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MINES BRANCH INVESTIGATION REPORT IR 70-1

1-0121 I

**INVESTIGATION OF
A TUNGSTEN-MOLYBDENUM-BISMUTH ORE
FROM YORK COUNTY, NEW BRUNSWICK,
FOR BURNT HILL TUNGSTEN AND
METALLURGICAL LIMITED**

by

G. I. MATHIEU AND R. W. BRUCE

MINERAL PROCESSING DIVISION

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G.I. Mathieu* and R.W. Bruce**

- - -

SUMMARY OF RESULTS

The ore sample contained tungsten, molybdenum and bismuth in economical amount with the following head assays: 1.02% WO_3 , 0.44% MoS_2 and 0.17% Bi. The tungsten occurred mainly as wolframite, the molybdenum as molybdenite, and the bismuth as native metal and bismuthinite. The wolframite and molybdenite had coarse mineralization (50 microns to 15 millimeters), whereas the bismuth minerals, at less than 50 microns in size, were finer-grained. Pyrite, marcasite and pyrrhotite were the main metallic impurities in the ore.

Grinding to minus 48 mesh was sufficient for liberation. At this fineness, 89% of the tungsten, 94% of the molybdenite and 85% of the bismuth were recovered in rougher concentrates. The wolframite was concentrated by gravity (either jigging, spiralling or tabling), while the molybdenite and bismuth minerals were recovered by selective flotation. Because of the friable nature of the bismuthinite and the native bismuth, it was not necessary to regrind the ore prior to their concentration.

To meet market specifications, it was necessary to upgrade the rougher concentrates by the following techniques:

- (1) tabling, magnetic separation and roasting (for desulphurization) of the tungsten concentrate;
- (2) cleaner flotation and acid leaching for the molybdenite concentrate;
- (3) gravity concentration or flotation separation for the bismuth.

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The average grade and recoveries after these treatments were as follows:

Product		Grade	Recovery
Tungsten Concentrate		66.4% WO ₃	77.1%
Molybdenite Concentrate		91.2% MoS ₂	94.2%
Bismuth	Concentrate	9.8% Bi	15.6 to 69.1%*
	Pregnant sol'n	20 g Bi/l	31.7 to 11.2%*

*Depending on the method used.

Further upgrading of the bismuth concentrate will be necessary, but could not be tested because of the small amount of concentrate produced.

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INTRODUCTION

Property

The ore sample submitted for investigation originated from the York County property of Burnt Hill Tungsten and Metallurgical Limited, New Brunswick. This property has been thoroughly developed over recent years and the company is now considering the installation of a mill for the treatment of the ore.

Purpose of Investigation

The investigation was initiated by Mr. D.F. Porteous, President, Burnt Hill Tungsten and Metallurgical Limited, P.O. Box 210, Victoria, Westmount, P.Q. Mr. Porteous requested the technical assistance of the Mineral Processing Division to develop a flowsheet for recovering the tungsten, molybdenum and bismuth contained in the ore.

Shipment

On January 6, 1969, a 420-lb lot of ore was received. This sample was said to be representative of the feed for a proposed milling plant.

Sampling and Analysis

The ore was crushed to minus $\frac{1}{2}$ in. and a few representative pieces were selected for mineralogical examination. Half of the remainder was then reduced to minus 10 mesh from which a head sample was riffled out for chemical analysis.

TABLE 1

Chemical Analysis* of Head Sample

Tungsten trioxide (WO ₃)	-	1.02%
Molybdenite (MoS ₂)	-	0.44%
Bismuth (Bi)	-	0.17%
Iron (Fe)	-	1.50%
Arsenic (As)	-	0.42%
Tin (Sn)	-	0.01%
Sulphur (S)	-	0.64%
Insoluble	-	78.80%
Gold (Au)	-	0.005 oz/ton
Silver (Ag)	-	0.30 "

*From Internal Reports MS-AG-69-155, 181, 245 and 412

A spectrographic analysis on a portion of the head sample indicated the presence of the elements listed below in their approximate order of decreasing abundance.

TABLE 2

Spectrographic Analysis* of Head Sample

I	-	Si, Fe, Al (>1%)
II	-	W, Ca, Mg, Ni, Mo (1% - 0.1%)
III	-	Ti, Bi, Mn, Cr, Cu (0.1% - 0.01%)
IV	-	Zr, Pb, Sn, Ag, Co (<0.01%)

*From Internal Report MS-AG-69-11

MINERALOGICAL EXAMINATION*

A few selected specimens and a portion of the head sample were sent to the Mineralogy Section of the Mineral Sciences Division for mineralogical studies. The results of these follows.

*From Investigation Report IR-69-19 by D. Owens.

Summary

Mineralogical studies made on a sample of tungsten ore from a deposit in York County, N.B., on behalf of Burnt Hill Tungsten and Metallurgical Limited, show that the ore consists of siliceous gangue, in which is disseminated a variety of ore minerals. The tungsten in the ore occurs almost entirely as wolframite, and to a very minor degree, as scheelite. The wolframite occurs mainly as small masses and relatively coarse grains in gangue, while the only scheelite identified consisted of a few grains in the head sample. Small amounts of molybdenum, bismuth and tin also are present in the ore. The molybdenum occurs in the form of molybdenite, the bismuth as native bismuth and bismuthinite, and the tin as cassiterite. Other minerals identified in the ore include pyrite, marcasite, pyrrhotite, sphalerite, arsenopyrite, chalcopyrite, galena, ilmenite, rutile, anatase, goethite, hematite, magnetite, tetrahedrite, quartz, fluorite, chlorite, mica, apatite, dolomite and topaz.

Method of Investigation

Polished sections were prepared from the hand specimens showing the heaviest ore mineralization, and these were examined microscopically to identify the ore minerals and to determine their grain size, occurrence and liberation characteristics. The 48- to 100-mesh and 100- to 250-mesh fractions were screened from the head sample and separated into sink and float products by means of heavy liquids. One polished section was prepared from each of the sink products and examined microscopically to permit a comparison of the ore minerals in the head sample with those in the hand specimens. The float products were analysed by X-ray diffractometer to identify their principal gangue minerals.

General Mineralogy of the Ore

The microscopical examination of the head sample shows that the major heavy minerals are pyrrhotite and wolframite. In addition, the head sample contains slightly smaller amounts of pyrite, marcasite and arsenopyrite, as well as from small quantities to trace amounts of molybdenite native bismuth, bismuthinite, cassiterite, scheelite, ilmenite, rutile, anatase, chalcopyrite, galena, sphalerite, goethite, hematite, magnetite and tetrahedrite. The major gangue mineral in the ore is quartz. Also present are much smaller amounts of fluorite, chlorite, mica, topaz, apatite, and dolomite.

It should be mentioned that the hand specimens, upon which the textural relationships of the minerals is based, do not appear to be entirely representative of the ore, as shown by the head sample. This fact is illustrated by the presence of a greater amount of pyrrhotite in the head sample than would be expected from its scattered occurrences in the hand specimens. For this reason, and because of the low ratio of heavy minerals to gangue, the associations of the minerals that are discussed in this report may not be entirely typical of the ore.

Detailed Mineralogy of the Ore

Tungsten-bearing minerals

Wolframite $(\text{Fe, Mn})\text{WO}_4$ is the dominant tungsten-bearing mineral in the ore. It occurs essentially as small masses, and as both individual grains and aggregates of elongate grains in gangue (Figures 1 and 2). The small masses vary from about 9 to 25 millimetres in size, while the individual grains and aggregates range from about 75 microns to 4 millimetres. (The word "size" as used in this report refers to the greatest dimension of the mineral grain being described.) The wolframite contains relatively few inclusions. These consist mainly of rutile (Figure 3) and ilmenite, which range from about 20 to 300 microns in size. The remaining inclusions in the wolframite are composed of a few grains each of pyrrhotite, pyrite (Figure 4) cassiterite (Figure 5), native bismuth, gangue, combined native bismuth and galena, and a few gangue veinlets. These inclusions are from 5 to about 300 microns in size.

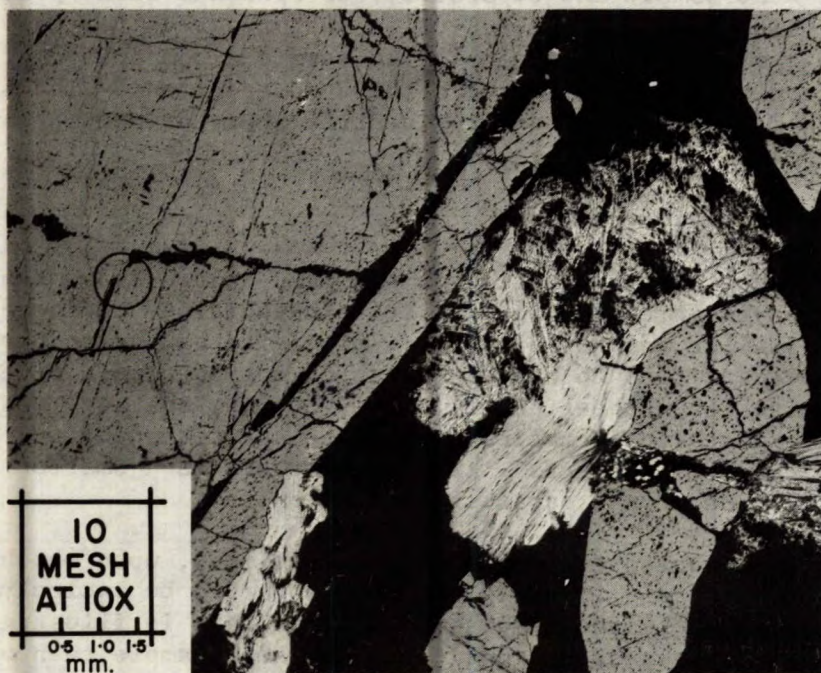


Figure 1. Photomicrograph of a polished section showing part of a small mass, and coarse grains, of wolframite (medium grey), and a few sheaf-like clusters of molybdenite grains (white) in gangue (black).

