A STUDY OF THE TREATMENT OF SOME ARIZONA MOLYBDENITE ORES

by

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PREFACE

The writer wishes to acknowledge his indebtedness to Dr. T. G. Chapman of the Department of Mining and Metallurgy, College of Mines and Engineering, University of Arizona, under whose personal supervision this work was done; also to Professor J. B. Cunningham of the Department of Mining and Metallurgy for helpful criticisms and suggestions. The writer is also indebted to Dr. R. L. Nugent of the Department of Chemistry, and Mr. E. A. Jacobs, registered assayer, Tucson, Arizona, for advice and suggestions on methods of chemical analyses.

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CHAPTER I.--INTRODUCTION

Since molybdenum has assumed a more important place among the metals produced in the Southwest owing to increased demand for the metal in the manufacture of alloy steels and to new uses discovered for the metal it is desirable that further experimental work be done with certain problems involving Southwestern ores.

Within the past year three problems involving the treatment of molybdenite ores and concentrates obtained from treating Southwestern ores have developed, and the object of the experimental work presented in this paper is to study these problems with a view of offering experimental evidence for their solutions.

The first problem is the difficulty encountered in concentrating Helvetia molybdenite ores due to inability to control flotation operations. The Helvetia mill started concentrating molybdenite ore in August, 1934. Difficulties soon developed in the control of the flotation circuit. Various remedies for the trouble were tried and it was finally determined that if the slime was removed, after grinding, the remaining material could be treated with proper control in the flotation circuit. The mill continued operations by removing the slime by means of a Wilfley table, treating the sands in flotation

cells, and storing the slime.

The second problem is more general in scope and involves the removal of copper from molybdenite ores. Two general methods are at present employed for removal of copper from molybdenite ores by flotation methods. One method consists of depressing molybdenite with starch while the copper is being floated; the molybdenite is then activated with kerosene and floated while the remaining copper is depressed with sodium cyanide. In the second method chalcopyrite is depressed by means of cyanide while the molybdenite is being floated.

The third problem involves the removal of sulphur and copper by leaching methods from the calcine produced by roasting molybdenite concentrate.

Very little material is available in the literature concerning the treatment of molybdenite ores along the lines described.

Considerable unpublished experimental work along the lines described has been done by members of the Department of Metallurgy of the University of Arizona. The object of the experimental work described in this paper is to obtain additional data on the work started at the University of Arizona.

CHAPTER II.--APPARATUS, MATERIALS, AND ANALYTICAL METHODS USED

The small-scale experimental work along flotation lines was done in Fahrenwald flotation machines of 500 and 2000 gram capacities. The 100-pound flotation test was made with a 5-cell continuous Fahrenwald machine.

Roasting tests were conducted in an iron pan 12 by 20-1/2 inches by 1-3/4 inches deep placed in the muffle of an oil-fired assay furnace.

Ores and concentrates used for experimental work were obtained from the Helvetia and Leviathan mines located in Arizona.

The Helvetia molybdenite ore occurs in a lime-garnet gangue, which is unusual, and this occurence of molybdenite probably accounts for some of the difficulties encountered in milling and processing Helvetia ores and concentrates. Chalcopyrite and pyrite occur in varying amounts with the molybdenite.

The Leviathan ore was used for the experimental work involving removal of copper by flotation methods. This ore contains molybdenite associated with chalcopyrite and pyrite in a granite gangue. The difficulty in removing copper contained

in this ore to a degree that permits the sale of the concentrate is due to the relatively large copper content and to the fact that a microscopic examination revealed an intimate association between the molybdenite and chalcopyrite.

Molybdenum analyses were made by the Bonardi method described in Bulletin 212, ANALYTICAL METHODS FOR CERTAIN METALS, by R. B. Moore published by the United States Bureau of Mines. This method is based on decomposition of the ore with acid into a soluble molybdate and a residue. The molybdate solution is filtered and interfering elements especially iron, arsenic, vanadium, and copper are removed. The resulting molybdate solution is then acidified and passed through a Jones reductor where the molybdenum is reduced from the sexavalent to the trivalent state. The solution containing the trivalent molybdenum compound is titrated with standardized potassium permanganate solution and the molybdenum content calculated.

