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A Thesis
Submitted to the Department of Mineral Dressing
in Partial Fulfillment
of the Requirements for the Degree of
Bachelor Science
in Metallurgical Engineering
Mineral Dressing Option

MONTANA SCHOOL OF MINES
BUTTE, MONTANA
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INTRODUCTION

The development of suitable beneficiation processes for treating domestic low-grade tungsten ores is a problem now facing the mineral industry. While we are now consuming more tungsten than normally because of the defense program, we are no longer able to import ores from the world's principal source, China. The problem then, is to increase our domestic production so as to acquire a greater degree of self sufficiency. Unfortunately, much of the tungsten available in this country exists in very low-grade ores. Our government, in an effort to stimulate production, has stabilized the price of tungsten concentrates for a five year period, and has granted generous amortization privileges to plant operators. Exploration and development loans are also available to producers.

Furthermore, the possibility exists of up-grading the initial concentrate to create a product capable of meeting the specifications by industry.

MONTANA TUNGSTEN RESOURCES

Numerous low-grade deposits of tungsten ores occur with a 100 mile radius of Butte. Several million tons of scheelite averaging about 0.35 per cent WO_3 are said to exist in Beaverhead County alone. Huebnerite ore has been noted in the Potosi District near Harrison, Montana, and also at the Black Pine Mine near Philipsburg. Until recently, little interest has been shown toward these deposits. However, with the curtailment of foreign sources and the Government's stimulus through price stabilization and exploration and production loans, the Montana resources have attracted wide interest. The low grade of the ore is offset by the apparently large tonnages available. Exploitation of these deposits within the near future appears likely.

TUNGSTEN BENEFICIATION

In order to briefly summarize the methods for beneficiation, it is necessary to outline broadly the mineralogy of the more important tungsten minerals.

The principal tungsten minerals are commonly divided into two groups: scheelite and wolframite. In the wolframite group are included a series of iron-manganese tungstates ranging from ferberite ($FeWO_4$) to huebnerite (MnO_4). Ferberite, arbitrarily includes tungstates containing not more than 20 per cent huebnerite, while huebnerite contains not more than 20 per cent ferberite. Other iron-manganese minerals of this group are designated as wolframite. The principal ore mineral in the scheelite group is scheelite ($CaWO_4$). Several other minerals in this group, tungstates of copper and lead, do have an affect on the beneficiated products if they occur in an ore.

The relatively high specific gravities of the tungsten minerals make them amenable to various forms of gravity concentration such as tabling and jigging. In fact, until about 20 years ago, flotation was relatively unknown as a means of tungsten beneficiation. Since recoveries by the gravity methods were low, only the better deposits could be exploited. At the present time, some plants are using flotation and magnetic separation in addition to gravity concentration methods. Others employ flotation as the only means of concentrating the tungsten minerals. Two plants are briefly discussed to illustrate the usual beneficiation procedures.

The process used at the Ima Mine (4) in Idaho affords an excellent example of the combined use of gravity concentration methods and flotation. An initial operation by flotation removes the sulphide minerals. Then, a series of jigging steps separate most of the huebnerite into low-grade concentrates. Finally, the combined concentrates are dried and passed through a magnetic separator. Extremely high grade concentrates are produced that easily meet the industrial specifications from the standpoint of tungsten trioxide content and allowable amounts of impurities.

The Getchell Mill (16) is illustrative of a plant employing an all-flotation process on a scheelite ore. Following grinding, the pulp is conditioned and sent directly to flotation. A series of flotation operations progressively increase the grade of the concentrates. Nevertheless, the final product is an extremely low-grade concentrate. This material is then sent to a chemical refinery for additional treatment. The overall recovery of tungsten trioxide by flotation and chemical refining is high, averaging from 85 to 90 per cent.

EXPERIMENTAL, PROCEDURE AND DATA

The objectives of the experimental work were (1) to familiarize the writer with the techniques of testing an ore, (2) to determine the effects of temperature and other variables upon the flotation of huebnerite, and (3) to investigate the possibilities of retreating the flotation concentrates. The temperature studies were a continuation of the work done by Shaffer. The purpose of the third objective was to examine the possibilities of up-grading the rougher concentrates by the elimination of the gangue material. In this effort, only preliminary data was obtained.