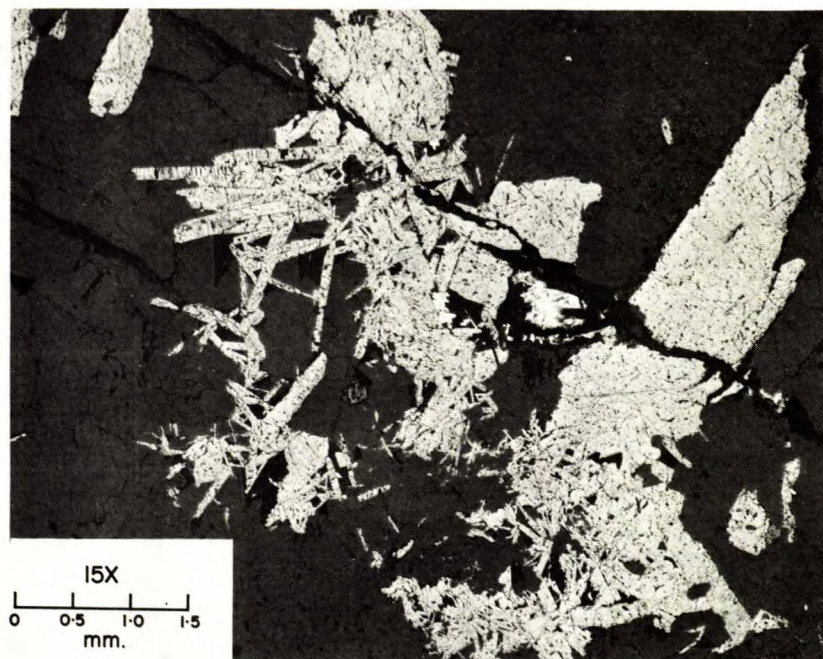


Figure 2. Photomicrograph of a polished section showing both individual grains and aggregates of wolframite grains (medium grey) in gangue (dark grey). A few inclusions of gangue are enclosed within the wolframite.

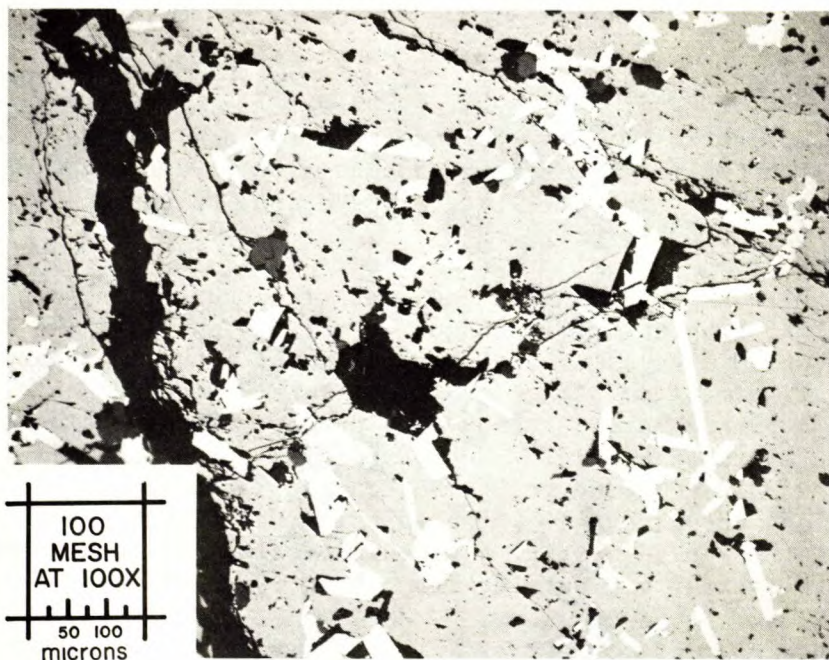


Figure 3. Photomicrograph of a polished section showing a cluster of rutile inclusions (greyish white) in wolframite (medium grey). A few grains of gangue (dark grey) are also present in the wolframite. The black areas are polishing pits and fractures.

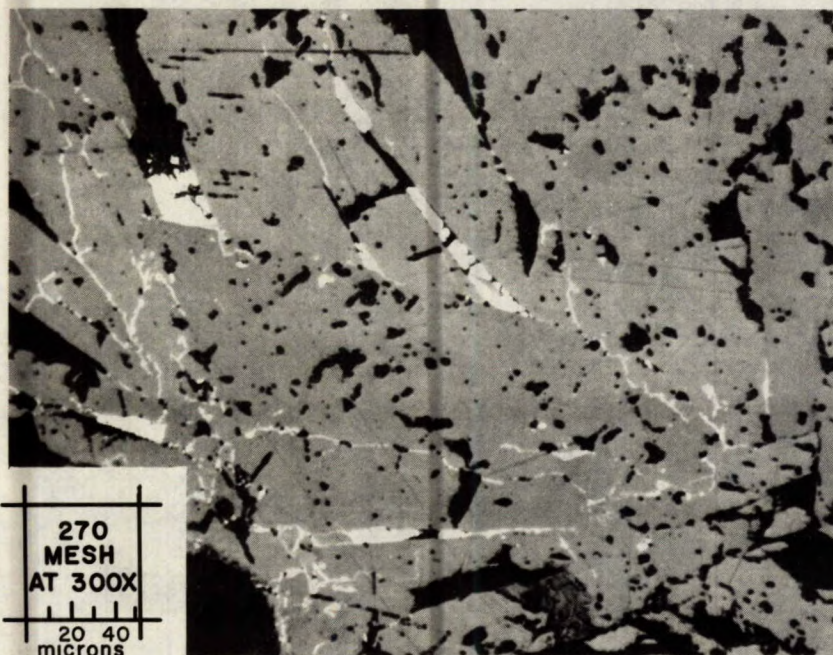


Figure 4. Photomicrograph of a polished section (in oil immersion) showing thin veinlets and small inclusions of pyrite (white) in wolframite (medium grey). The black areas are polishing pits.

Other ore minerals

A small quantity of cassiterite occurs in the ore. It is present largely as inclusions in wolframite (Figure 5) and also in a few gangue grains which are themselves enclosed in wolframite. The grains of cassiterite vary in size from about 20 to 300 microns.

Molybdenite is also present in the ore. It occurs mainly as individual and aggregates of sheaf-like grains in gangue (Figures 1 and 6). The individual grains vary from about 30 microns to 2 millimetres, while the aggregates range from about 2.5 to 5 millimetres. A few grains of molybdenite are also present as inclusions in some of the large arsenopyrite grains. These inclusions are from about 40 to 450 microns in size. The molybdenite grains themselves contain few inclusions. These are composed chiefly of gangue, which occurs as thin blade-like grains along the cleavage of the molybdenite. The blade-like gangue inclusions often run the length of the molybdenite grains, whereas the other inclusions are generally smaller, varying from about 10 to 40 microns in size.

Small, but significant, amounts of native bismuth and bismuthinite are also present in the ore. The native bismuth occurs as inclusions in gangue (Figures 7 and 8), arsenopyrite, wolframite, bismuthinite (Figure 8) and molybdenite; as combinations with galena in gangue (Figure 7) and in wolframite; and as combinations with bismuthinite in gangue (Figure 9). Of these, the most numerous occurrences are the inclusions of native bismuth in gangue, and its combinations with galena and bismuthinite. The size of the native bismuth is quite small; although the grains range in size from 5 to about 100 microns, most are smaller than 50 microns. A few of the grains of native bismuth contain one or more inclusions of pyrrhotite (Figure 9).

The bismuthinite is present in the ore essentially as grains disseminated in gangue, and as combined grains with marcasite in gangue (Figures 8 and 9). These grains vary in size from 2 to about 50 microns. A number of bismuthinite grains also occur as inclusions in molybdenite, and as combined grains with galena and with native bismuth in gangue (Figure 9). The bismuthinite infrequently contains small inclusions of native bismuth (Figure 8), whose grain size is of the order of 40 microns or less.