The copper contents of calcines were determined by the electrolytic method. The procedure is described in STANDARD METHODS OF CHEMICAL ANALYSIS, Volume 1, fourth edition, by W. W. Scott, published by D. Van Nostrand Company, and was used with the following addition. The weighed sample was boiled in a solution of sodium hydroxide which converted the

molybdenum trioxide into soluble sodium molybdate and left the copper in the residue. After filtering the residue was treated with nitric acid and then evaporated with sulphuric acid. The water soluble copper and iron solution after filtering was then handled as in the electrolytic method.

CHAPTER III.--EXPERIMENTAL WORK

QUALITATIVE EXPERIMENTAL WORK ON HELVETIA ORE

As previously mentioned, considerable difficulty was encountered in operating the Helvetia concentrator due to inability to control the flotation circuit. The first reagents used comprised lime, xanthate, pine oil, and cyanide. With these reagents the tailing loss of coarse molybdenite was excessive. Kerosene was then employed to recover the coarse molybdenite, and the addition of this reagent caused a "wild froth" condition in the flotation circuit. Attempts to correct this difficulty by varying the kinds and amounts of reagents failed. The difficulty was finally traced to the lime-garnet slime in conjunction with kerosene, pine oil, or hard water. The removal of the slime on a Wilfley table, as previously mentioned, permitted the satisfactory recovery within the limits of grinding employed of the molybdenite contained in the sand. The slime was stored until further experimental work could be done to develop a method for its treatment.

The object of the experimental work described in this chapter was to study the effects of various reagents in order to find a combination that would permit the treatment of the entire ground product without the removal of the slime, by flotation methods, or in the event that this was not found feasible, to find a reagent combination that would permit the

treatment of the slime.

The experimental work for this phase of the work involved making 16 flotation tests in a 500-gram capacity Fahrenwald machine. The material used was slime, separated from ground Helvetia ore by means of a laboratory-size Wilfley table. The slime was not dried before making the tests. The tests were qualitative in nature as it was desired to study the effects of adding various reagents on the physical properties of the froth produced. The results of these tests are given in Table 1.

Referring to Table 1, the various reagents used were for the purposes of conditioning the water, dispersing the gangue slime, or activating the molybdenite.

The qualitative results of most of the tests, as indicated in Table 1, were negative. General conclusions may be stated as follows:

1. - The results of tests 8 and 13 indicate that hard water is at least to some extent responsible for the poor results obtained in treating this material when kerosene is used as an activator of the molybdenite.

2. - The results of tests 6 and 14 indicate that the use of increasing amounts of kerosene cause more gangue to be floated and increases the size of the bubbles comprising the froth.

Table 1 - The effects of various reagents on the character of froth produced from Helvetia slime

