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Benefication of a Tungsten Ore

James Alexander Shaffer Jr.

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BENEFICIATION OF A TUNGSTEN ORE

by

James Alexander Shaffer, Jr.

A Thesis

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

MONTANA SCHOOL OF MINES

BUTTE, MONTANA

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BENEFICIATION OF A TUNGSTEN ORE

INTRODUCTION

Tungsten is a metal of high strategic value in the defense effort. It is used chiefly to improve creep strength in steels, although a significant percentage enters into the manufacture of cemented-carbide tool bits. Therefore, in this age of mechanized warfare, quality and quantity of defense production depend greatly on tungsten.

An investigation has been made on a Montana tungsten ore. In the interest of stimulating production of tungsten from domestic ores, the investigation has included, in addition to the application of basic theory, some consideration of practical milling requirements.

Ores containing tungsten minerals in commercially recoverable quantities often present unique beneficiation problems. Although the commonly-found tungsten minerals (scheelite, CaWO_4 ; ferberite, FeWO_4 ; wolframite, $(\text{Fe},\text{Mn})\text{WO}_4$; and huebnerite, MnWO_4) have many similar chemical and physical properties, treatment of ores containing these minerals may vary, and must be dictated, in most cases, by their association with other valuable ore constituents and with various gangue minerals.

Massive deposits of tungsten minerals are infrequently

found. These minerals usually occur in contact-metamorphic deposits or in quartz veins, in the form of finely-disseminated acicular crystals, crusts and coatings, and tabular grains. They may be associated with heavy-metal sulfides, especially those of copper, lead, silver, and molybdenum. Gangue minerals include quartz, the various complex silicates, and, at times, apatite. Placer deposits, including large occurrences in China, are known.

The commercial value of a deposit depends on the amount of tungsten and other valuable minerals present, the amount of mineral economically recoverable, and current metal prices. It follows that a high recovery of mineral from a low-grade deposit may make a valuable property out of one otherwise worthless, and that good recovery of the mineral in a relatively high-grade deposit will yield the maximum return.

Tungsten concentrates are marketed on the basis of tungstic acid (WO_3) content; most buyers require an assay of at least 60% WO_3 . Impurities, especially the heavy metals, phosphorus, and sulfur, should be brought down to but a small fraction per cent. Depending on supply and demand, poorer grades, with higher impurity content, may be marketed, with attendant penalties.

An investigation has been made on a tungsten ore from

the properties of the Potosi Tungsten Mining Company, near Pony, Montana. Beneficiation studies have been conducted on this ore by gravity methods, including heavy-media separation, tabling, and jigging; and by somewhat detailed flotation testing. The proper commercial application of one or a combination of several of these methods will, it is believed, produce a saleable concentrate, with a high recovery of the tungsten minerals.

SURVEY OF RECOVERY METHODS

Gravity Concentration

Gravity methods have long been used for tungsten recovery. The concentration criterion for these methods ranges from about 2.0 to 3.5, indicating a possibility of effective separation. High recoveries and good concentrate grade can be made in the sand sizes. Owing, however, to the friability of the tungsten minerals, they slime badly during comminution; the slimes are slow-settling because of their extreme fineness and are usually lost in tailings from operations which depend wholly on gravity methods. Since several per cent of a tungsten mineral may approach colloidal size after a fine-grinding operation, the loss of this amount of mineral may adversely affect the economic feasibility of the entire operation.

According to Taggart¹, a gravity flowsheet may include stage crushing, screening, and classification to produce several closely-graded products, followed by separation on tables or in jigs, with recirculation of the middling for re-treatment. If sulfides or other heavy minerals are present, further steps, including flotation, digestion and precipitation, roasting, and magnetic separation, may be required.

Flotation

Flotation methods on tungsten ores, although more recent in development than gravity treatment, have passed the experimental stage at properties where their use has been indicated. At Ima² and Nevada-Massachusetts³, flotation is recovering a large amount of mineral formerly lost in the gravity process.

Although tungsten minerals are metallic salts of tungstic acid, their properties are those of the non-metallic minerals; as such, they are amenable to the action of anionic flotation reagents, including fatty acids and their alkali-metal salts. In contrast to usual sulfide flotation practice, the use of anionic collectors depends greatly on the depression of the gangue minerals. Most anionic collectors are non-selective unless the proper addition agents are used with them. It follows that one of the major phases of flotation testing, as always, includes the choice of reagents, the determination of their quantities, and the control of the flotation environment, in order to produce the desired results.

Tungsten reagents may be grouped into four classifications⁴: 1) addition agents; 2) promoters (collectors); 3) accessory promoters; and 4) frothers. Typical addition agents are soda ash, for gangue depression, pH regulation, and selectivity; sodium silicate, as a dispersant; sodium

cyanide, as a depressant of sulfides; and quebracho or tannin, as a depressant of carbonate gangue minerals.

Promoters are usually long-chain fatty acids, their emulsions, or their salts. Theories concerning the action of these reagents will be discussed later; suffice it here to say that they render the mineral surface hydrophobic, and, in the presence of the proper addition agents, leave the gangue surfaces hydrophilic. Probably the most important collectors are oleic acid and its salts, specifically sodium oleate. Oleic acid itself is secondarily soluble and must be added in, say, an alcohol solution, whereas the salt is, of course, water-soluble, and may be added dry, if desired. Stage addition of these reagents may be most effective; a certain advantage, however, seems to accrue by the introduction of some of the collector into the grinding circuit, possibly due to increased attraction of the collector to newly-produced (and therefore comparatively clean, as well as, possibly, atomically un-neutralized) surfaces.