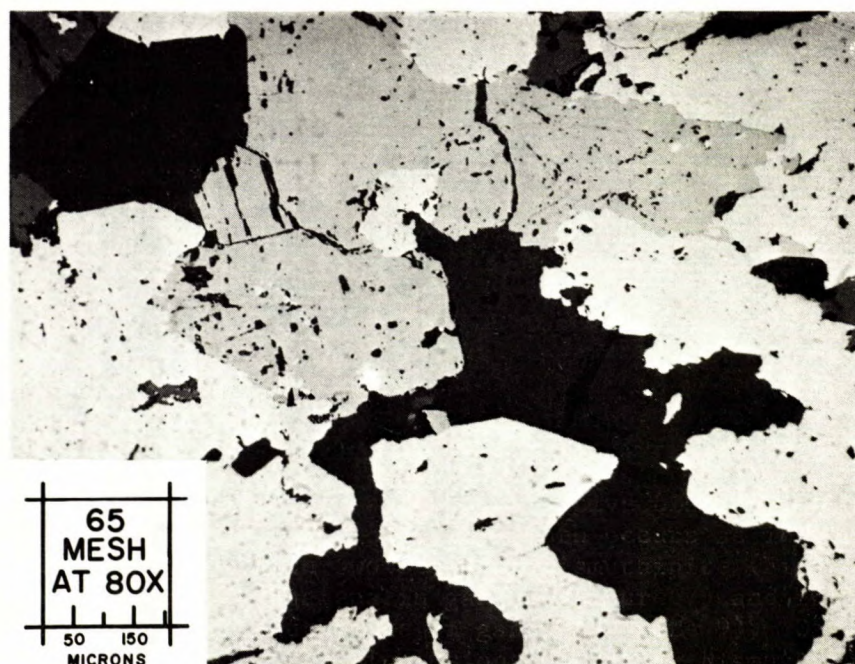


Figure 5. Photomicrograph of a polished section showing grains of cassiterite (medium grey) and gangue (dark grey) in wolframite (light grey).

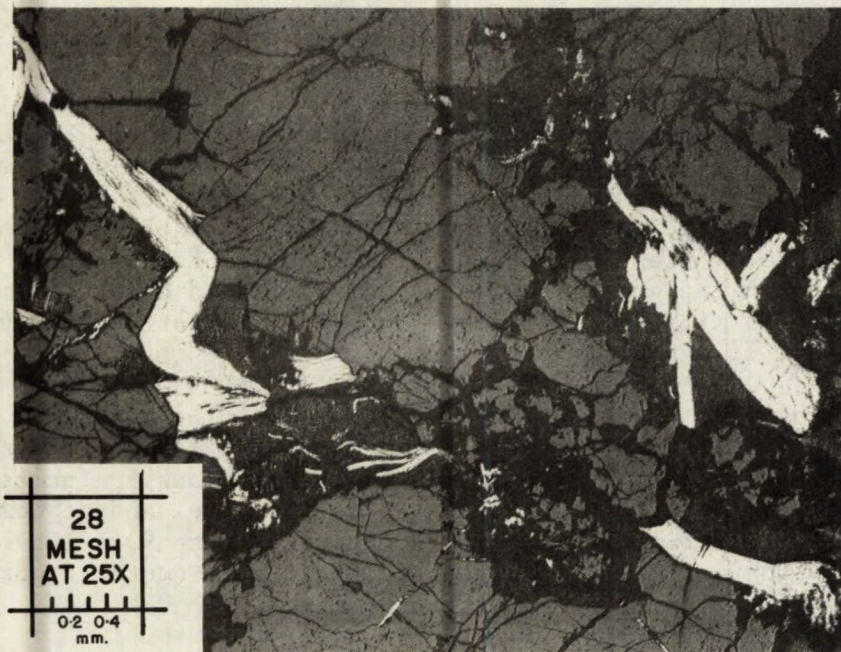


Figure 6. Photomicrograph of a polished section showing a few grains of molybdenite (white) in gangue (dark grey).

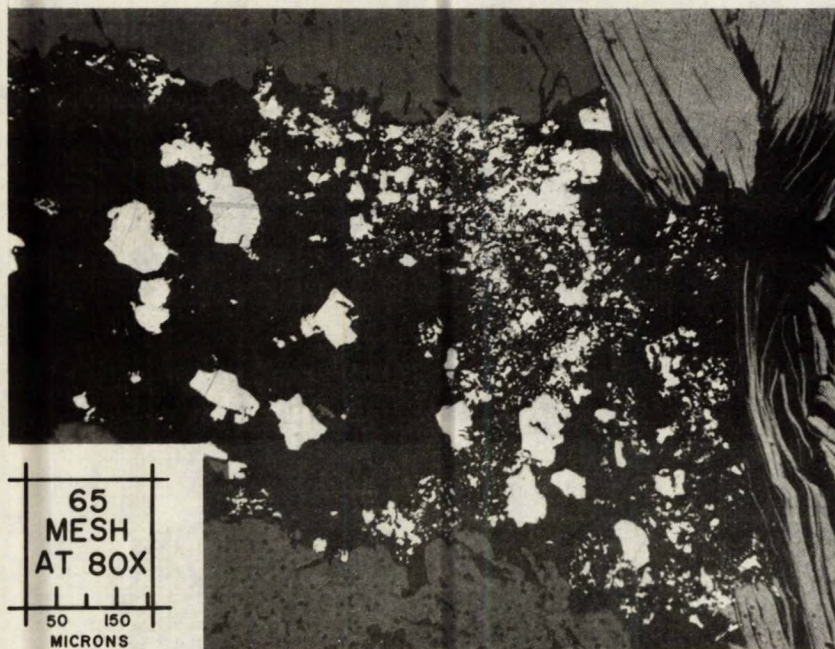


Figure 7. Photomicrograph of a polished section showing an area of gangue (black) between wolframite (dark grey) and molybdenite (medium grey and fibrous), in which are disseminated minute grains of native bismuth (white) and larger grains of galena (greyish white). Some of the galena and native bismuth grains are combined.

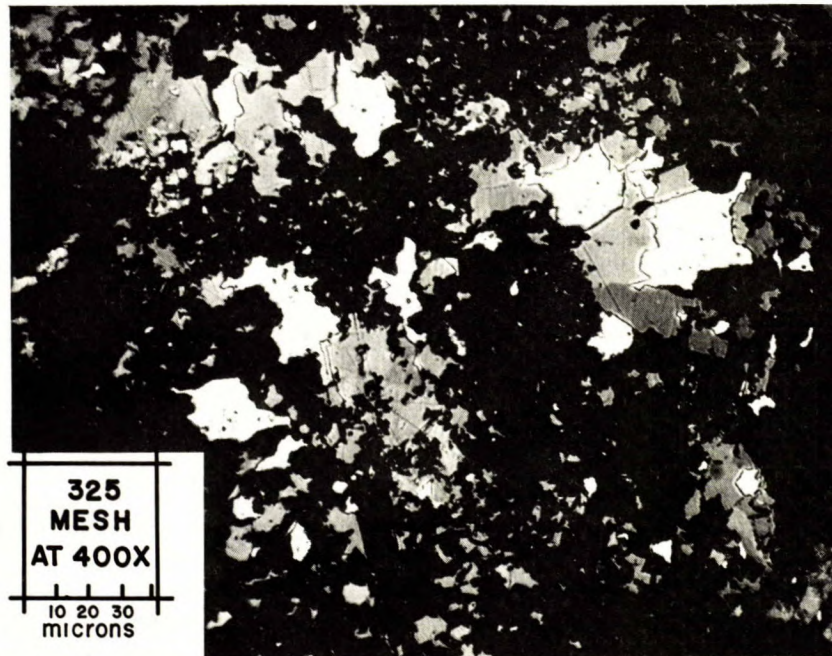


Figure 8. Photomicrograph of a polished section (in oil immersion) showing inclusions of native bismuth (white) in gangue (black) and bismuthinite (grey). A few of the native bismuth grains are combined with bismuthinite. Some of the grains (grey) are marcasite but none of these are in direct contact with the native bismuth.

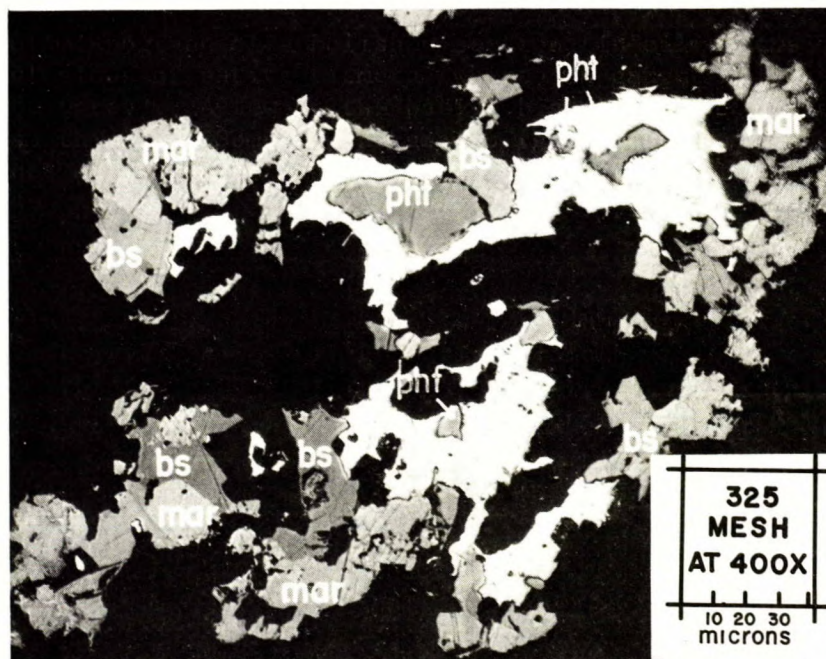


Figure 9. Photomicrograph of a polished section (in oil immersion) showing combined marcasite (mar) and bismuthinite (bs) in association with native bismuth (white) in gangue (black). A few inclusions of pyrrhotite (pht) occur in the native bismuth.