Test No.	Weight of Helvetia slime used, grams	Reagents used: Collectors: Kind	Collectors: Lbs. per ton of slime	Frothers: Kind	Frothers: Lbs per ton of slime	Miscellaneous: Kind	Miscellaneous: Lbs per ton of slime	Character of froth produced
1	200	Amyl xanthate Kerosene	0.1 0.5	GNS No. 5 pine	0.28	Borax glass	2.0	Large bubbles with gangue; molybdenite was not effectively floated.
2	200	Amyl xanthate Kerosene	0.1 0.5	GNS No. 5 pine	0.28	Alum, added in stages of 1.0 lbs per ton each	3.0	Brittle froth; molybdenite not effectively floated.
3	200	Amyl xanthate Kerosene	0.1 0.5	GNS No. 5 pine	0.28	Sodium carbonate added in stages, first two of 1 and 2nd two of 5 lbs. per ton each	12.0	First two additions caused decrease in bubble size, second two caused no change. Froth carried gangue; molybdenite was not effectively floated.
4	200	Amyl xanthate Kerosene	0.1 0.5	GNS No. 5 pine	0.28	Soap	1.0	Large volume of tough gray froth; molybdenite was not effectively floated.
5	200	Amyl xanthate Kerosene	0.1 0.5	GNS No. 5 pine	0.28	Soap	0.1	Watery froth which carried much gangue.
6	200	Amyl xanthate Kerosene	0.1 0.5	GNS No. 5 pine	0.28	Sodium silicate	1.0	Medium sized bubbles; molybdenite not effectively floated.
7	200	Amyl xanthate Kerosene	0.1 0.5	GNS No. 5 pine	0.28	Potassium hydroxide	1.0	Large bubbles; molybdenite not effectively floated.
8[1]	200	Amyl xanthate Kerosene added in three stages of 0.5 lbs per ton	0.1 1.5	GNS No. 5 pine added in three stages, first stage 0.28 next two 0.14 lbs. per ton	0.56	-	-	After first stage of kerosene and pine oil the bubbles were small and carried molybdenite and gangue. After the second and third addition of kerosene and pine oil more molybdenite appeared on the froth, but the bubbles were larger and carried more gangue.
9	200	Amyl xanthate Kerosene	0.1 0.5	GNS No. 5 pine	0.28	Sodium silicate Sodium carbonate	1.0 2.0	Small bubbles with gangue; molybdenite not effectively floated.
10	200	Minerec (acid) Kerosene	0.05 0.5	GNS No. 5 pine	0.28	Sulphuric acid	1.0	Watery froth, large bubbles with gangue.
11	200	Amyl xanthate Kerosene	0.1 0.5			Copper sulphate	1.0	Large bubbles; molybdenite not effectively floated.
12	200	Amyl xanthate Kerosene	0.1 0.5	GNS No. 5 pine	0.28	Tartaric acid	1.0	Small bubbles; molybdenite not effectively floated.
13[1]	200	Amyl xanthate Kerosene	0.1 1.5	GNS No. 5 pine	0.28	-	-	Large bubbles with some gangue.
14	200	Amyl xanthate Kerosene	0.1 1.5	GNS No. 5 pine	0.42	Sodium silicate	1.0	Large bubbles gray with gangue.
15	200	Amyl xanthate	0.1	GNS No. 5 pine	0.28	Sodium carbonate	1.0	Froth had satisfactory appearance and less gangue was floated than in previous tests.
16	200	-	-	GNS No. 5 pine	0.28	-	-	Froth had satisfactory appearance and was similar to the froth of test 15.

[1] The slime was washed with two 600 cc. washes of distilled water before treatment and distilled water was used in the flotation machine.

3. - The results of test 3 indicate that sodium carbonate has a beneficial effect on the character of the froth.

4. - The results of test 6 indicate that sodium silicate has a beneficial effect on the character of the froth.

5. - The results of test 16 indicate that amyl xanthate is not effective in the flotation of molybdenite, or at least, this reagent is not necessary when pine oil is used as a frothing reagent.

6. - All other reagents employed gave negative results.

QUANTITATIVE EXPERIMENTAL WORK ON HELVETIA ORE

Test 17 was made to secure an indication of the results that might be expected in treating the Helvetia ore by separating the slime and sand and floating each in separate circuits.

A 1000-gram sample of Helvetia ore, ground to 4.2 per cent plus 48- mesh, was deslimed in a gold pan and the sand and slime floated separately.

The sand was floated for 20 minutes in a 500-gram capacity Fahrenwald machine with 1.5 pounds kerosene, 1.0 pound sodium carbonate, and 0.3 pound G.N.S. No. 5 pine oil per ton of sand treated. The rougher concentrate was cleaned for 15 minutes in the same flotation machine with 1.0 pound of sodium cyanide per ton of sand treated, added in five equal stages, for the depression of chalcopyrite.

The slime was floated for 20 minutes in a 500-gram capacity Fahrenwald machine with 0.1 pound amyl xanthate, 1.0 pound sodium carbonate, and 0.3 G.N.S. No. 5 pine oil per ton of slime treated. The rougher concentrate was cleaned for 15 minutes in the same flotation machine with 1.0 pound of sodium cyanide per ton of slime treated, added in five equal stages. The results of this test are given in Table 2.

