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1965/182

INVESTIGATION INTO PRODUCTION OF REFINED BISMUTH

(A.M.D.L. Report No.388)

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Introduction

Marketing of crude bismuth metal produced by leaching ore from the Tennant Creek area proved difficult. The relatively low return for crude bismuth compared with prices listed for pharmaceutical grade material prompted the Bureau to sponsor this research into an electro-refining process suitable for the production of bismuth metal of acceptable grade at Tennant Creek.

The report has been included in the Bureau's Record series so that it may enjoy the wider distribution afforded by the "open file" system. It has not been altered in any way.

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AMDL Report 388
November, 1964

INVESTIGATION INTO PRODUCTION OF REFINED BISMUTH

by

R. E. Wilmshurst

to

THE BUREAU OF MINERAL RESOURCES

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1. INTRODUCTION

Early in 1962, a request was received from Mr C.N. Strong of Tennant Creek for the development of an electro-refining process to produce pharmaceutical grade bismuth from crude metal. The latter was produced from tailings dumps in the Tennant Creek area by a process similar to that described by Cathro and Koch[1][(a)]. In his process, Mr Strong leached the ore by percolation with sodium chloride-sulphuric acid solution. The leach solution, together with liquor used to wash the leach residue, was then treated with scrap iron. Bismuth metal in a finely divided "sponge" form was precipitated in this cementation step, and was subsequently melted into ingots. The product, although technically a good quality metal, was not of sufficiently high purity for use in the manufacture of pharmaceuticals.

In September, 1962, Mr Strong approached the Commonwealth Bureau of Mineral Resources for support in financing the investigation. This support was given and work on the project commenced in January, 1963.

Specifications for pharmaceutical bismuth are laid down in the British Pharmaceutical Codex, but this authority uses arbitrary tests extensively, without giving numerical limits for specific impurities. Tests of this nature are convenient as acceptance tests to determine the suitability of any given material, but are inadequate for use in investigational work. Evaluation of the tests and correspondence with Bismuth Products Pty. Ltd. led to the following tentative limits for impurities in pharmaceutical grade bismuth metal:

Arsenic	not more than	2	ppm
Lead	- ditto -	0.04	%
Copper	"	50	ppm
Silver	"	0.01	%
Antimony	"	10	ppm
Tellurium	"	2	ppm

The experimental work described in this report was aimed at production of a metal to this specification by an electro-refining process suitable for use at Tennant Creek.

1.1 Electro-refining of Bismuth

Electro-refining of bismuth has been practised for many years but little detailed information has been published. Gruzensky and Crawford[2] surveyed the various electrolytes recommended from time to time and found only two to be satisfactory. One of these, a hydrofluosilicic acid solution, gave excellent results but was unstable and unsuitable for large scale use, particularly in remote areas. The alternative hydrochloric acid-bismuth chloride solution gave satisfactory results except that removal of lead was not achieved; this was rectified by the addition of sulphuric acid. Kern and Jones[3] recommended a similar solution, and this was used also by Cathro and Koch (loc cit) in refining of Tennant Creek bismuth.

(a) See Section 8 for References.

Metal from Tennant Creek has been variable in composition, with analyses generally in the following ranges:

Copper	0.03 - 0.20 %
Lead	0.05 - 0.10 %
Zinc	(a) < 0.01 %
Silver	< 50 ppm
Iron	< 0.01 %

The work of Cathro and Koch, in conjunction with consideration of standard electrode potentials, indicates that simple electro-refining applied to this metal would have the effect shown in Table 1.

TABLE 1: LIKELY PURIFICATION OF BISMUTH

Element	Crude Metal	Reduction Factor	Refined Metal
Cu	0.2 %	5	0.04 %
Pb	0.1 %	450	2 ppm
Zn	0.01 %	high	low
Fe	50 ppm	high	low
Ag	0.01 %	1.3	70 ppm

These figures suggest that electro-refining alone is unlikely to produce a metal to the required specification. Pyrometallurgical methods of removing these impurities were therefore investigated. Some consideration was also given to modifying the existing operations at Tennant Creek to improve the crude metal purity.