Other minerals in the ore

The other minerals in the ore include pyrite, marcasite, pyrrhotite, sphalerite, arsenopyrite, chalcopyrite, galena, ilmenite, anatase, rutile, goethite, hematite, magnetite and tetrahedrite. Of these, the hematite, magnetite and tetrahedrite were found only in the sink products of the head sample, where in each instance they numbered only a few grains each.

The pyrite and marcasite usually occur in association with each other as disseminations in gangue, although they also occur as separate grains in gangue. The intergrowths of marcasite and pyrite vary from about 0.1 to 4 millimetres in size, while the individual marcasite grains range from 10 to 200 microns, and the pyrite grains attain 260 microns. The inclusions in these two minerals consist mainly of gangue and occasionally of anatase, pyrrhotite, ilmenite and chalcopyrite. These latter inclusions vary from about 5 to 75 microns, whereas the gangue inclusions reach 1.2 millimetres in size. Some association of marcasite with bismuthinite in gangue was also noted (Figure 9).

Although pyrrhotite is one of the major heavy minerals in the head sample, only a few occurrences were found in the hand specimens. In the hand specimens the pyrrhotite is present largely as disseminated grains in gangue. These disseminations generally are from 5 to 120 microns in size. In a few instances slightly coarser pyrrhotite also occurs in association with sphalerite (Figure 10), where it reaches a size of just over one millimetre. A few grains of pyrrhotite also occur as inclusions in sphalerite, pyrite and marcasite, and vary in size from about 10 to 150 microns. In addition, a number of inclusions of sphalerite and chalcopyrite are present in the pyrrhotite, and these vary from 10 to 225 microns in size.

Only a few occurrences of sphalerite were noted in the examination of the hand specimens. In each case the sphalerite is present as fairly large grains in gangue, and is generally found with pyrrhotite (Figure 10). The sphalerite ranges in size from about 75 microns to 3 millimetres. The sphalerite contains a few inclusions of pyrrhotite, chalcopyrite and gangue, none of which are greater than 150 microns in size. A few grains of sphalerite also occur as inclusions in the pyrrhotite.

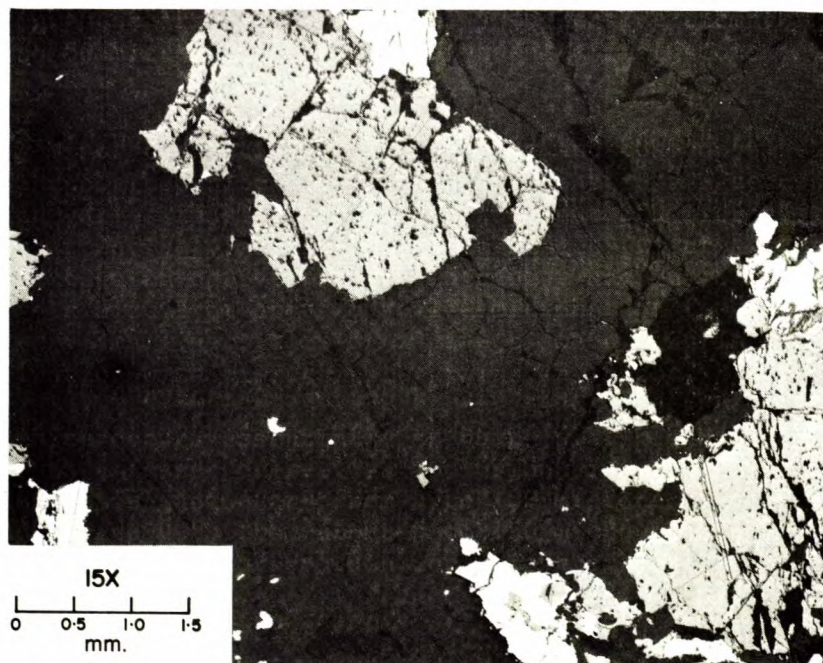


Figure 10. Photomicrograph of a polished section showing small masses and grains of sphalerite (medium grey) in gangue (dark grey). A few small areas of pyrrhotite (white) one of which contains sphalerite inclusions, are associated with the sphalerite.

More arsenopyrite is present in the head sample than was indicated from the examination of the hand specimens. In the hand specimens, the arsenopyrite occurs as a few quite large grains in gangue, which range in size from about 0.1 to 4 millimetres. A few inclusions of native bismuth and of molybdenite occur in these arsenopyrite grains. The native bismuth grains vary from about 5 to 50 microns, while the molybdenite inclusions are as large as 450 microns.

Only minor quantities of both galena and chalcopyrite are present in the ore. The chalcopyrite occurs as inclusions in gangue, sphalerite and pyrrhotite, and varies in size from a few to about 250 microns. The galena is present almost entirely as inclusions in gangue (Figure 7), and occasionally as combined grains with native bismuth in gangue and in wolframite. The grains of galena vary in size from about 5 to 180 microns. A few grains of galena also contain very small particles of native bismuth, and in a few instances occur in combination with bismuthinite grains in gangue.

Ilmenite occurs essentially as quite small lath-like grains disseminated in gangue and, to a lesser degree, as inclusions in wolframite and pyrite. The grains of ilmenite in gangue are from 5 to 100 microns in size, while those in wolframite and pyrite vary from about 5 to 150 microns. Some of the ilmenite grains are partly replaced or contain inclusions of rutile.

Rutile occurs as inclusions in wolframite (Figure 3) and gangue, and to a small degree as inclusions in, or replacing, ilmenite grains. The grains of rutile are generally lath-shaped, and vary in size from about 20 to 200 microns.

Anatase is also present in the ore. It occurs exclusively as individual and as clusters of grains in gangue. These grains are usually acicular in shape, and range from about 3 to 300 microns in size. A few small grains are also enclosed in pyrite.

Only one occurrence of goethite was found in the ore. It occurs as a thin narrow veinlet in gangue and measures about 40 microns in width.

Gangue minerals

The principal gangue mineral in the ore is quartz; the others, which include fluorite, topaz, mica, chlorite, dolomite and apatite, occur in small, and different, amounts.

Conclusions

The mineralogical investigation of the ore leads to the following conclusions: Wolframite accounts for nearly all of the tungsten in the ore, and scheelite is present in only trace amounts. The wolframite is generally coarse-grained and should be largely liberated without great difficulty. The tin in the ore occurs as cassiterite, and although most of it was observed in the wolframite, traces also occur in the gangue minerals. The molybdenite occurs essentially in the gangue; and most of the grains are quite large and a fairly high degree of liberation should be achieved. Native bismuth and bismuthinite, on the other hand, are so fine-grained that they may present some problems in liberating.

OUTLINE OF INVESTIGATION

In the first part of the investigations recovery of each valuable constituent was studied independently of the other. This method was aimed at finding the liberation characteristics and the best method for concentration of the tungsten, molybdenum and bismuth minerals, while keeping the analytical work to a minimum. The wolframite was concentrated by various gravity and magnetic separation methods; the molybdenite, bismuthinite and native bismuth were concentrated by flotation.

Flowsheets incorporating the best features found in the preliminary investigation were then developed and tested. Finally, attempts were made (1) to upgrade the wolframite concentrate to market specification by removal of its excessive sulphur content by roasting, and (2) to reduce the impurity level and recover the bismuth in the molybdenite concentrate by acid leaching.

DETAILS OF INVESTIGATION

Part I: Testwork on Individual Constituents

A - Recovery of Tungsten

i) Rougher Concentration by Gravity Processes, Tests 1-3

Three samples (two 8,000-g and one 25,000-g) were cut from the crushed ore. The first 8,000-g sample was ground to minus 14 mesh and concentrated using a Denver Laboratory Mineral Jig (Model 1 M); the 25,000-g sample was reduced to minus 28 mesh and treated by a Humphreys Spiral; the third sample was passed over a Deister laboratory table at minus 48 mesh.

The results of these concentration tests are shown in Table 3.

TABLE 3

Results of Gravity Concentration of Tungsten

Test	Product	Weight %	Analysis (%) WO ₃	Distribution (%) WO ₃
1 (Jig at -14 mesh)	Jig conc	6.9	11.48	88.2
	Jig bed	3.2	0.24	0.9
	Tailing	89.9	0.11	10.9
	Feed (calcd)	100.0	0.90	100.0
2 (Spiral at -28 mesh)	Spiral conc	14.6	5.41	87.9
	Middling	14.9	0.27	4.1
	Tailing	70.5	0.13	8.0
	Feed (calcd)	100.0	0.97	100.0
3 (Table at -48 mesh)	Table conc	12.1	7.43	90.6
	Middling	6.4	0.18	1.2
	Tailing	81.5	0.10	8.2
	Feed (calcd)	100.0	0.99	100.0

*From Internal Reports MS-AC-69-219

Other tests were done using either a jig with finer-ground material or a table with a coarser feed, but no significant improvement in results was achieved.

ii) Size Analysis of Gravity Tailings

To determine the size-distribution of the tungsten in the tailings produced by the various gravity techniques, a 400-g sample was cut from each tailing, screened on a series of Tyler sieves and the fractions analysed for tungsten trioxide.

