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RECOVERY OF MOLYBDENITE IN A COPPER CONCENTRATE FROM McINTYRE PORCUPINE MINES, LIMITED, SCHUMACHER, ONTARIO

IR 65-66

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by

G. I. MATHIEU

MINERAL PROCESSING DIVISION

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RECOVERY OF MOLYBDENITE IN A COPPER
CONCENTRATE FROM McINTYRE PORCUPINE
MINES, LIMITED, SCHUMACHER, ONTARIO

by

G. I. Mathieu*

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SUMMARY OF RESULTS

The copper concentrate received from McIntyre Porcupine Mines contained approximately 0.6% MoS₂. The molybdenite occurred mostly as free grains varying from 5 to 60 microns in size, but occasionally was intergrown with chalcopyrite.

Phosphorus pentasulphide or arsenic trioxide were both found to be suitable for separating the molybdenite from the copper minerals by selective flotation. The latter proved to be slightly more effective and was used in a test incorporating four cycles of flotation. This technique produced a concentrate assaying 73.2% MoS₂ and 3.5% Cu with a molybdenite recovery of from 60% to 78%. Attempts to upgrade the molybdenite concentrate to 90% MoS₂ were unsuccessful.

Other reagents such as sodium cyanide and ferrocyanide were found to be ineffective in separating the molybdenite from the copper minerals.

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INTRODUCTION

McIntyre Porcupine Mines Limited are currently milling, in addition to a gold ore, approximately 1500 tons of copper ore per day in a separate circuit. The copper concentrate produced from this ore carries from 0.7% to 0.9% MoS₂. The company is planning to increase the tonnage in the copper circuit to 2000 tons per day and under these circumstances is interested in the possibility of recovering the molybdenite from their final copper concentrate.

Purpose of Investigation

Mr. J. C. Carter, Chief Metallurgist, McIntyre Porcupine Mines, Limited, Suite 1500, 25 King Street West, Toronto 1, Ontario, requested an investigation aimed at recovering the molybdenite from the copper concentrate. He pointed out that the handling and disposition of a series of cleaner tailings in upgrading rougher molybdenite concentrate might become a problem and should receive due consideration in the investigation. A molybdenite concentrate assaying 90% MoS₂ with less than 0.5% Cu was desired.

Shipment

A sealed drum containing approximately 1100 lb of copper concentrate, in a moist state, was received on April 21, 1965.

Sampling and Analysis

A sample weighing 150 lb was shovel sampled from the barrel and was split into 32 fractions having a dry weight of approximately 2,000 g. One of these was used as a head sample, the others being retained separately in plastic bags for future test work. During the course of the investigation, another 150 lb sample had to be cut and split into fractions for further test work.

Chemical analysis of the head sample gave the following results:

TABLE 1

Chemical Analysis* of Head Sample

Copper	(Cu)	-	29.71%
Molybdenite	(MoS ₂)	-	0.65%
Iron	(Fe)	-	26.76%
Sulphur	(S)	-	30.15%
Insoluble		-	7.65%

*From Internal Report MS-AC-65-594

Some of the molybdenite assays on test products in this report were done by both the Mineral Sciences Division and McIntyre mine staff. Although good checks were obtained on high grade molybdenite products, there was a large discrepancy in the analyses of the tailing products (0.17% MoS₂ versus 0.03% MoS₂). These differences were never resolved and although they have no bearing on the final grade of molybdenite concentrate produced, they represent a difference of up to 20% in the molybdenite recovery figures.

A spectrographic analysis on a portion of the head sample identified the following elements listed in their approximate order of decreasing abundance.

TABLE 2

Spectrographic* Analysis of Head Sample

I	-	Fe, Cu.
II	-	Si, Mo, Na.
III	-	Al, Mg.
IV	-	Mn, Ag.

*From Internal Report MS-AC-65-478.

Mineralogical Examination*

A portion of the head sample was submitted to the Mineralogy Section of the Mineral Sciences Division for mineralogical examination. One polished section was prepared from the sample and the minerals were identified by microscopical and X-ray diffraction studies. It was found that the sample is composed of chalcopyrite and small amounts of bornite, tennantite, molybdenite, sphalerite, pyrite, quartz, muscovite and talc. The minerals are largely present as free grains but chalcopyrite contains a few inclusions of pyrite. The molybdenite grains vary from about 5 to 60 microns in size and are mostly free, with the exception of 5% to 10% occurring as intergrowths with chalcopyrite.

*From Internal Reports MS-65-53 and 94.

OUTLINE OF INVESTIGATION PROCEDURES

As a preliminary step, a screen and infrasizer analysis was made to determine the size distribution of the molybdenite.