The beneficiation studies reported here represent an investigation of the concentration of huebnerite by flotation. The ore from the Potosi Mining District near the town of Harrison, Montana, averaged 8.2 per cent WO_3 and should be properly termed a low-grade concentrate. In addition to huebnerite and the principal gangue mineral, quartz, a small amount of sulphide minerals were present. From a flotation standpoint an interesting problem in beneficiation exists.

Table I

Screen Analysis of Rod Mill Product

(10 minute grind)

Mesh	Weight (Grams)	Weight %	% Cum.*
-35	0.2	0.03	0.03
-35 + 38	7.4	1.23	1.26
-48 + 65	77.4	12.82	14.08
-65 + 100	140.6	23.29	37.37
-100 + 150	94.0	15.57	52.94
-150 + 200	74.3	12.31	65.25
-200	209.8	34.75	100.00
Total	603.7	100.00	

(15 minute grind)

Mesh	Weight (Grams)	Weight %	% Cum.*
+35	0.2	0.03	0.03
-35 + 48	1.0	0.17	0.20
-48 + 65	6.9	1.14	1.34
-65 + 100	64.7	10.72	12.06
-100 + 150	118.3	19.61	31.67
-150 + 200	105.5	17.48	49.15
-200	306.8	50.85	100.00
Total	603.4	100.00	

* % Cum. - per cent by weight

Liberation Studies

The ore, as received, had been previously reduced to about 3-inch size. Further reduction was made with the laboratory crusher and the rolls to all minus 10-mesh. Batch grinding in a rod mill completed the grinding phase.

Aliquot samples of the minus 10-mesh material were ground for 10 and 15 minutes respectively in a laboratory rod mill. Each sample was screened by the wet-dry method. Briquetted samples of each screen-fraction were polished and examined under a binocular microscope. This preliminary examination indicated that huebnerite was liberated from the gangue minerals in the minus 65 mesh material. Careful counting of the free and locked particles disclosed that about 95 per cent of the huebnerite was freed in the minus 48 plus 65 product. The results of the liberation studies are presented in Table I.

Flotation At Elevated Temperatures

The importance of elevated temperatures to the efficient flotation of huebnerite has been emphasized by Shaffer. In an attempt to verify his work, several tests were made in which the pulp was maintained at elevated temperatures during flotation.

Table II

Flotation at Elevated Temperatures

Test	p^H	Temp(°C)	% WO_3	Recovery (%)
1	9.5	60	14.6	83.1
2	9.6	50	27.1	67.5
3	9.6	40	21.6	71.9
28	9.7	35	47.7	80.6

The data obtained is not entirely in agreement with the observations of Shaffer. While his objective in using elevated temperatures was to bring about greater overall recovery, the lack of selectivity with increase in temperature was prominently displayed.

Sodium oleate was used as the collector and sodium silicate (Metso Brand) was added as the quartz depressant. These are the same reagents as used by Shaffer. Cooke believes that temperature brings about hydrolsis of sodium oleate at the mineral interface. The observations made by Shaffer were not substantiated. Nevertheless, the writer wishes to point out that further temperature studies are required before a definite opinion can be expressed. From a temperature of 40°C and upward the several variables affecting flotation should be studied in detail. Since the absorbability of the mineral surface for sodium oleate is likely to be increased with temperature, the variable of the amount of collector appears to be very critical. For example, there seems to be a minimum amount of sodium oleate required before flotation is attained at all. The tests also showed an increase in the amount of quartz floated. Apparently the quartz is activated more readily at higher temperatures. Thus, another problem occuring with elevated temperatures is the finding of a satisfactory quartz depressant.

Flotation at Ambient Temperatures

By ambient temperatures is meant that no appreciable changes were made in the mineral pulp. The temperature for each test was maintained at, or very near to, 26°C. The other variables including amount, type, method of addition, conditioning time, and the effects of alkalinity were investigated.

Of the collectors available, oleic acid and sodium oleate are commonly employed for non-metallic flotation. Both of these reagents were investigated. However, sodium oleate was used exclusively in all the tests recorded. Armeen SD, in a few tests, showed practically no selectivity and further testing with this reagent was discountinued. Only two depressants for the quartz were studied, sodium fluoride and sodium silicate.

The quantity of sodium oleate added varies greatly with pulp conditions and with method of use. (14) The collector required for a given amount of fine feed was found to be greater than that needed for the same weight of coarser material. Grinding in a batch process tends to produce a greater amount of fines; the weight of collector required in actual practice may be considerable less than that used in the tests recorded herein. Table III illustrates the variation in recovery and grade with increasing collector addition.