TABLE 4

Size-distribution of Tungsten in Tailings

Size Mesh	Jig Tailing			Spiral Tailing			Table Tailing		
	Weight %	Analysis* % WO ₃	Dist'n % WO ₃	Weight %	Analysis* % WO ₃	Dist'n % WO ₃	Weight %	Analysis* % WO ₃	Dist'n % WO ₃
+20	22.2	0.038	9.4	-	-	-	-	-	-
-20+28	21.8	0.022	5.3	-	-	-	-	-	-
-28+35	17.5	0.030	5.8	19.5	0.038	7.1	-	-	-
-35+48	10.1	0.018	2.0	17.5	0.036	6.0	-	-	-
-48+65	6.8	0.023	1.8	17.1	0.025	4.1	26.2	0.057	11.9
-65+100	4.7	0.025	1.3	11.7	0.004	0.5	18.4	0.053	7.8
-100+150	4.1	0.05	2.3	8.9	0.014	1.2	14.2	0.064	7.3
-150+200	3.1	0.12	4.1	6.4	0.010	0.6	10.3	0.059	5.0
-200+325	4.2	0.49	22.8	8.6	0.081	6.7	11.1	0.07	6.2
-325	5.5	0.74	45.2	10.3	0.75	73.8	19.8	0.39	61.8
Total	100.0	0.090	100.0	100.0	0.110	100.0	100.0	0.120	100.0

*From Internal Report MS-AC-69-208

The above results show that the greatest losses are found in the minus 325 mesh fractions, particularly when the spiral and table were used.

iii) Cleaning Rougher Concentrates by Tabling and Magnetic Separation

The jig and table concentrates from the previous tests plus one third of the spiral concentrate were combined and reduced to minus 48 mesh for this test. The cleaning procedure consisted of tabling the material to remove the gangue minerals and of passing the resultant concentrate through a Jones high-intensity magnetic separator to reject the non-magnetic impurities, particularly the pyrite.

All the products were analysed for tungsten trioxide, molybdenite and bismuth. A composite sample of the middling and tailing products from the previous tests was also prepared and analysed for the calculation of the metal distribution.

TABLE 5

Results of Gravity and Magnetic Cleaning of Tungsten Concentrate

Product	Weight %	Analysis %			Distribution %		
		WO ₃	MoS ₂	Bi	WO ₃	MoS ₂	Bi
Jones conc	1.19	55.54	0.15	1.04	72.7	0.4	7.7
Jones middling	0.53	3.05	1.49	6.52	1.8	1.8	21.4
Jones tailing	0.69	0.93	1.69	6.03	0.7	2.8	25.8
Table cl tailing	8.79	1.35	1.41	0.22	13.1	29.5	12.0
Gravity middlings and tailings (combined)	88.80	0.12	0.31	0.07	11.7	65.5	33.1
Feed (calcd)	100.00	0.91	0.42	0.16	100.0	100.0	100.0

*From Internal Report MS-AC-69-232

From this part of the investigation on the tungsten recovery, the following observations can be made:

(1) Overall recovery of wolframite (without cleaning) did not differ significantly in any of the three gravity methods used for concentration. However, with the plus 65-mesh fractions, the tungsten content of the tailing was the lowest in jigging; in the -65+200-mesh fractions, the tailing with the lowest tungsten content was obtained from the Humphrey Spiral; and with the minus 200-mesh fractions, the best results were achieved by tabling. Therefore, preliminary sizing with the use of a combination of gravity methods will likely give maximum recovery of wolframite.

(2) An appreciable proportion of the Jones concentrate was in the form of pyrrhotite. This impurity should be removed by low-intensity magnetic separation prior to the final cleaning of the wolframite with the Jones apparatus.

(3) The high content of molybdenite and bismuth in the intermediate products would necessitate diversion of these to appropriate circuits for their metal recoveries.

B - Recovery of Molybdenite

Two 4,000-g samples of crushed ore were stage-ground to minus 35 and 48 mesh, respectively. Each sample was floated separately during the rougher stage, but the concentrates were combined for the cleaning stages. The flotation procedure is shown in Table 6 and the results obtained in Table 7.

TABLE 6

Reagents and Conditions of Molybdenite Flotation

Operation	Time min	Reagent	lb/ton	pH
Conditioning	2	Kerosene	0.040	7.6
		Pine oil	0.015	
		Dowfroth 250	0.015	
Rougher flotation	8	Kerosene	0.040	7.5
		Pine oil	0.015	
		Dowfroth 250	0.015	
Cleaner "	4	Kerosene	0.010	7.4
(twice)		Pine oil	0.010	
Recleaner "	3	Kerosene	0.005	7.4
(twice)		Pine oil	0.005	

TABLE 7

Results of Molybdenite Flotation

Product	Weight %	Analysis*			Distribution		
		MoS ₂	Bi	WO ₃	MoS ₂	Bi	WO ₃
MoS ₂ recl conc	0.47	70.900	6.91	0.26	87.8	19.9	1.4
Recl + cl tailings	2.13	1.110	0.88	0.48	6.2	11.5	1.2
Flot tailing (-35 m)	48.76	0.029	0.12	0.85	3.7	35.8	49.3
Flot tailing (-48 m)	48.64	0.018	0.11	0.83	2.3	32.8	48.1
Feed (calcd)	100.00	0.38	0.16	0.84	100.0	100.0	100.0

*From Internal Reports MS-AC-232 and 460

The above results show that a better recovery of molybdenite was achieved with the minus 48-mesh grind. Mineralogical examination of the molybdenite concentrate revealed that its bismuth content was in the form of bismuthinite, occurring partly free and partly closely associated with the molybdenite particles.

C - Recovery of Bismuth

The tailings from the previous test were used as feed for the bismuth concentration. Rougher flotation was first made on each sized fraction separately, but the concentrates were combined for the cleaning stages. The procedure followed and the results obtained are shown in Tables 8 and 9, respectively.

TABLE 8

Reagents and Conditions of Bismuth Flotation

Operation	Time min	Reagent	lb/ton	pH
Rougher flotation	8	Xanthate Z-6	0.08	7.4
		Dowfroth 250	0.02	
Cleaner flotation (twice)	4	Xanthate Z-6	0.008	7.4
		Dowfroth 250	0.004	
Recleaner flotation	3	Xanthate Z-6	0.002	7.3

TABLE 9

Results of Bismuth Flotation

Product	Weight %	Analysis* %				Distribution %			
		Bi	WO ₂	Fe	As	Bi	WO ₂	Fe	As
Bi recl conc	0.98	9.10	0.34	31.7	11.3	75.3	0.4	19.6	30.3
Recl + cl tailings	1.42	0.84	0.65	29.8	8.1	10.0	1.1	26.6	31.4
Flot tailing (-35 m)	48.20	0.021	0.83	0.83	0.15	8.5	49.4	25.2	19.8
Flot tailing (-48 m)	48.40	0.015	0.82	0.94	0.14	6.2	49.1	28.6	18.5
Feed (calcd)	100.00	0.120	0.81	1.59	0.37	100.0	100.0	100.0	100.0

*From Internal Reports MS-AC-460 and 467.

These results show that the bismuth concentrate was highly contaminated with pyrite and arsenopyrite. Further steps will have to be taken either to prevent flotation of these impurities or to remove them from the concentrate.

Part II - Flowsheet Testing

The information obtained in the previous tests led to the development of Flowsheet I and II. However, trial of these two flowsheets prompted changes incorporated in Flowsheet III.

A - Flowsheet I

The features of this flowsheet were:

- (1) concentration of wolframite prior to molybdenite and bismuth minerals flotation;
- (2) removal of pyrrhotite from the wolframite concentrate using a Jones separator set at low intensity;
- (3) recirculation of the middlings into the molybdenite flotation circuit;
- (4) attempt to separate the bismuth minerals from the pyrite and arsenopyrite using a Haultain superpanner.

The details of the test are shown in Table 10 and Figure 11, while the results obtained appear in Table 11.