The major part of the investigation was concerned with the selective flotation of a molybdenite concentrate. For this purpose, three main types of copper depressants were tried, namely, sodium or ferrocyanide phosphorus pentasulphide and arsenic trioxide.

To simulate plant practice with recirculation of the cleaner tailings, a locked cycle test was done using the best procedure outlined by previous test work.

Finally, attempts were made to upgrade the final molybdenite concentrate by the following techniques:

- (i) further cleaning under various conditions;
- (ii) reverse flotation of the gangue minerals;
- (iii) heavy liquid separation.

DETAILS OF INVESTIGATION

Screen and Infrasizer Analysis (Test 1)

A 500g sample of copper concentrate was sized using screens and infrasizer apparatus. The fractions were analysed for molybdenite with the following results.

TABLE 3

Molybdenite Distribution in Sized Fractions

Size	Weight %	Analysis*% MoS ₂	Distribution % MoS ₂
+ 100 mesh	3.4	0.14	0.8
-100 + 150 "	9.1	0.16	2.5
-150 + 200 "	12.0	0.25	5.1
-200 + 40 microns	29.0	0.49	24.1
- 40 + 20 "	22.1	0.94	35.2
- 20 + 10 "	11.0	0.95	17.7
- 10 "	13.4	0.64	14.6
Feed (calcd)	100.0	0.60	100.0

*From Internal Report MS-AC-65-594.

Selective Flotation of Molybdenite

(i) Sodium Cyanide or Ferrocyanide

Sodium cyanide and ferrocyanide were tested as possible selective depressants for copper minerals. However, no satisfactory results were achieved with these reagents. A few tests were also made in which the copper concentrate was either boiled for 2 hrs or heated for 1 hr at 280°C prior to the flotation in presence of both cyanides. These techniques, aimed at removing the residual collectors, failed to improve appreciably the molybdenite-copper separation. The investigation was then directed towards the use of other reagents for the depression of the copper minerals.

(ii) Phosphorus Pentasulphide

This series of tests was made with the Noake's reagent which consists of 13 parts of caustic soda to 10 parts of phosphorus pentasulphide in aqueous solution (10% P₂O₅). Only the results from the two most significant tests of the series will be reported in detail.

Tests 2 and 3

A 2,000 g sample of copper concentrate (Test 2) and a 8,000 g sample (Test 3) were floated under the conditions shown in Table 4 and with the results summarized in Table 5.

TABLE 4

Reagents and Conditions of Flotation

Operation	Time min.	Reagents	lb / ton		pH
			Test 2	Test 3	
Conditioning	5	*P-Pentasilphide	3.50	3.50	8.1
		Kerosene	1.00	1.00	
Rougher flotation	15	Butanol High Boiler Frother	0.02	0.02	
1st and 2nd cleaner	10	P-Pentasilphide	1.00	0.50	9.8
		Kerosene	0.40	0.20	
3rd and 4th cleaner	5	P-Pentasilphide	0.50	0.25	9.7
		Kerosene	0.20	0.10	
5th and 6th cleaner (Test 3 only)	4	Sodium silicate		0.05	9.5
		Sodium cyanide		0.05	
		P-Pentasilphide		0.20	
		Kerosene		0.05	

*Phosphorus pentasilphide added as Noake's reagent.

Note: The reagents and the flotation time in cleaning were used in each of the two stages.

TABLE 5

Results of Flotation with Phosphorus Pentasulphide

Test	Product	Weight %	Analysis* %			Distribution % MoS ₂
			MoS ₂	Cu	Insol	
2	MoS ₂ conc	0.49	59.4	3.7	-	55.6
	3rd + 4th cl tailing	1.37	4.6	-	-	12.0
	1st + 2nd cl tailing	13.97	0.55	-	-	14.7
	Flotn tailing	84.17	0.11	-	-	17.7
	Feed (calcd)	100.00	0.52	-	-	100.0
3	MoS ₂ conc	0.35	72.4	3.7	10.9	50.0
	5th + 6th cl tailing	0.32	14.2	26.0	-	8.9
	3rd + 4th cl tailing	1.13	2.9	31.4	-	6.5
	1st + 2nd cl tailing	8.63	0.27	31.2	-	4.6
	Flotn tailing	89.57	0.17	-	-	30.0
	Feed (calcd)	100.00	0.51	-	-	100.0

*From Internal Reports MS-AC-65-867 and 916, and by McIntyre Porcupine Mines, Limited.

(iii) Arsenic Trioxide

A 5% As₂O₃ solution was prepared by dissolving in water a mixture consisting of one part of sodium sulphide to four parts of arsenic trioxide.