Table III

Effect of Collector Concentration

Test	p^H	Sodium Oleate (lb per ton)	Wt. %	$\%WO_3$	Recovery (%)
26	9.7	2.33	1.1	Not Assayed	
23	9.7	3.00	6.6	52.2	76.3
27	9.7	3.7	13.3	35.8	96.1

The results of the series of tests strongly suggest that if the quantity of reagent is carefully controlled, the p^H maintained at 9.7, and an adequate quantity of sodium silicate is used, satisfactory flotation can be attained.

Admittedly, the optimum amount of sodium silicate for the depression of the quartz was not determined. Other depressants should be investigated. Sodium fluoride proved unsatisfactory under the conditions with which it was used. A preliminary washing of the raw ore would be beneficial in removing or minimizing the elements responsible for the quartz activations. It has been proved that sodium oleate will not be a collector for quartz unless an ion, usually a heavy metal ion, is present. Some writers believe that such ions form relatively insoluble soap films at the surfaces of the quartz particles.

Stage Addition of Collector: Stage addition of collector has been noted by Taggert (14) as often very desirable to the effective flotation of tungsten minerals. The importance of addition of collector by increments was well illustrated by Tests 25 and 12 wherein the addition of approximately equal amounts of collector, with and without stage feeding, resulted in widely divergent recoveries. In Test 12, first 2 lb per ton of reagent was added followed by the addition of 0.83 lb per ton after a conditioning period of 8 minutes. In Test 25, all the reagent added was placed in the cell prior to the start of the conditioning period.

Table IV

Stage Addition of Collector

Test	p^H	Sodium Oleate (lb per ton)	Wt %	$\%WO_3$	Recovery (%)
25	9.7	3.17	4.6	51.8	36.4
12	9.7	2.83	15.8	52.2	92.3

Stage addition does increase the recovery with no appreciable change in grade of concentrate obtained.

Conditioning Time: The total conditioning time was found experimentally to lie in the range between 8 minutes and 29 minutes. Twenty two minutes conditioning proved no better than did twelve. The latter time was adopted for all tests except those made at higher than ordinary temperatures. Over 40°C, it is necessary to shorten conditioning to about 1.5 minutes.

In the Table below, the conditioning times are presented in two columns: (1) the time after the first addition of reagents and (2) after the second addition.

Table V

Variation in Conditioning Time

Test	Temp (°C)	Time		Wt %	% WO_3	Recovery (%)
		(1)	(2)*			
15	26	4	4	11.5	58.4	72.4
16	26	4	4	14.6	55.9	89.7
12	25	8	4	15.8	52.2	92.3
13	25	8	4	15.8	52.2	94.9
10	26	18	4	17.7	49.9	93.1
11	26	18	4	18.1	46.1	93.0
5	23	25	4	9.2	42.7	42.7
6	23	25	4	14.5	54.4	90.1
7	26	25	4	11.6	51.5	68.9
8	26	25	4	14.8	48.9	84.9
1	60	1.5	0.5	45.4	14.6	83.1

*Time (1) the time, in minutes, after the first addition of reagents.

(2) the time after the first addition of reagents.

Hydrogen Ion Concentration: The maintenance of the proper p^H of the pulp is essential when sodium oleate is employed as the collector. A critical point exists about p^H 9.0, below which, the frothing characteristics of the collector become noticeably apparent. Coinciding with the increase in froth is the rapid decrease in grade of the concentrate. Above p^H 9.2, the frothing diminishes and considerable latitude exists as to alkalinity.

Table VI

Hydrogen Ion Concentration

Test	p^H	Temp(°C)	Wt %	%WO_3	Recovery (%)
13	9.7	25°	15.8	52.5	94.9
19	9.2	26°	19.8	41.1	96.9
20	8.8	26°	37.7	23.1	92.6

Rougher Concentrate Retreatment: The concentrates obtained in the tests previously noted and other concentrates prepared after the more effective flotation conditions were known, were used in this part of the investigation. These concentrates ranged in WO_3 content from 40 to 55 per cent and were regarded as rougher concentrates. The principal contaminating material was found to be quartz.

From a weight standpoint, less quartz than huebnerite was present in the concentrate. The removal of the quartz seemed desirable. The first step in the process was the removal of the collector from the huebnerite particles. Several cleaning methods were considered: (1) an acid treatment followed by washing with water, (2) digestion with a caustic followed by washing with water and (3) treatment with an organic solvent. Undoubtedly, light roasting of the material would remove the organic reagent but this method was not considered practical because of the expense of dewatering, heating, and repulping.