2. SUMMARY

In response to a request from Mr C.N. Strong of Tennant Creek and under the sponsorship of the Commonwealth Bureau of Mineral Resources, an electro-refining process for metallic bismuth has been developed. Simple electro-refining using an acidic chloride electrolyte was incapable of producing pharmaceutical grade bismuth from crude metal. Various pyrometallurgical techniques were examined and a hybrid process developed.

Melting of the crude metal with sodium hydroxide and sodium cyanide, casting the resultant metal into anodes, and electro-refining in the chloride bath, followed by a sulphur drossing step gave pharmaceutical quality bismuth metal.

(a) < Less than.

A large parcel of bismuth metal has been refined by this process to give over 200 pounds of pharmaceutical quality metal. The process is capable of good yields of metal and the electro-refining operation has a high current efficiency.

The weaknesses inherent in electro-refining processes are considered to make them adaptable only with difficulty for small-scale use in remote areas such as Tennant Creek.

3. MATERIAL EXAMINED

The ore used in leaching experiments was from the Jubilee Mine, near Tennant Creek. This material contained approximately 3 per cent bismuth.

In both the small scale and pilot scale refining experiments, a parcel of 350 pounds of crude bismuth metal from Mr Strong was used. This parcel consisted of 14 ingots each of 25 pounds nominal weight. As preliminary experiments had indicated that copper and silver were the elements most likely to cause difficulty in refining, each ingot was assayed for these metals. The results of these assays are set out in Table 2.

TABLE 2: ANALYSES OF CRUDE BISMUTH INGOTS

Ingot No.	Silver ppm	Copper %
1	23(a)	0.074(b)
2	16	0.076
3	12	0.113
4	18	0.062
5	8	0.099
6	10	0.063
7	18	0.035
8	20	0.070
9	18	0.110
10	18	0.098
11	18	0.159
12	18	0.160
13	14	0.119
14	16	0.206

(a) Mean, values from 22 ppm to 26 ppm in various parts of ingot.

(b) Mean, values from 0.051 to 0.093%.

4. EQUIPMENT

The pilot scale electro-refining experiments were conducted in a multiple cell bank constructed for the purpose. This vessel was 3 feet square in plan and 18 inches deep, and was divided by vertical partitions into ten cells 18 inches by 7 inches in plan and 18 inches deep. Welded steel construction was used and all internal surfaces of the tank were covered by epoxy resin reinforced with glass fibre.

Two copper cathodes, approximately one sixteenth of an inch thick, were suspended in each cell compartment with an area 15 inches square immersed in the electrolyte. Only five cells were used and these were connected electrically in series. The current for electrolysis was obtained from a silicon diode rectifier set rated to deliver 50 amperes at 2 volts DC from a 240 volt 50 cycle AC input. A variable auto-transformer in the AC circuit served to control the rectifier output.

5. EXPERIMENTAL PROCEDURE AND RESULTS

5.1 Preliminary

An experimental pyrometallurgical treatment was begun at Tennant Creek by Mr Strong. The procedure is given as described by him in Figure 1.

The metal corresponding to Sample B was cast into an anode and electro-refined. Sample C was the cathode deposit.

Analyses by AMDL of these samples, for copper and silver only, are given in Table 3.

TABLE 3: ANALYSIS OF BISMUTH METAL

Sample	Copper ppm	Silver ppm
A	160	10
B	30	20
C	15	10
D	3300	10
E	170	10
F	490	10
G	55	10
H	65	20
J	110	4
K	27	4

Samples G and H, also from Tennant Creek, are respectively before and after a cyanide leaching treatment of sponge metal. Samples J and K are from a similar experiment conducted at AMDL.

In general the following conclusions can be drawn:

a. the copper tends to concentrate in the skimmings (Sample D);

b. the sulphur and cyanide flux treatment reduces copper appreciably (Samples A-B and D-E);

c. electro-refining following the flux treatment produces a metal of purity approaching the required level;

d. copper can probably be removed also by cyanide leaching of the cemented bismuth sponge before smelting.

5.2 Laboratory Investigations

5.2.1 Improvement of Existing Process

To simulate the existing leaching process, 250 grams of the ore sample submitted by Mr Strong was crushed to pass a ¼-inch screen, and then leached twice by percolation with the same 500 ml of leach solution. This solution contained 10 per cent w/v NaCl and 4 per cent w/v H_2SO_4. A further 100 ml of fresh solution was used as a wash.