TABLE 10

Reagents and Conditions

Operation	Time min	Reagent	lb/ton	pH
MoS ₂ flotation: Rougher	7	Kerosene Pine oil Dowfroth 250	0.08 0.03 0.03	7.5
Cleaner (5 times)	3½	Kerosene Pine oil Sodium cyanide Sodium silicate	0.01 0.005 0.01 0.01	8.1
Bismuth flotation: Rougher	8	Xanthate Z-6 Dowfroth 250	0.08 0.02	7.4
Cleaner (5 times)	3½	Xanthate Z-6 Dowfroth 250	0.005 0.002	7.4

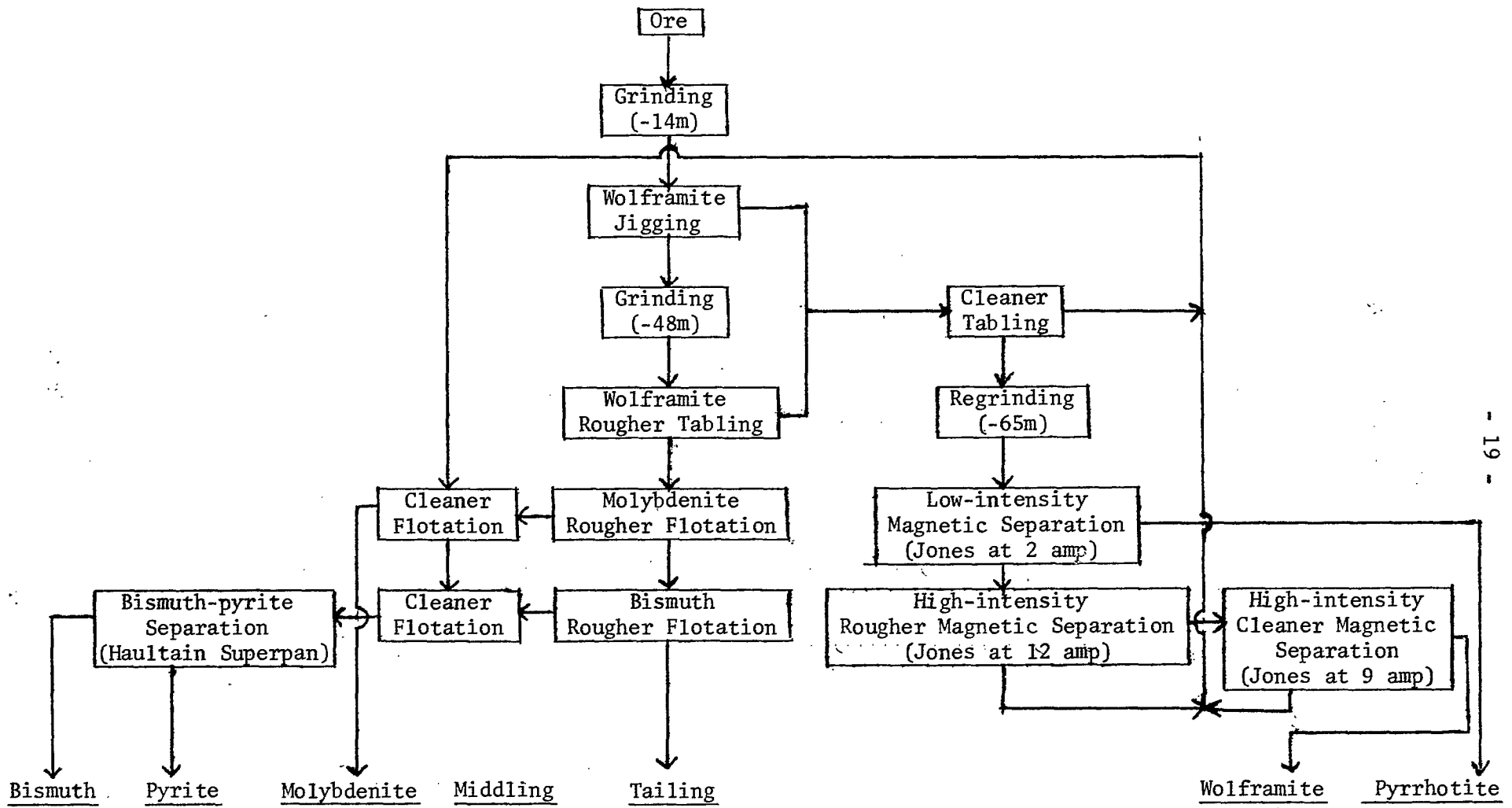


FIGURE 11 - FLOWSHEET I

TABLE 11

Results with Flowsheet 1

Product	Weight %	Analysis*					Distribution				
		WO ₃	MoS ₂	Bi	Fe	As	WO ₃	MoS ₂	Bi	Fe	As
Wolframite conc	1.05	60.0	0.15	1.10	10.9	1.15	76.6	0.4	7.8	7.6	4.3
Molybdenite conc	0.48	0.46	78.0	4.73	7.8	0.23	0.3	94.5	15.6	2.5	0.4
Bismuth conc	0.34	0.58	0.28	11.10	28.7	7.62	0.2	0.3	25.5	6.5	9.1
Pyrrhotite conc	0.04	6.40	0.11	0.47	42.4	2.84	0.3	0.0	0.1	1.1	0.4
Pyrite conc	0.33	0.34	0.21	6.55	29.3	9.77	0.1	0.2	14.6	6.4	11.3
Middling	9.81	1.50	0.06	0.39	3.7	1.54	17.9	1.5	25.8	24.0	52.9
Tailing	87.96	0.043	0.014	0.018	0.89	0.07	4.6	3.1	10.7	51.9	21.6
Feed (calcd)	100.00	0.82	0.41	0.15	1.51	0.29	100.0	100.0	100.0	100.0	100.0

Additional analysis on wolframite conc - 2.75% S

*From Internal Report MS-AC-69-460, 467 and 506.

B - Flowsheet II

The main characteristics of the procedure were as follows:

- (1) flotation of molybdenite and bismuth prior to wolframite gravity concentration;
- (2) separation of the pyrrhotite from the wolframite concentrate using a Jones separator set at low intensity;
- (3) attempt to reject the pyritic minerals from the bismuth concentrate by selective flotation (using sodium cyanide).

Detailed procedure and results are given in Figure 12 and in Tables 12 and 13.

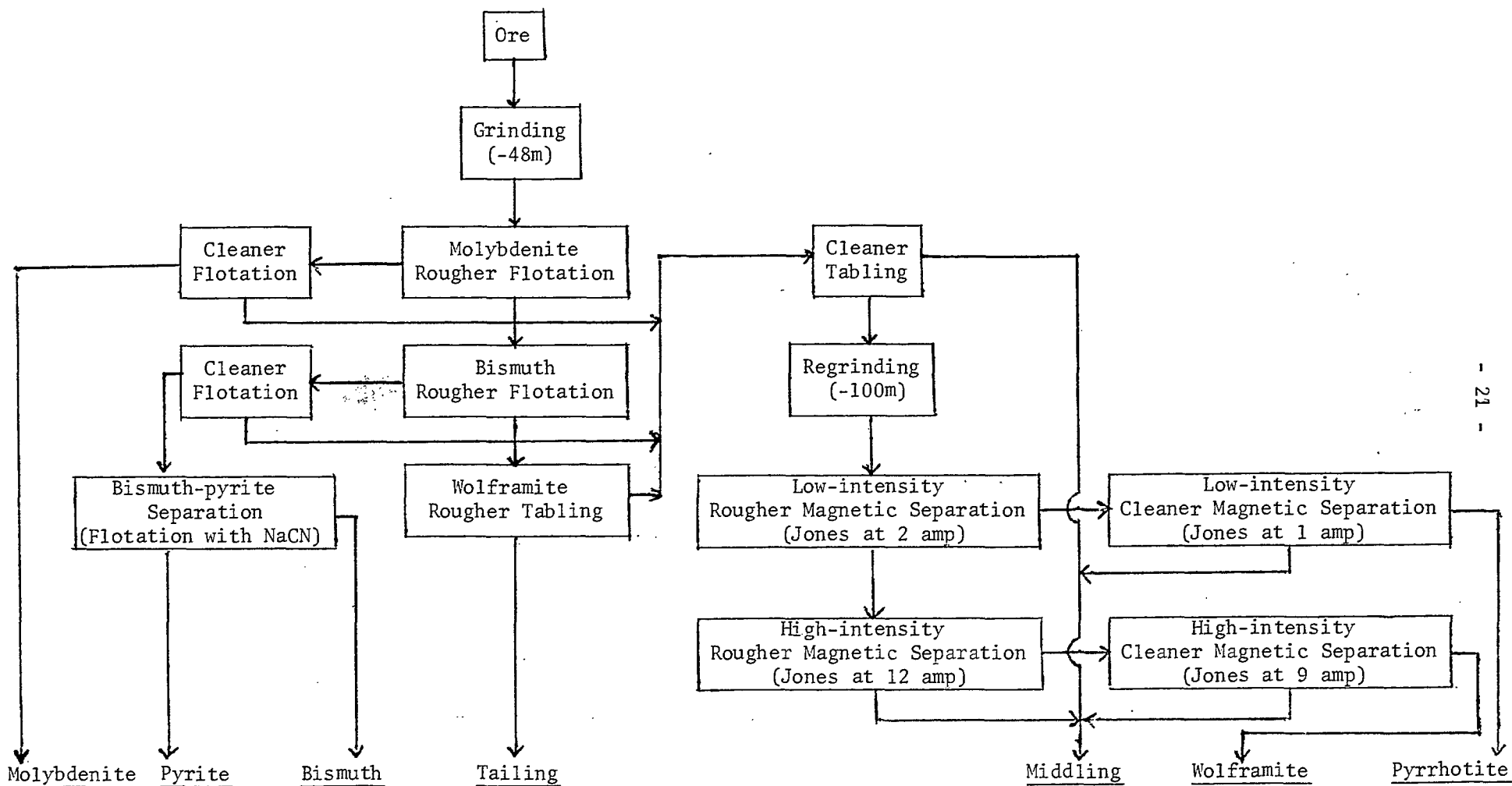


FIGURE 12 - FLOWSHEET II

TABLE 12
Reagents and Conditions

Operation	Time min	Reagent	lb/ton	pH
MoS ₂ flotation: Rougher	7	Kerosene Pine oil Dowfroth 250	0.08 0.03 0.03	7.6
Cleaner	3½	Kerosene Pine oil Sodium cyanide Sodium silicate	0.01 0.005 0.01 0.01	8.0
Bismuth flotation: Rougher	8	Xanthate Z-6 Dowfroth 250	0.08 0.02	7.5
Cleaner		Xanthate Z-6 Dowfroth 250	0.005 0.002	7.4
Pyrite-bismuth separation: Rougher		NaCN	0.15	9.7