The concentrates to be cleaned were repulped in an acid solution at a p^H of 3.0 and were vigorously agitated for 25 minutes while the pulp was maintained at a temperature of 50°C. Following agitation, the pulp was filtered and thoroughly washed with distilled water. Upon return of the material to the flotation cell, the huebnerite minerals floated immediately to the surface. The scrubbing treatment had evidently failed to remove the collector.

The treatment to remove the collector with caustic solution was identical to that outlined for the acid wash with the exception that the p^H of the pulp was maintained at 10.8 by the use of suitable amounts of sodium hydroxide. The alkaline solution was no more effective in removing the collector than was the acid bath.

A thorough washing with acetone apparently removed all the collector reagent from the huebnerite for the tungsten mineral was not observed to float after a short agitation period in the flotation cell. The acetone, itself, must be completely removed from the concentrates or uncontrollable frothing occurs.

SUMMARY

The advantages of elevated temperatures were not apparent from the experimental evidence gathered in this investigation. However, the many variables which should be thoroughly investigated at each temperature were not considered in sufficient detail. For this reason, the influence of temperature upon the effectiveness of the flotation process remains questionable and will require further study.

Stage addition of collector is helpful. Likewise reagent addition is critical. Insufficient collector addition resulted in extremely low recoveries while low-grade concentrates were produced when an excess of reagent was present.

An initial conditioning time of 8 minutes was found to be satisfactory when followed by a 4 minute conditioning period after the second stage addition of collector. Four minutes conditioning proved to be not enough; whereas, an 18 minute period was no better than 8. Twenty five minutes of conditioning gave erratic results.

Hydrogen ion concentration is another of the important variables affecting the flotation process. With sodium oleate as collector, a critical point exists at about p^H 9.0 Overfrothing occurs below the critical point with corresponding reduction in grade. Both good recovery and grade were obtained in the p^H range of from 9.2 to 9.8.

An organic solvent such as acetone is effective for the removal of the collector from the huebnerite surfaces. Methods of digesting the concentrates in a strong acid and a strong alkaline solution proved to be ineffective. 23220

RECOMMENDATIONS

Other organic compounds for the flotation of huebnerite should be studied in an effort to secure a reagent with more selectivity for this tungsten mineral. A better reagent for the depression of quartz would be equally important. Furthermore, better understanding of the environmentally conditions necessary for quartz depression would facilitate the separation. The retreatment of the initial concentrates merits more thorough investigation.

Considerable flexibility in the up-grading process is permissable. If retreatment could be developed, the grade of the initial concentrate would not be too critical. Conversely, if experimental evidence points that retreatment is not feasible, a more specific collector would be needed.

CONCLUSION

On the basis of the experimental evidence obtained, the writer believes that an all-flotation process for huebnerite is feasible. Careful plant control will be required to produce concentrates of high enough grade to meet industrial specifications. Such variables as p^H, number of cleaning operations, and the maintenance of uniform temperature will require careful consideration.

ACKNOWLEDGMENT

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APPENDIX

Table No. VII

Test	p^H	Temp (^oC)	Condition (minutes)	Weight %	% WO_3	Recovery (%)
1	9.5	60	2.0	45.5	14.6	83.1
2	9.7	50	2.75	22.2	27.1	67.5
3	9.6	40	3.5	28.8	21.6	71.9
28	9.7	35	12.0	9.5	47.7	80.6

Reagents

Test	Metso lb/ton	Sodium Oleate (lb/ton)			
		1	2	3	Total
1	1.5	1.0	0.16		1.16
2	1.5	1.0	0.33		1.33
3	1.5	1.0	0.66		1.66
28	1.5	2.0	1.00		3.00

Remarks:

Note the low grade of the products obtained at the higher temperatures. Sodium carbonate used for p^H control.

Table No. VIII

Test	p^H	**Temp** (^{o}C)	**Condition** (minutes)	**Weight %**	**% WO_3**	**Recovery** (%)
26	9.7	26	12	1.1	Not assayed	
23	9.7	26	12	6.6	52.2	76.3
27	9.7	26	12	13.3	35.8	96.1

Reagents

Test	**Metso** lb/ton	**Sodium Oleate (lb/ton)**			
		1	**2**	**3**	**Total**
26	1.5	2.0	0.33		2.33
23	1.5	2.0	1.00		3.00
27	1.5	2.0	1.70		3.7

Remarks:

A minimum amount of collector must be added for flotation to occur at all. If an excess is present in the cell, overfrothing with attendant low grade occurs.