Tests 4 and 5

These tests were similar to Tests 2 and 3, respectively, except that arsenic trioxide was used instead of phosphorus pentasulphide. The results obtained are shown in Table 6.

TABLE 6

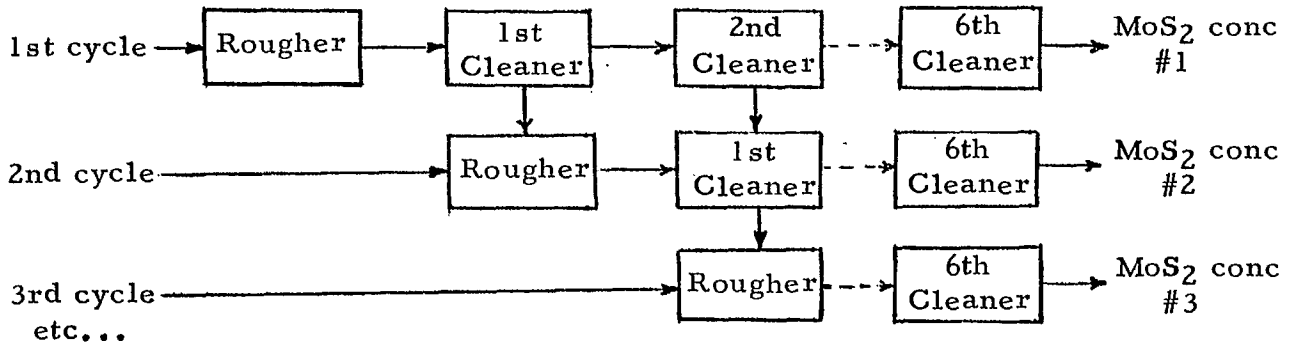
Results of Flotation with Arsenic Trioxide

Test	Product	Weight %	Analysis* %			Distribution % MoS ₂
			MoS ₂	Cu	Insol	
4	MoS ₂ conc	0.45	65.3	4.1	-	64.3
	3rd + 4th cl tailing	0.62	2.0	-	-	2.7
	1st + 2nd cl tailing	16.57	0.36	-	-	13.1
	Flotn tailing	82.36	0.11	-	-	19.9
	Feed (calcd)	100.00	0.46	-	-	100.0
5	MoS ₂ conc	0.39	74.5	3.8	9.9	56.7
	5th + 6th cl tailing	0.27	7.5	28.3	-	4.0
	3rd + 4th cl tailing	4.03	0.49	32.9	-	3.8
	1st + 2nd cl tailing	9.64	0.38	28.3	-	7.1
	Flotn tailing	85.67	0.17	-	-	28.4
	Feed (calcd)	100.00	0.52	-	-	100.0

*From Internal Reports MS-AC-869 and 916, and by McIntyre Porcupine Mines, Limited.

(iv) Integration of Four Cycles of Flotation (Test 6)

This test was aimed at predicting the behavior of the middling particles recirculated in plant practice. It consisted of four identical cycles of flotation in which the cleaner tailings were reintroduced in the next cycles according to the scheme shown below:



In each flotation cycle, the new feed was about 4,000 g. Flotation procedure and results obtained are shown in Tables 7 and 8.

TABLE 7

Reagents and Conditions for Each Flotation Cycle

Operation	Time min.	Reagents	lb/ton	pH
Conditioning	5	Arsenic trioxide	3.50	6.5-7.2
		Kerosene	1.00	
Rougher flotation	15	Butanol High Boiler	0.02	
1st + 2nd cleaner	10	Arsenic trioxide	0.75	7.5-9.0
		Kerosene	0.30	
3rd + 4th cleaner	5	Arsenic trioxide	0.35	9.4-9.8
		Kerosene	0.15	
5th + 6th cleaner	4	Sodium silicate	0.10	9.6-10.1
		Sodium cyanide	0.10	
		Arsenic trioxide	0.20	
		Kerosene	0.05	

Note: The reagents and the flotation time shown were used in each flotation stage.