TABLE 13
Results with Flowsheet II

Product	Weight %	Analysis*					Distribution				
		WO ₃	MoS ₂	Bi	Fe	As	WO ₃	MoS ₂	Bi	Fe	As
Wolframite conc	1.01	59.2	0.05	0.34	13.7	0.69	79.2	0.1	3.0	8.5	2.7
Molybdenite conc	0.53	0.21	70.8	6.86	15.7	0.76	0.1	92.5	31.1	5.1	1.4
Bismuth conc	0.37	0.61	0.31	10.07	26.9	6.62	0.3	0.3	31.8	6.1	9.4
Pyrrhotite conc	0.03	0.46	0.19	0.38	64.3	0.30	0.0	0.0	0.1	1.2	0.0
Pyrite conc	0.25	0.32	0.19	6.31	31.7	11.32	0.1	0.1	13.5	4.8	10.9
Middling	11.10	0.44	0.16	0.10	3.5	0.59	6.5	4.4	9.5	23.8	25.3
Tailing	86.71	0.12	0.012	0.015	0.95	0.15	13.8	2.6	11.0	50.5	50.3
Feed (calcd)	100.00	0.76	0.41	0.12	1.63	0.26	100.0	100.0	100.0	100.0	100.0

Additional analysis on wolframite conc: 2.98% S

*From Internal Reports MS-AC-232, 491, 511 and 568.

Because of the high bismuth reporting in the pyrite concentrates with both flowsheets, these were carefully examined under the microscope to find the cause of the losses. It was found that the bismuth lost with the gravity process (Flowsheet I) was mostly in the form of fine bismuthinite, while that lost with the selective flotation technique (Flowsheet II) appeared mainly as native metal. This indicates (1) that bismuthinite is not heavy enough to be separated by gravity from coarser grains of pyrite, and (2) that sodium cyanide has a depressing action on native bismuth only.

These observations, coupled with the fact that the molybdenite carries in any event sufficient bismuth to necessitate its removal by acid leaching, were utilized in Flowsheet III.

C - Flowsheet III

The features of this flowsheet were as follows:

- (1) flotation of the bismuthinite along with the molybdenite using sodium cyanide for pyrite and arsenopyrite depression;
- (2) recovery of wolframite and "depressed" native bismuth by tabling;
- (3) removal of the wolframite from the table concentrate by magnetic separation;
- (4) concentration of the native bismuth by further gravity treatment.

The details of the test are shown in Table 14 and Figure 13, and the results in Table 15.

TABLE 14

Reagents and Conditions

Operation	Time min	Reagents	lb/ton	pH
MoS ₂ -Bi flotation: Rougher	10	Kerosene	0.06	8.9
		Xanthate Z-6	0.06	
		Pine oil	0.03	
		Dowfroth 250	0.03	
		Sodium cyanide	0.30	
		Sodium silicate	0.15	
Cleaner (twice)	4	Kerosene	0.01	8.7
		Xanthate Z-6	0.005	
		Pine oil	0.005	
		Sodium cyanide	0.05	
		Sodium silicate	0.02	
Recleaner (four times)	3	Xanthate Z-6	0.002	8.8
		Sodium cyanide	0.01	

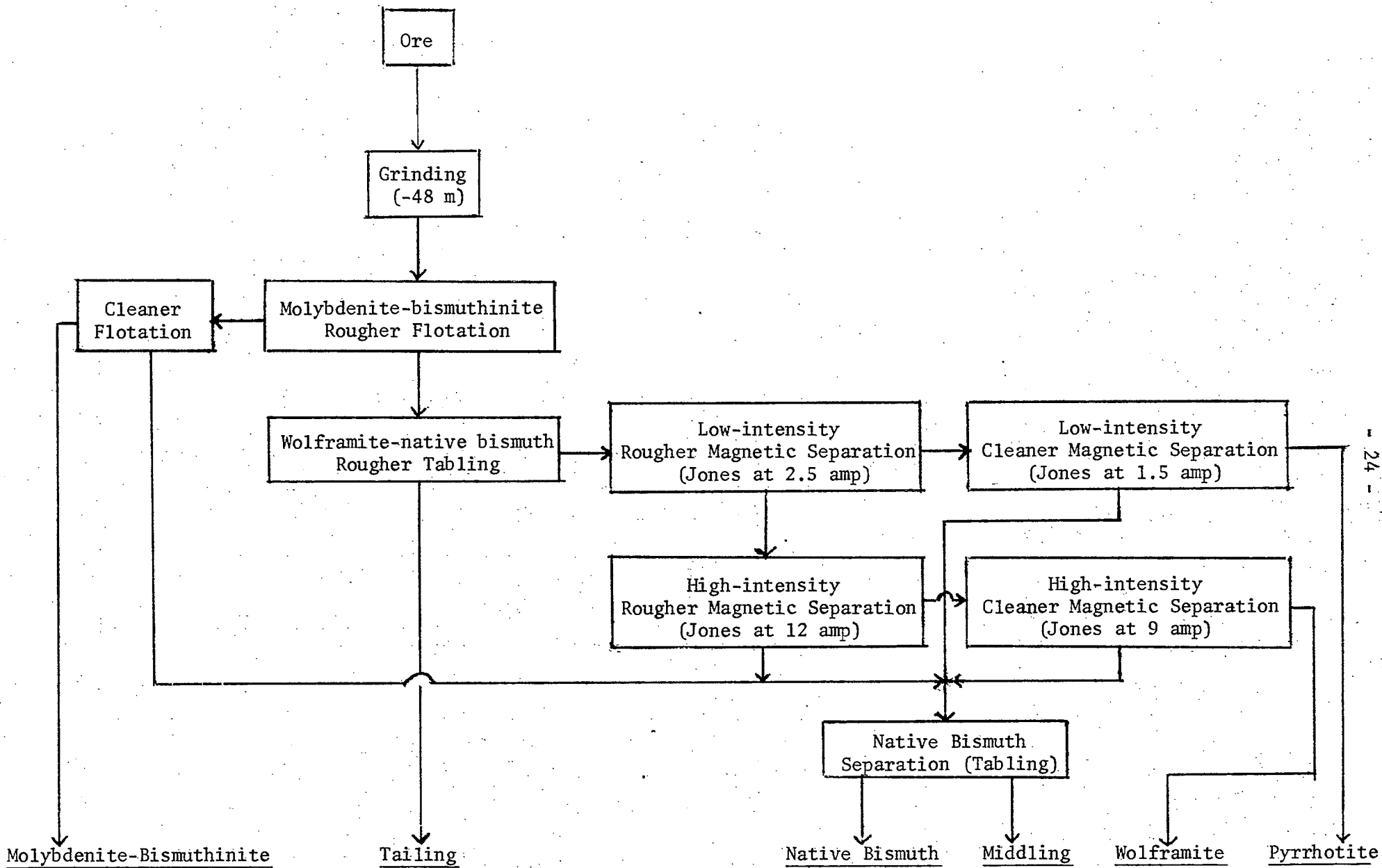


FIGURE 13 - FLOWSHEET III

TABLE 15
Results with Flowsheet III

Product	Weight %	Analysis %					Distribution %				
		WO ₃	MoS ₂	Bi	Fe	As	WO ₃	MoS ₂	Bi	Fe	As
Wolframite conc	0.89	66.7	0.04	0.08	8.7	0.32	76.1	0.1	0.5	5.9	2.0
MoS ₂ - Bi conc	0.67	1.53	54.30	13.20	6.9	4.12	1.3	95.7	69.5	3.5	19.5
Native Bi conc	0.20	0.76	0.17	7.11	23.9	4.07	0.2	0.1	11.2	3.7	5.7
Pyrrhotite conc	0.03	0.43	0.14	0.44	54.0	1.95	0.0	0.0	0.1	1.2	0.4
Middling	4.60	1.56	0.05	0.11	4.1	0.19	9.2	0.6	4.0	14.4	6.2
Tailing	93.61	0.11	0.014	0.02	1.0	0.10	13.2	3.5	14.7	71.3	66.2
Feed (calcd)	100.00	0.78	0.38	0.13	1.31	0.14	100.0	100.0	100.0	100.0	100.0

Additional analysis on wolframite conc: 0.93% S

*From Internal Reports MS-AG-69-582 and 759.

Further gravity cleaning would be necessary to upgrade the native bismuth concentrate to a marketable grade (about 40% Bi). However, the extremely small amount of this product precluded such an operation on a laboratory table unit. An investigation of this would be possible only on pilot plant scale.

The somewhat higher bismuth content of the tailing obtained in Flowsheet III were due to intergrowths of bismuthinite and native bismuth, and to very fine native bismuth which resisted gravity separation. If the latter proved to be rather abundant in plant operation, reactivation of the native bismuth by sulphuric acid for its subsequent flotation might well be necessary. The relatively small amount of fine bismuth produced during stage grinding of the ore to minus 48 mesh was insufficient to permit practical testing of the technique on laboratory scale.