Referring to Tables 2 and 3 the data indicates the conclusions which follow:

Table 2 - Effect of desliming on flotation treatment of Helvetia ore

Product	Weight, grams	Tons in 100	Assays, per cent MoS_2	Pounds MoS_2 in 100 tons of mill feed	Per cent of total MoS_2
Ore	1000	100	Head 1.50	2700	100
			Product 1.35		
Sand			(1)		
Head	695.78	69.58	1.48	2054	76.09
Concentrate	8.72	0.87	86.34	1506	55.78
Middling	6.06	0.61	6.37	77	2.85
Tailing	681.	68.1	0.35	471	17.46
Slime			(1)		
Head	296.57	29.66	1.09	646	23.91
Concentrate	5.02	0.50	27.19	273	10.11
Middling	19.55	1.96	2.46	96	3.56
Tailing	272.	27.20	0.51	276	10.24

(1) Calculated

Table 3 - Summary of results given in Table 2

Product	Weight, grams	Tons in 100	Assays, per cent MoS_2	Pounds MoS_2 in 100 tons of mill feed	Per cent of total MoS_2
Heads	1000	100	Head 1.30 Product 1.35	2700	100
Combined concentrates	13.74	1.37	64.70	1778	65.89
Combined middlings	25.61	2.56	3.40	174	6.42
Combined tailings	953	95.3	0.39	748	27.69

1. - The concentrate produced from the sand was not high enough in molybdenite content to meet the usual market requirements, but it could no doubt be raised to the required grade by a second cleaning operation.

2. - The concentrate produced from the treatment of the slime was much below the grade required for marketing, but additional cleaning stages might also remedy this difficulty.

3. - The molybdenite loss in the tailing was high. This loss in the case of the sand was believed to be due to the coarse grinding employed rather than the inefficiency of the flotation operation. In the treatment of the slime additional flotation time might improve the results.

EXPERIMENTAL WORK ON LEVIATHAN ORE BY SELECTIVE FLOTATION METHODS

R. C. Bacon[1] made a series of flotation tests on Leviathan ore when it was ground to 2.6 per cent plus 65-mesh. These tests did not produce a molybdenite concentrate sufficiently low in copper content to meet the market requirements. Without cleaning the flotation concentrate a recovery of 85.2 per cent of the molybdenite was made in a concentrate that contained 12.8 per cent of copper when 1.0 pound of cyanide per ton of ore treated was used for the depression of chalcopyrite. With a cleaning operation in which 1.5 pounds of cyanide per ton of original ore was used a recovery of 73.9 per cent of the molybdenite was made in a concentrate that contained 2.14 per cent of copper. Microscopic examination by Bacon of the products of various tests indicated an intimate association between the molybdenite and chalcopyrite.

In order to check Bacon's results on a continuous treatment basis a 100-pound flotation test was made on the Leviathan ore ground somewhat finer than was the ore for Bacon's tests. Ore, ground to 1.5 per cent plus 65- mesh and 67.0 per cent minus 200- mesh, was fed into the conditioner of a 5-cell Fahrenwald flotation machine at the rate of one pound per minute. Reagents added to the conditioner were 1.0 pound sodium carbonate, 1.0 pound kerosene, and 0.33 pound sodium cyanide per ton of

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[1] Bacon, R. C., Personal communication.

ore treated, with sufficient C.N.S. No. 5 pine oil to produce the desired amounts of froths.

A concentrate was removed from the first cell and a middling product from the remaining four. The concentrate was dried and then cleaned twice in one cell of the 5-cell machine. During each cleaning operation sodium cyanide was added in four equal stages, the total cyanide used amounting to four pounds per ton of concentrate cleaned.

The ore used for this test contained 1.51 per cent of copper. The finished concentrate produced contained 4.04 per cent of copper. Of the total copper originally in the ore 3.16 per cent was in the concentrate indicating that 96.84 per cent of the copper was depressed in the flotation operation by cyanide. Since the copper content of the concentrate was more than the maximum allowable for the marketing of the concentrate a complete accounting of the copper and molybdenum contents of the products of this test was not made. The loss of molybdenite caused by cleaning operations in Bacon's tests and an inspection of the middling products from the 100-pound test indicated that the separation of chalcopyrite and molybdenite cannot be readily accomplished in this ore without undue losses of molybdenite. A microscopic examination of the concentrate from the continuous 100-pound test showed free chalcopyrite and at least some of the chalcopyrite associated with

the molybdenite.