TABLE 8

Results with Four Cycles of Flotation

Product	Weight %	Analysis* %			Distribution %	
		MoS ₂	Cu	Insol	MoS ₂	Cu
MoS ₂ conc #1	0.09	75.5	3.3	10.6	12.7 (16.5)	-
MoS ₂ conc #2	0.10	74.6	3.4	10.7	13.9 (18.2)	-
MoS ₂ conc #3	0.12	72.6	3.5	10.5	16.3 (21.2)	-
MoS ₂ conc #4	0.13	71.2	3.9	10.6	17.3 (22.5)	-
4th cycle:						
5th + 6th cleaner tailing	0.08	36.9	11.5	-	5.5 (7.2)	-
4th + 3rd cleaner tailing	0.49	0.48	35.9	-	4.4 (5.7)	0.6
1st + 2nd cleaner tailing	8.11	0.08	35.6	-	1.2 (1.6)	9.3
Flotn tailing #1	21.51	0.17 (0.03)	30.8	-	6.8 (1.6)	21.3
Flotn tailing #2	24.02	0.17 (0.03)	30.8	-	7.6 (1.7)	23.8
Flotn tailing #3	22.43	0.18 (0.03)	30.8	-	7.5 (1.6)	22.2
Flotn tailing #4	22.92	0.16 (0.04)	30.7	-	6.8 (2.2)	22.8
Feed (calcd)	100.00	0.54 (0.41)		-	100.0 (100.0)	100.0
MoS ₂ conc (combined)	0.44	73.2	3.5	10.6	60.2 (78.4)	-
Flotn tailing (combined)	90.88	0.17 (0.03)	30.8	-	28.7 (7.1)	90.1

*From Internal Report MS-AC-906 and by McIntyre Porcupine Mines, Limited.

**Estimated

Note: Results in brackets are from McIntyre analyses.

Remarks: Assuming that the molybdenite contained in the cleaner tailing of the 4th cycle should be recovered eventually as suggested by the constant percentage of MoS₂ in the flotation tailing, the molybdenite recovery in plant practice should attain 71%. (If McIntyre analyses of tailing are used, the recovery would be 93%).

Mineralogical studies* on the combined concentrate produced in Test 6 can be summarized as follows:

- 1 - The concentrate consisted of molybdenite, chalcopyrite, pyrite, bornite, muscovite, talc, magnesite, quartz and feldspar.
- 2 - Molybdenite was present as flakes that varied in size from 5 to 60 microns, and about 90% of them were free. Most of the remaining ones were intergrown with chalcopyrite, while a few others contained inclusions of chalcopyrite, pyrite and bornite.
- 3 - The principal gangue minerals were muscovite and, to a lesser extent, talc and magnesite.

Upgrading of Molybdenite Concentrate

To obtain a sufficient and representative feed for this part of the investigation, the concentrates produced in Tests 5 and 6 were combined, mixed and divided into four equal fractions.

(i) Further Cleaning under Various Conditions

In this series of tests, attempts were made to upgrade the molybdenite concentrate by further cleaning stages with sodium silicate and sodium cyanide after the following treatments:

(a) regrinding, (b) boiling, (c) heating and (d) conditioning with lactic acid. However, none of these tests appeared sufficiently good enough to justify analyses of the products. The test products were combined, heated at 280°C to drive off the chemicals and redivided for further investigation.

(ii) Reverse Flotation of Gagnue Minerals (Test 7)

This test was aimed at floating the mica and possibly the talc with a diamine while depressing the molybdenite with dextrin. Flotation procedure and results obtained are shown in Tables 9 and 10.

*From Internal Report MS-65-94.

TABLE 9

Reagents and Conditions of Reverse Flotation

Operation	Time min	Reagent	lb/ton of ore	pH
Conditioning	3	Dextrin	0.10	7.0
Rougher flotation	4	Diamine	0.01	6.9
Cleaner flotation	2	Dowfroth 250	0.01	7.2
		Dextrin	0.05	
		Diamine	0.005	
		Dowfroth 250	0.005	

TABLE 10

Results of Reverse Flotation

Product	Weight %	Analysis* %			Distribution %			
		MoS ₂	Cu	Insol	MoS ₂ **		Cu	Insol
					In Test	Overall		
1st non-float	86.3	76.0	4.1	8.7	88.1	53.0	88.1	75.6
2nd non-float	7.1	72.9	2.5	13.6	7.0	4.2	4.5	9.8
Float	6.6	57.1	4.6	22.0	4.9	3.0	7.4	14.6
Feed (calcd)	100.0	74.4	4.0	9.9	100.0	60.2	100.0	100.0

*From Internal Report MS-AC-65-1013.

**Calculated from a 60.2% recovery in Test 6.

These results (even if rather poor) should be improved by further testing with more careful control of reagents and other conditions, but no material was available to further pursue investigation of this technique.

(iii) Heavy Liquid Separation

To assess the possibility of removing the gangue minerals from the molybdenite concentrate, a heavy liquid separation test was made with tetrabromoethane (sp gr 2.96).

