		- - -	
Fe	.015		.0016	
Al	Spectrographic trace		- - -	
Ti	do.		- - -	

Table 13 compares industrial copper and nickel electrolysis operating data with the Boulder City laboratory data.

The comparison does not take into account the fact that the electrolytic work at the Federal Bureau of Mines laboratories was done on such a small scale that the normal tank-house current losses due to poor contacts, solution leakage, etc., did not occur. The efficiency figures tabulated at 95+ percent would undoubtedly be lower in the course of normal tank-house practice. In studying this comparison, the low thermal-energy requirements in the preparation of the converter anode must be taken into consideration, as well as the energy requirement for electrolysis. The thermal-energy requirement for prepartion of a 95+ percent nickel metal anode from a nickel-copper matte is far greater than the electrolytic-energy requirement for electrolysis of this nickel anode.

TABLE 13. - Comparison of Industrial and Experimental Operating Data

Process	Current Density	Ampere Efficiency Percent	Voltage Across Cell	Kw/hr. per Lb. Metal	Flow Number
Copper - Electrorefining[14]	10 to 20		0.23 to 0.45	0.16	
Copper - Electrowinning[15]	10 to 12	65 - 90	1.8 to 2.5	1.0 to 1.5	
Copper-matte Anode Electrolysis - U.S.B.M.	10	100	.5	.19	
Nickel - Stanley refining process[16] . . .	11 to 12	93 to 94	2.4 to 2.5	1.1	
Nickel - Hybinette refining process[17] . . .	10	85	3 to 4	1.7	
Nickel - Electrowinning - U.S.B.M.	18.5	100	4.2	1.74	4
Nickel - Electroinning - U.S.B.M.	18.5	77.5	3.8	2.3	0.75

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[14] Brockman, C.S., "Electrochemistry", N.Y., Von Nostrand, 1931, p. 119.

[15] Perry, J.H., "Chemical Engineer's Handbook", N.Y., McGraw Hill, 1934; Sec. 25, by C. L. Mantell, p. 2358.

[16] Perry, J.H., "Chemical Engineer's Handbook", N.Y., McGraw Hill, 1934, Sec. 25, by C. L. Mantell, p. 2354.

[17] Gowland, W.A., and Bannister, C.O., "The Metallurgy of Nonferrous Metals", Sp. Cit., p. 551.

CONCLUSIONS

1. A process has been developed for the production of electrolytic nickel and copper from copper-nickel converter matte. While the energy required for the two electrolytes is somewhat higher than the normal energy requirements for the present commercial processes, this is more than offset by a saving in thermal energy.

2. Copper of satisfactory chemical composition and physical characteristics has been deposited electrolytically from a solution containing as little as 5 grams of copper per liter and as much as 30 grams of nickel per liter.

3. Nickel of satisfactory physical and chemical characteristics has been deposited from nickel sulfate electrolytes by means of insoluble anodes. The time of deposition has been maintained long enough to allow deposits of a thickness comparable with the usual commercial cathodes.

4. The precious metals values from the ore are entirely recovered in the copper cell.

5. Indications are at present that the precipitation of nickel carbonate before the nickel electrolysis may be eliminated.

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