The leach liquor was found by analysis to contain 12.1 grams of bismuth per litre. It was divided into three equal parts. Part 1 was cemented for 24 hours with sheet steel. Part 2 was cemented for 2 hours with 1 gram of bismuth sponge, filtered and then cemented with iron as in Part 1. Part 3 was treated with 0.1 gram of sodium sulphide, stirred for 2 hours, filtered and cemented with iron as in Part 1.

Cementation with metallic bismuth was expected to remove copper from the solution, while the partial sulphide treatment of Part 3 should precipitate copper and some bismuth as sulphide. As the amount of metal in each experiment was quite small, the bismuth sponge products were oxidised to Bi_2O_3 before analysis.

The results are as follows:

		Cu ppm	Ag ppm
Part 1:	Control only	61	<3[a]
Part 2:	Bismuth cementation	48	3
Part 3:	Sulphide	46	<3

Both the treatments therefore reduced the concentration of copper in the product, but not sufficiently to indicate that either technique was suitable without further development.

(a) < Less than.

5.2.2 Refining of Ingot Metal

The metal used in the experiments was from an ingot previously sampled and found to contain 16 ppm of silver and 0.206 per cent copper. This metal was treated by a number of different techniques with the following results.

Simple Electro-refining. A sample of the metal was cast into a sheet 8 inches square and approximately $^1/_8$-inch thick. This was electro-refined on to a waxed copper sheet at a current density of 10 amperes per square foot. The electrolyte contained 50 g per litre HCl, 70 g per litre bismuth (added as $BiCl_3$) and 0.1 g per litre pyrogallol. The electrodes were $1^1/_4$ inches apart, and the solution was agitated gently. Operating voltage was 0.13 volt. The cathode deposit was granular, with a tendency to growth in fingers, but adequately adherent. The analyses of this metal indicated 61 ppm copper and 3 ppm silver.

This experiment confirmed that simple refining was not adequate.

Use of Parkes Process. One hundred grams of metal and 10 grams of powdered reagent grade zinc were melted and held at 450°C for 2 hours with occasional stirring. After settling and solidification, the top half of the specimen was rejected and the bottom half sampled. A control test without zinc was carried out simultaneously.

The analyses were:

	Cu ppm	Ag ppm
Control	9	11
Experiment	2	3

The results suggest that the zinc treatment was successful in removing copper and silver to acceptable limits but, more important, that careful settling without zinc was also effective.

Use of Sulphur Drossing. A sample of metal was fused with 1 per cent of its weight of elemental sulphur, using a salt bath for ease of temperature control. The melt was skimmed and cast into an anode. The electro-refining process described above was carried out and gave a metal containing 4 ppm copper and 3 ppm silver.

This technique therefore gave a metal acceptable with regard to both copper and silver.

Cyanide Fluxing. A sample of metal was fused with 1 per cent of its weight of sodium cyanide. Some difficulty was experienced and contact was not ideal. The treated metal was cast into an anode and refined. Two products were collected - one with the electrolyte described above, and the other after addition of 75 g per litre of H_2SO_4 to the solution. The products contained:

Product							
With Sodium Cyanide				With Sodium Cyanide plus H_2SO_4			
Copper,	Cu	15	ppm	Copper,	Cu	19	ppm
Silver,	Ag	<3(a)	ppm	Silver,	Ag	<3	ppm
Lead,	Pb	0.015%		Lead,	Pb	0.015 %	

The cyanide treatment effectively reduced the copper and silver concentrations. The addition of sulphuric acid to the electrolyte made no difference to the concentration of lead in the products.

5.3 Discussion

The experiments above indicated that simple electro-refining of the bismuth ingot metal was not likely to produce a metal to the required specification. Preliminary treatment with sulphur, sodium cyanide or metallic zinc, followed by electro-refining, should produce an acceptable metal. In the latter case the refining would be necessary to remove zinc left in solution in the bismuth. Of these methods, the zinc treatment would probably give a lower yield than the others, because of difficulty in separating the two metals. The sulphide treatment would give a greater loss of bismuth in the skimmings than the cyanide method, and the latter is therefore preferred.