TABLE 11

Results of Heavy Liquid Separation

Product	Weight %	Analysis* %			Distribution%			
		MoS ₂	Cu	Insol	MoS ₂		Cu	Insol
					In Test	Overall		
Sink	91.4	79.5	3.7	5.4	96.6	58.1	94.9	49.7
Float	8.6	29.8	2.1	58.1	3.4	2.1	5.1	50.3
Feed (calcd)	100.0	75.2	3.6	9.9	100.0	60.2	100.0	100.0

*From Internal Report MS-AC-1013.

**Calculated from a 60.2% recovery in Test 6.

The high molybdenite contained in the float was due to the tendency of this mineral to stick to the walls of the separation vessel and end up in the float fraction when the vessel was washed out.

SUMMARY AND CONCLUSIONS

Head sample analysis of the copper concentrate submitted by McIntyre Porcupine Mines gave the following results:

MoS ₂	Cu	Fe	S	Insol
0.65%	29.7%	26.8%	30.1%	7.6%

Microscopic examination indicated that about 90% of the molybdenite was present as free grains, most of the remainder being intimately associated with chalcopyrite. Muscovite and talc, which are particularly critical in molybdenite selective flotation, were also identified. Furthermore, infra-sizer analysis showed that 67.9% of the molybdenite was finer than 40 microns; and that 32.3% was finer than 20 microns at which size the flotation selectivity of the molybdenite is greatly reduced.

The results obtained in the investigation can be summarized as follows.

TABLE 12

Compilation of Results

Procedure	MoS ₂ Concentrate			
	Analysis %			Recovery % MoS ₂
	MoS ₂	Cu	Insol	
(1) Selective flotation with P ₂ O ₅	72.4	3.7	10.9	50.0
(2) Selective flotation with As ₂ O ₃	74.5	3.8	9.9	56.7
(3)* Four cycles of flotation with As ₂ O ₃	73.2	3.5	10.6	60.2 (78.* ₄)
(4) Procedure (3) and reverse flotation of gangue minerals with dextrin and diamine	76.0	4.1	8.7	53.0 (69.* ₁)
(5) Procedure (3) and heavy liquid separation with tetrabromoethane	79.5	3.7	5.4	58.1 (75.* ₇)

*Concentrates from 1st, 2nd, 3rd, and 4th cycles analysed 75.5, 74.6, 72.6 and 71.2% MoS₂, while flotation tailings assayed 0.17, 0.17, 0.18 and 0.16% MoS₂ respectively.

**Calculated from analyses by McIntyre Mines.

The original objective of a 90% MoS₂ grade was not attained due to the limitations of small scale test work which resulted in very small amounts of molybdenite concentrate available for subsequent cleaning or further investigation. However, the investigation has shown that the following points are pertinent in the processing of this material towards this goal.

(1) Arsenic trioxide was the most effective depressant for the copper minerals being slightly better than phosphorus pentasulphide for the selective flotation of the molybdenite.

(2) The results of the locked cycle test suggested that:

(a) Recirculation of the cleaner tailing in plant practice should result in a substantial increase in molybdenite recovery with a slight decrease in the grade of the final concentrate.

(b) The weight of the cleaner tailings after the 4th cycle indicates that the circulating load has a tendency to build up. This problem can be overcome in plant operation by diverting the 1st and/or 2nd cleaner tailing, which is low in molybdenite (0.08% MoS₂ and 35.6% Cu), back to rougher tailing.

(3) The main impurities in a 73% MoS₂ concentrate are chalcopyrite, mica, and talc. These impurities are unlikely to be removed by further conventional cleaning with arsenic trioxide because of the close association between the remaining chalcopyrite and molybdenite, and the natural floatability of the above mentioned gangue minerals.

(4) The treatment of 73% MoS₂ concentrates by reverse flotation or heavy liquid separation rejected enough mica and talc to anticipate a 90% MoS₂ concentrate in the eventuality of a quasi-complete removal of the copper minerals.

(5) The removal of the residual copper minerals in the molybdenite concentrate from 3.5% to 0.5% Cu, does not appear to be practical by mineral processing methods. The main difficulty encountered is that an appreciable amount of this copper is combined with molybdenite grains. The removal of this residual copper might be feasible by a hydrometallurgical process.

To summarize, the investigation has shown that a 70% to 75% MoS₂ grade with good molybdenite recovery can be produced from the copper concentrate by multiple cleaning using arsenic trioxide as a copper depressant and kerosene as a molybdenite collector. The gangue minerals present in this concentrate, particularly the talc and mica, can probably be best removed by utilizing a reverse flotation technique. The production of a final molybdenite concentrate of marketable grade might then be accomplished by leaching the residual copper, although it was not possible to investigate these final cleaning steps in the laboratory, this could be done more readily by plant testing.

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