Part III - Sulphur Removal from Tungsten Concentrate

The sulphur content of the wolframite concentrates produced by any of the three flowsheets was in excess of market specification, (i.e. <0.5%). This part of the investigation was aimed at reducing the sulphur content of the wolframite concentrate. To obtain sufficient material and more representative results, the tests were carried out on a combined sample produced during the testing of the three flowsheets, which contained 2.22% S with 61.9% WO₃.

A - Magnetizing Roast

A 50-g sample of wolframite concentrate was roasted for 1 hour at 400°C in a muffle furnace in an attempt to convert the pyrite to a magnetic product. After cooling to room temperature, a sample of the roasted material was sent for analysis while the remainder was passed through a Jones separator set at 2 amperes. The following results were obtained in this test.

TABLE 16

Result of Magnetizing Roast and Magnetic Separation

Product	Weight %	Analysis*		Distribution	
		WO ₃	S	WO ₃	S
Roasting:					
Conc (as rec'd)	100.0	61.9	2.22	-	-
" (roasted)	98.4	62.8	1.35**	-	-
Magnetic separation:					
Jones non-mag***	91.2	65.7	0.44	94.7	33.9
" middling	5.7	50.5	0.74	4.5	3.6
" mag	3.1	17.2	23.84	0.8	62.5
Feed (calcd)	100.0	63.3	1.18**	100.0	100.0

*From Internal Reports MS-AC-69-597 and 810.

**The difference between those two figures indicates that very little sulphur was converted into sulphate water-soluble form during the roasting stage.

***Additional analyses: Bi - 0.064%, Cu <0.01%, As - 0.69%, MoS₂ - 0.019%.

B - Dead Roast

A 50-g sample of tungsten concentrate was placed into a furnace set at 400°C. The temperature was then increased to 800°C over a period of 1½ hours and held at that temperature for an additional 30 minutes. The roasted product was allowed to cool slowly to room temperature and sent for chemical analysis.

TABLE 17

Result of Sulphur Removal by High-Temperature Roasting

Product	Analysis*, %	
	WO ₃	S
WO ₃ conc (prior roasting)	61.9	2.22
Roasted concentrate**	66.4	0.14

*From Internal Reports MS-AC-69-597 and 810.

**Additional Analyses: Bi - 0.04%, Cu < 0.01%, As - 0.35%
MoS₂ - 0.016%.

It was found that the tungsten lost during the roasting stage was negligible.

Part IV - Leaching of Molybdenite Concentrate

This part of the investigation was aimed at removing impurities and recovering bismuth from the molybdenite concentrates. Samples representative of the concentrates produced during the testing of the three flowsheets were combined for the testwork.

A - Hydrochloric Acid Leach

A 50-g lot of mixed molybdenite concentrate was agitated for 1½ hour in 200 mls of 37% hydrochloric acid maintained at 70°C. The pulp was then filtered and washed several times with water. The leached concentrate was dried and analysed for molybdenite, bismuth, copper, iron, arsenic and tungsten. A comparison of the analytical results before and after leaching is shown in Table 18.

TABLE 18

Results of Hydrochloric Acid Leach

Element	Flotation Concentrate	HCl Residue
MoS ₂	67.70%	70.10%
Bi	8.26"	4.41"
Cu	0.51"	0.39"
Fe	10.13"	0.14"
As	1.70"	0.98"
WO ₃	0.73"	0.08"
Pb	2.56"	0.07"

*From Internal Reports MS-AC-69-597, 611 and 810.

Mineralogical examination* of the leached concentrate showed that it contained pyrite and arsenopyrite as major contaminants, but it also carried small amount of native bismuth and traces of chalcopyrite. Therefore, the use of an oxidizing agent would be required during the leaching in order to dissolve the pyritic sulphides and the native bismuth (the bismuthinite being entirely soluble in the hydrochloric acid). Nitric acid was used for this purpose.

*From Internal Report MS-69-45 by D. Owens.

B - Hydrochloric and Nitric Acid Leach

A 50-g sample was leached under conditions similar to those of the preceding test, but with an addition of 50 mls of concentrated nitric acid for the final 30 minutes of the treatment. The following results were obtained.

TABLE 19

Results of Hydrochloric and Nitric Acid Leach

Element	Flotation Concentrate	HCl + HNO ₃ Residue
MoS ₂	67.70%	91.20%
Bi	8.26"	0.04"
Cu	0.51"	0.05"
Fe	10.13"	0.16"
As	1.70"	0.25"
WO ₃	0.73"	0.04"
Pb	2.56"	0.02"

*From Internal Reports MS-AC-69-597 and 611.

No attempt was made to recover the bismuth from the pregnant solution. This is done in practice by diluting to neutral pH with water. The bismuth then precipitates as bismuth oxychloride.

CONCLUSIONS

From the results of independant studies of each valuable mineral (wolframite, molybdenite, bismuthinite and native bismuth), three combined flowsheets were developed and tested for the treatment of the Burnt Hill complex ore. A summary of the sequence of operations and the results obtained are shown below:

Flowsheet	Procedure	Product	Analysis %				Recovery %	
			WO ₃	S	Bi	As	WO ₃	Bi
I	(a) Gravity concentration and magnetic separation of wolframite	WO ₃ conc	WO ₃	S	Bi	As	WO ₃	
			60.0	2.7	1.1	1.1	76.6	
	(b) Flotation of molybdenite	MoS ₂ conc	MoS ₂	Bi	Fe	As	MoS ₂	Bi
			78.0	4.7	7.8	0.2	94.5	15.6
	(c) Flotation and gravity concentration of bismuthinite and native bismuth	Bi conc	Bi	Fe	As	WO ₃	Bi	
			11.1	28.7	7.6	0.6	25.5	
II	(a) Flotation of molybdenite	MoS ₂ conc	MoS ₂	Bi	Fe	As	MoS ₂	Bi
			70.8	6.9	15.7	0.8	92.5	31.1
	(b) Flotation of bismuthinite and native bismuth	Bi conc	Bi	Fe	As	WO ₃	Bi	
			10.1	26.9	6.6	0.6	31.8	
	(c) Gravity concentration and magnetic separation of wolframite	WO ₃ conc	WO ₃	S	Bi	As	WO ₃	
			59.2	3.0	0.3	0.7	79.2	
III	(a) Flotation of molybdenite and bismuthinite	MoS ₂ -Bi conc	MoS ₂	Bi	Fe	As	MoS ₂	Bi
			54.3	13.2	6.9	4.1	95.7	69.7
	(b) Gravity concentration and magnetic separation of wolframite	WO ₃ conc	WO ₃	S	Bi	As	WO ₃	
			66.7	0.9	0.1	0.3	76.1	
	(c) Gravity concentration of native bismuth	Bi conc	Bi	Fe	As	WO ₃	Bi	
			7.1	23.9	4.1	0.8	11.2	

From the preceding results, the following points pertinent to the successful processing of the Burnt Hill ore were established:

1. Initial concentration of molybdenite and bismuth (rather than tungsten as in Flowsheet I) results in a slightly better overall recovery, but in more contaminated concentrates.
2. Appreciable bismuth reports with the molybdenite even when using selective flotation (Flowsheets I and II).
3. Flotation of bismuthinite with molybdenite and separate concentration of native bismuth (Flowsheet III) proves to be necessary for a maximum recovery of bismuth (80.9%). Furthermore, this flowsheet is simpler and requires less steps than the others (compare Figures 11, 12 and 13 on pages 29, 32 and 36, respectively).
4. Further upgrading of the bismuth concentrate would be necessary to obtain a marketable product (40% Bi).
5. Desulphurization of the tungsten concentrates and removal of the main impurities from the molybdenite concentrates are imperative to meet market specifications.

Because of the small quantity of bismuth concentrate (0.2 to 0.4% by weight), it was not possible to clean this product on a table. A pilot plant investigation would be necessary to determine if this concentrate could be upgraded to a marketable grade. On the other hand, roasting was investigated to eliminate the sulphur from the tungsten concentrates and acid leaching was tested to reduce the impurity level in a combined molybdenite and molybdenite-bismuthinite concentrate, with the following results:

Roasting (WO ₃ conc)					Acid Leaching (MoS ₂ -Bi conc)				
Element	Feed	Magnetizing Roast and Separation	Calcine (800°C)	Specifi- cations*	Element	Feed	HCl Residue	HCl + HNO ₃ Residue	Specifi- cations*
WO ₃ (%)	61.90	65.70	66.40	65.0+	MoS ₂ (%)	67.7	70.10	91.20	85.0+
S "	2.20	0.44	0.14	0.50	Bi "	8.3	4.40	0.04	0.20
Bi "	0.50	0.06	0.04	0.25	Cu "	0.5	0.40	0.05	0.45
Cu "	0.02	0.01	0.01	0.05	Fe "	10.1	9.10	0.16	3.00
As "	0.72	0.69	0.35	0.10	As "	1.7	1.00	0.25	0.15
Mo "	0.50	0.02	0.02	0.80	Pb "	2.6	0.07	0.02	0.15

*From "Mineral Facts and Problems", U.S. Bureau of Mines, 1965.

Therefore, roasting of the tungsten concentrate and hydrochloric-nitric acid leaching of the molybdenite concentrates are necessary if marketable-grade products are to be achieved. Furthermore, as arsenic proved to be an impurity difficult to eliminate entirely by either roasting or acid leaching, attempts should be made to limit its concentration during the flotation stage by a more liberal addition of sodium cyanide.

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