THE LEACHING OF CALCINE PRODUCED BY ROASTING LEVIATHAN MOLYBDENITE CONCENTRATE

A sample of the concentrate produced in the 100-pound flotation test previously described contained in an iron pan was placed in the muffle of an oil-fired assay furnace for four hours. The following readings of temperatures were observed.

Time, p.m.	Temperature, degrees centigrade
1:00	150
1:30	300
1:45	350
2:00	415
2:15	410
2:30	415
2:45	460
3:00	460
3:15	460
3:30	590
4:00	560
4:15	595
4:30	595
4:45	590
5:00	590

The weight of the calcine was 91 grams. A sample of the calcine weighing 50 grams was placed in a bottle with 100 cc. of distilled water and the bottle placed on a set of revolving rolls for two days. The pulp was filtered and the residue washed with 200 cc. of distilled water. The residue was then dried and weighed. The weight was 45.4 grams, the loss of weight during leaching being 4.6 grams. Before leaching, the calcine

contained 4.44 per cent of copper, after leaching the residue contained 4.59 per cent of copper. The copper removed by leaching amounted to 6.31 per cent of the total.

A second roasting test was made in the manner described using a 100-gram sample of the same concentrate. The material was roasted for five hours and the following readings of the temperatures were observed.

Time	Temperature, degrees centigrade
11:15 a.m.	300
11:30	350
11:45	340
12:00	400
12:15 p.m.	405
12:30	405
12:45	450
1:00	455
1:15	420
1:30	430
1:45	450
2:00	450
2:15	460
2:30	450
2:45	480
3:00	480
3:15	490
3:30	490
3:45	495
4:00	495

The weight of the calcine produced was 93.1 grams. A sample of the calcine, weighing 50 grams, was leached with distilled water for two days as described in the previous test. The residue after filtering and washing with 250 cc.

of distilled water weighed 45.9 grams, the loss of weight during leaching being 4.1 grams. Before leaching the calcine contained 5.05 per cent of copper, after leaching the residue contained 5.04 per cent of copper. The copper removed by leaching amounted to 8.34 per cent of the total.

While the roasting and leaching methods used did not successfully remove the copper from the molybdenum calcine the slight improvement in the results obtained in the second test indicates that the temperature at which the roasting is done affects the solubility of the copper compounds formed. Although the writer believes that further work along the lines used might bring improved results it is doubtful if large enough amounts of the copper can be rendered water soluble by roasting to reduce the copper content of the calcine to a point permitting the marketing of the product when the copper content of the flotation concentrate is appreciable.

CONCLUSIONS

The qualitative work on Helvetia ore indicated that while some of the reagent combinations showed a beneficial effect on the character of the froths produced when these combinations were used with kerosene no reagent combination was found that would permit the use of enough kerosene to float the coarse molybdenite in the ore in the presence of the slime portion of the ore. Unless some other reagent combination is developed it will be necessary to continue to deslime the ore after grinding and treat the sand and slime products in separate flotation circuits.

The quantitative test on desliming Helvetia ground ore and treating the sand and slime products separately by flotation methods indicates that although kerosene appears to be essential in the flotation of the coarse molybdenite in the sand it is not essential in the flotation of the fine molybdenite in the slime.

The data given involving the removal of copper by selective flotation in the treatment of Leviathan ore indicates that it will be difficult to produce a concentrate of low copper content from this ore. The copper content of the ore is so high that even when 96 plus per cent of the copper is depressed by cyanide the copper content of the concentrate greatly

exceeds the maximum allowable for the marketing of the concentrate.

A treatment scheme such as is used at Cananea might be successful in treating this ore, but it would mean a double flotation treatment, the first to depress molybdenite while floating chalcopyrite and the second to depress the remaining chalcopyrite while floating the molybdenite.

As previously indicated the removal of copper from molybdenite concentrate by roasting followed by leaching to remove the water soluble copper does not offer much promise of success.

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