The removal of copper by careful settling was not fully understood, and may have been due partly to segregation on cooling. However, it was observed in the experimental work that some sulphur was present in the ingot material - a sample of skimmings from an ingot was found to contain 0.2 per cent of sulphur, presumably as copper and bismuth sulphides. This probably accounted for copper removal by settling. Use of the method for refining is feasible but bismuth losses would be high.

The presence of the sulphide was noticeable also in the electro-refining process. A black crystalline deposit, identified as bismuth sulphide, appeared at times on the anode and in the anode sludge. This phenomenon was also associated in some way with the appearance of a white coating of bismuth oxychloride on the anode in some experiments. This coating, if left unchecked, blanketed the anode surface and increased the cell voltage to 0.25 volt or higher. Both of these effects are probably associated with gradual loss of free acid from the electrolyte.

At this point a complete refining process could be formulated. To check the validity of this proposed process, a separate "proving" experiment was carried out.

A sample of ingot metal was melted in a steel vessel using as flux a mixture of equal weights of sodium hydroxide and sodium cyanide. The total weight of flux was 2 per cent of the weight of bismuth. The mixture was held at 400-500°C for 10 minutes with occasional stirring, and then allowed to cool slowly. As solidification commenced about 2 per cent of the bismuth was skimmed off using a steel gauze and discarded. The bulk of the metal was reheated and cast into anodes.

(a) < Less than.

The anode metal was electro-refined using a hydrochloric acid electrolyte containing 70 grams of bismuth, 50 grams of free acid, and 0.1 gram pyrogallol per litre. Copper cathodes were used and were coated with a thin film of paraffin wax to assist in removal of the deposit. The current density was 10 amperes per square foot, and the electrolyte was agitated gently. No diaphragm or anode bag was used.

Over a period of 90 hours, 2020 grams of metal was deposited at a current efficiency of 94 per cent. In the following 72 hours, 1620 grams of metal was deposited at virtually 100 per cent efficiency. Analyses of the two deposits, designated A and B respectively, are shown in Table 4 below.

TABLE 4: ANALYSES OF BISMUTH METAL

Element	Deposit A ppm	Deposit B ppm	Limit ppm
Lead	<10[a]	<10	400
Copper	12	30	50
Silver	2	6	100
Antimony	<5	<5	10
Arsenic	0.4	1.2	2
Tellurium	<1	1.1	2

(a) < Less than.

These results confirmed that the process was effective.

6. PILOT SCALE REFINING OF BISMUTH METAL

Following the development of the process to the stage outlined in the previous Sections, refining of the larger parcel of metal was begun.

The crude metal was treated by the sodium hydroxide-sodium cyanide fluxing technique, and cast into anodes with an active area 15 inches square. These were mounted in the cell bank described previously using in each cell one anode suspended between two copper cathodes and approximately 1½ inches away from each. The conditions for electrolysis were the same as given in the preceding section.

Refining was carried out until there was insufficient crude metal available to form 5 anodes. The operation was then continued using 4 cells then 3, then 2, and finally a single cell. Refining was stopped when there was insufficient crude metal to give a single anode.

During the whole of this period, metal was deposited on the cathodes at high current efficiencies, except in some cases where the deposit on the cathodes bridged the space between the two electrodes. When this happened the cell was effectively short circuited and refining ceased. In an effort to prevent this difficulty glycerol was tried as an alternative to the pyrogallol used to modify the character of the deposit throughout the earlier experimental work. Little if any improvement was evident. On some occasions the weight of metal deposited on the cathodes before the cell became unworkable was quite small.

Removal of the deposit from the cathodes was not difficult but always involved some chance of contaminating the product with cathode material. The risk was proportionately greater when the cathode deposit was thin and refining had been interrupted by bridging of the electrodes.

No purification of the electrolyte was attempted at any stage, but additions of hydrochloric acid were required at intervals to replace acid lost by evaporation and by side reactions in the cells. At the completion of the run the cathode deposits were melted down using sodium hydroxide flux and cast into ingots which were sampled for analysis. Results of the analyses are shown in Table 5.