Table No. IX

Test	p^H	Temp (°C)	Condition (minutes)	Weight %	% WO_3	Recovery (%)
5	9.7	23	29	9.2	42.7	42.7
6	9.7	23	29	14.5	54.4	90.1
7	9.7	27	29	11.6	51.4	68.9
8	9.7	27	29	14.8	48.9	84.9

Reagents

Test	Metso lb/ton	Sodium Oleate (lb/ton)			
		1	2	3	Total
5	1.5	2.0	0.66		2.66
6	1.5	2.0	0.66		2.66
7	1.5	2.0	0.66		2.66
8	1.5	2.0	0.66		2.66

Remarks:

Sodium Carbonate used for p^H control. Agreement in recoveries is lacking in this series of tests.

Table No. X

Test	p^H	Temp (°C)	Condition (minutes)	Weight %	% WO_3	Recovery (%)
9	9.7	27	22	15.8	46.0	90.4
10	9.7	27	22	17.7	49.9	93.1
11	9.7	27	22	18.1	46.1	93.0

Reagents

Test	Metso lb/ton	Sodium Oleate (lb/ton)			
		1	2	3	Total
9	1.5	2.0	0.83		2.83
10	1.5	2.0	0.83		2.83
11	1.5	2.0	0.83		2.83

Remarks:

Excellent agreement in both grade and recovery indicated here. Sodium carbonate added for p^H control.

Table No. XI

Test	p^H	Temp (°C)	Condition (minutes)	Weight %	% WO_3	Recovery (%)
12	9.7	25	12	15.8	52.2	92.3
13	9.7	23	12	15.8	52.5	94.9
14	9.7	26	12	16.7	48.3	91.8
15	9.7	26	8	11.5	58.4	72.6
16	9.7	26	8	14.6	55.9	89.7

Reagents

Test	Metso lb/ton	Sodium Oleate (lb/ton)			
		1	2	3	Total
12	1.5	2.0	0.83		2.83
13	1.5	2.0	0.83		2.83
14	1.5	2.0	0.83		2.83
15	1.5	2.0	0.83		2.83
16	1.5	2.0	0.83		2.83

Remarks:

The most suitable conditioning time appears to from 12 to 22 minutes. Recovery decreased when conditioning was shortened to 8 minutes.

Table No. XII

Test	p^H	Temp (°C)	Condition (minutes)	Weight %	% WO_3	Recovery (%)
25	9.7	26	12	4.6	51.8	36.4
12	9.7	25	12	15.8	52.2	92.4

Reagents

Test	Metso lb/ton	Sodium Oleate (lb/ton)			
		1	2	3	Total
25	1.5	3.17			3.17
12	1.5	2.0	0.83		2.83

Remarks:

The value of stage addition is emphasized here. In test 25, all the collector was added to the cell at the start of conditioning while in test 12 addition was by two stages.

Table No. XIII

Test	p^H	Temp (°C)	Condition (minutes)	Weight %	% WO_3	Recovery (%)
17	9.7	26	12	18.6	45.3	91.2
18	9.7	26	12	12.3	56.8	77.8

Reagents

Test	Metso lb/ton	Sodium Oleate (lb/ton)			
		1	2	3	Total
17	1.5	2.0	0.83		2.83
18	1.5	2.0	0.66		2.66

Remarks:

The flotation feed for tests 17 and 18 was ground only 10 minutes as compared with 15 minutes for all the other tests recorded. If sufficient collector is added, ten minutes appears to be sufficient.

Table No. XIV

Test	p^H	Temp (°C)	Condition (minutes)	Weight %	% WO_3	Recovery (%)
13	9.7	25	12	15.8	52.5	94.9
19	9.2	26	12	19.8	41.1	96.9
20	8.8	26	12	37.8	23.1	92.6

Reagents

Test	Metso lb/ton	Sodium Oleate (lb/ton)			
		1	2	3	Total
13	1.5	2.0	0.83		2.83
19	1.5	2.0	0.67		2.67
20	1.5	2.0	0.67		2.67

Remarks:

The amount of gangue material floated with the huebnerite increases sharply when the p^H falls below 9.0. With sodium oleate, lower p^H values result in overfrothing.

Sodium Carbonate and HCI added for p^H control.