TABLE 5: ANALYSIS OF REFINED BISMUTH
Expressed in parts per million

Ingot Number	Ag	Cu	As	Te	Pb	Sb
1	5	76	2	1	40	10
2	9	69	2	1	18	10
3	5	140	2	1	35	10
4	6	99	2	1	15	10
5	3	37	2	1	10	10
6	2	37	2	1	15	10
7	7	755	2	1	8	10
8	4	110	2	1	18	10
9	3	170	2	1	15	10
10	6	125	2	1	8	10
11	6	150	2	1	10	10

These analyses indicate that the refined metal was satisfactory in all respects except that it contains considerably more copper than is permissible. Following the earlier work it was thought that this might be removable by a skimming technique. Accordingly all of the refined metal was re-melted using caustic soda flux, and small amounts of skimmings were taken as the metal solidified. These skimmings were kept separate, the bulk of the metal being re-heated and cast again into ingots. Results of the analysis of these ingots for copper are given in Table 6.

TABLE 6: ANALYSIS OF SKIMMED BISMUTH
Expressed in parts per million

Ingot Number	Cu
1	1070
2	320
3	290
4	440
5	750
6	500
7	460
8	260
9	670

Results of this operation were disappointing in that the amount of copper had increased rather than decreased. The increase may have been due in part to sampling errors but was almost certainly caused largely by contamination from an unidentified source. Clearly the metal was still unsatisfactory.

At this stage a sulphur drossing technique was used to reduce the copper content of the bismuth. The ingot material was melted once again using sodium hydroxide flux and, while molten, the metal was treated with elemental sulphur. The weight of sulphur used was 1 per cent of the weight of the metal in any given melt and it was added slowly with stirring to the bismuth. The molten metal was then allowed to cool, was skimmed, reheated, and recast into ingots. Results of further analyses are given in Table 7.

The amount of copper present was then well within the specified limit with the exception possibly of the ingot designated 9A. However, other ingots were so far below the limit that the metal could all be considered satisfactory after a single blending operation.

The weights of finished refined metal, skimmings, and crude residual metal were respectively 214, 6 and 34 pounds. While the overall yield could be regarded as poor, considerable quantities of bismuth were discarded at various stages of the operation because it was considered that recovery would cost appreciably more than the value of the recovered metal. In practice excellent yields of metal should be possible.

TABLE 7: ANALYSIS OF DROSSED METAL

Ingot Number	Cu ppm	Weight of Ingot lb
1A	5	24
2A	16	24
3A	8	20
4A	20	21
5A	17	19
6A	17	21
7A	22	20
8A	15	20½
9A	59	22½
10A	20	22½

7. DISCUSSION

The investigation was restricted in scope as the original request was for development of an electro-refining process. The experimental work demonstrated clearly that a simple electro-refining process was not capable of producing metal of the required purity. Consequently a combination process was developed in which pyrometallurgical steps were combined with electro-refining to produce pharmaceutical grade bismuth. The overall process has been used to refine substantial quantities of metal and has been shown to be effective.

In spite of the reasonable results which were obtained from the refining process, electro-refining can scarcely be considered a satisfactory refining process in the present context. Its inability to remove certain impurities and the possibility of impurity build-up in the electrolyte with subsequent falling-off in efficiency of refining are strong arguments against a process of this type. Control of the nature of the cathode deposits by use of various additives to the electrolyte is an art rather than a science. With experience a satisfactory technique could probably be developed. However, there seems to be an inherent weakness in any process which involves plating of metal on to a cathode of material which would be an undesirable contaminant in the product. Removal of the deposits from the copper cathodes was relatively easy but when the copper specification is so stringent the danger of contamination beyond the specified limit is always present. Possibly this could be averted by use of an alternative cathode material. With further development, use of bismuth cathodes may be feasible but this has not been attempted in the present investigation. However, it is considered that a pyrometallurgical process along conventional lines using such operations as sulphur drossing, skimming, partial oxidation, chlorination and so on, could give metal of an acceptable quality rather more simply than the refining processes described above. Nevertheless it has been shown that a combination process employing sulphur drossing, skimming and electrorefining can produce pharmaceutical grade bismuth from crude metal produced in the Tennant Creek area.

8. REFERENCES

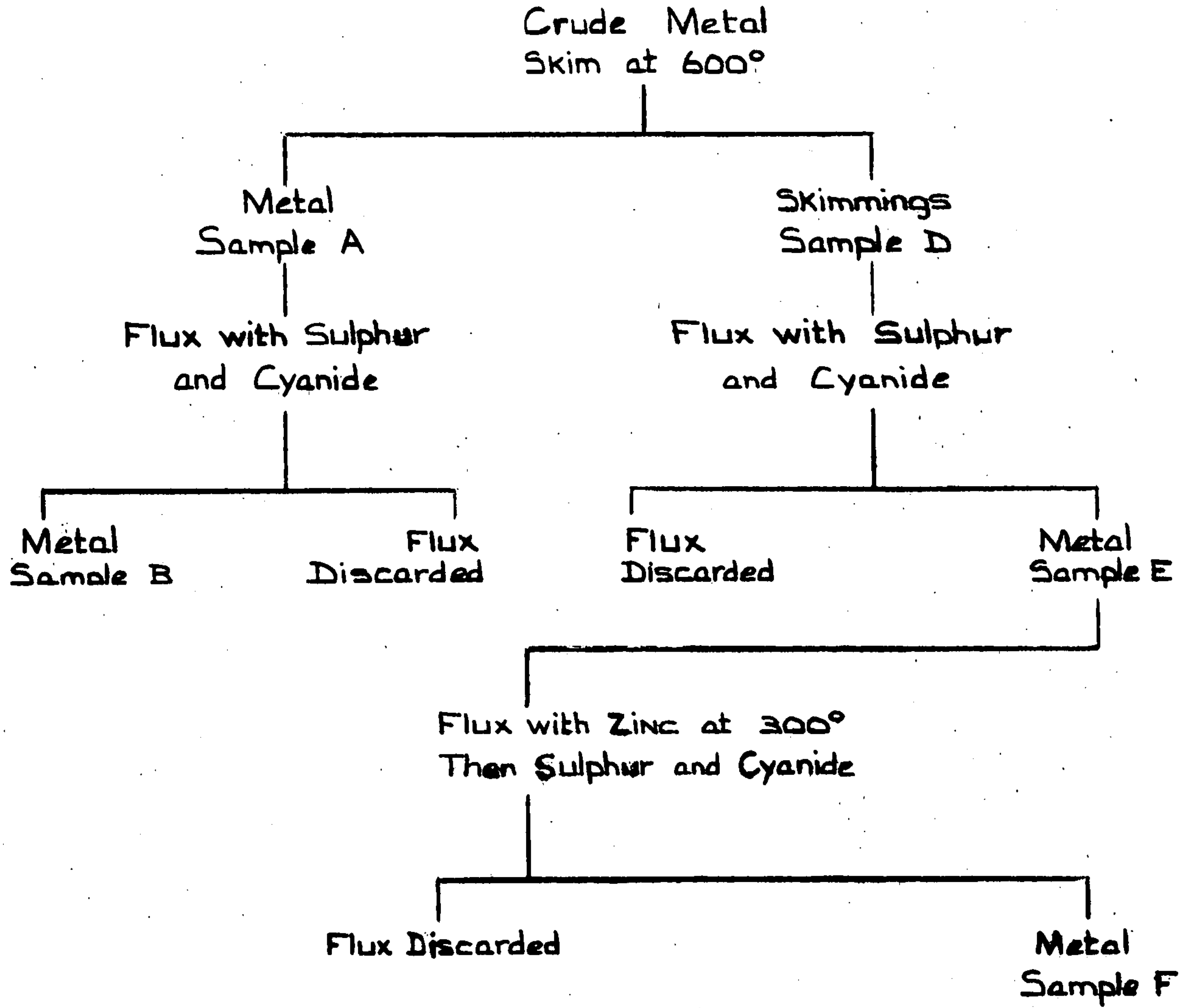
1. CATHRO, K. J., and KOCH, D. F. A., "Recovery of Bismuth from Chalcopyrite Calcines", paper presented at the A. I. M. M. Hydrometallurgy Symposium, Adelaide, February, 1960. See also Aust. J. App. Sci. 13, (3) 175 (1962).

2. GRUZENSKY, P. M., and CRAWFORD, W. J., U. S. Bureau of Mines, Report of Investigation 5182.

3. KERN, E. F., and JONES, T. R., Trans. Amer. Electrochem. Soc. 57, 255 (1930).

FIGURE 1.

EXPERIMENTAL PYROMETALLURGICAL TREATMENT



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