Accessory promoters are usually anionic wetting agents, such as Aerosol OT, which affect the surface tension of the pulp, and, consequently, the amount, quality, and selectivity of the froth. Frothers are not always necessary. In some ores, oleic acid, a promoter with frothing properties,

will yield a suitable froth; if stabilization or modification of the froth is desired, cresylic acid or pine oil may be added as a primary frother.

Tungsten ores differ greatly from one property to another, and frequently change tenor or association in the same property. An intelligent program of laboratory testing should be instituted, from which initial recommendations for treatment can be made, and which will afford a continuous check on mill recoveries. Determinations of optimum conditions of time temperature, pH, and pulp density, together with the effect of the mill water supply on anionic collectors, must be carefully watched and checked at frequent intervals. Variation of one of these factors in the mill may cause serious dislocation of the entire process of recovery.

LABORATORY TESTWORK

Sample Preparation

The sample submitted consisted of 500 lb of ore, in pieces of about 1 lb weight, with a minimum of fines and of moisture, and with no material which would not enter the jaws of the 2" x 6" sample crusher. A random selection of about half of this material was crushed in the jaw crusher at a one-inch open setting. The crushed ore was then thoroughly mixed, coned and quartered, and several 6-kg sample lots were split from it. Representative hand samples were selected for mineralogic examination and for determination of average specific gravity.

Three of the split-out sample lots were reserved for heavy-media separation tests; the remaining lots were crushed to -10 mesh by a roll crusher in closed circuit with a 10-mesh screen. Although further reduction (from -1 inch) could have been made with the jaw crusher, rolls were employed because of their selective action on the larger particles and the short time of the mineral in the crushing zone, to minimize the production of extremely fine material.

Liberation Studies

On the products of a screen analysis of the -10-mesh

material, the particle-count method disclosed but 10% liberation of the 20-mesh fraction, whereas the 48-mesh fraction showed 80%, and the 100-mesh fraction more than 90% liberation.

Mineralogy

Inspection of a hand sample showed large and small bladed crystals of a tungsten mineral in a quartz matrix; microscopic examination of a polished section disclosed that the tungsten mineral consisted of an iron or manganese tungstate in a quartz gangue, with slight interstitial staining of a substance identified as molybdic oxide. No apatite, calcite, dolomite, or heavy-metal sulfides were observed. Subsequent assay showed the manganese-iron ratio to be approximately 20:1, further identifying the tungsten mineral as huebnerite.

Heavy-media Separation

The average specific gravity of the ore, as determined from 14 samples selected at random, was found to be 2.88. Accordingly, a test was made at medium gravities, in 0.05 steps, from 2.75 to 2.90, tabular results of which may be found in the Appendix. The medium employed was acetylene tetrabromide, with specific gravity regulation by the addition of carbon tetrachloride. The first 6-kg sample showed an assay of 4.9% WO_3 in the float product on 2.75

specific gravity. Since this assay was higher than the heads at many successfully-operating properties, it was decided to abandon heavy-media separation as a beneficiation method, and further testing by this means was discontinued.

Tabling and Jigging

One of the -10-mesh sample lots was subjected to a tabling test on the 40" x 18" laboratory Wilfley table. A concentrate assaying 60.3% WO_3 was made, but overall recovery was only 61.6% of the total tungsten mineral. Slime losses amounted to more than 7%, despite the care used in crushing, and tailing losses (including middling) totaled 31.4%. Good milling practice would doubtless recirculate the middling, or locked particles, with provision for further comminution before return to the tabling operation.

A portion of one of the -10-mesh samples was jigged on a Denver laboratory jig. Feeding difficulties caused poor and non-reproducible results, and this form of testing was abandoned.

Flotation Testing

Preliminary examination of the ore disclosed few apparent obstacles to successful flotation. Presence of but one gangue mineral and one tungsten mineral suggested

a simple reagent combination, without the necessity for use of complicated gangue depressants or froth modifiers; good liberation in the flotation sizes indicated the probability of high recovery.

Flotation samples of 600 gm each were prepared by grinding -10-mesh material from the rolled sample lots in rod or pebble mill. Samples were batch-ground in the rod mill for 10 minutes, and stage-ground in the pebble mill to all -65 mesh. Although the Galigher Agitair flotation machine seemed to be able to lift the coarser fraction of a sample easier than the Fagergren, the latter's advantages of a fine froth column and ease of cleaning outweighed its difficulty in lifting coarse material, and it was used in all but the last test.

Two series of flotation tests were conducted. In the first series, a 5% solution of oleic acid in methyl alcohol provided 0.01 lb of the reagent per ore-ton treated. Sodium silicate (Metso) and soda ash were added to the rod mill, together with the amounts of oleic acid indicated. The major testing variables were pH and oleic acid addition, one being held constant while the other was varied. Grinding conditions (time, type of mill) were varied on one or two tests, with, apparently, only mechanical significance. The use of specially distilled water in the

first series of tests had no noticeable effect on recovery or concentrate grade.

The second series of tests was made using sodium oleate as the collector. The amount of this reagent was held constant at about 10^{-3} molar (slightly more than 2 lb per ore-ton), and pH was varied. The pulp was ground with soda ash and Metso, as before, temperature of the pulp was raised to 60 C, and the collector was added in the dry form. After a 2-min conditioning period, 1 drop of cresylic acid was added, and the froth was removed, at 60 C.

The first series of tests disclosed that a recovery of 90% was easily obtainable; a satisfactory rougher concentrate, of 40% grade, was made, although one or two tests showed but little upgrading of the ore. The second series showed total recoveries of as high as 97.8%, with a maximum grade of rougher concentrate of more than 44%. It was found that cooling of the pulp to 30 C after the conditioning period practically nullified any selecting action of the reagents.

It should be noted that the maximum recoveries and rougher-concentrate grades made in these tests may be considered very satisfactory from the standpoint of single-stage flotation.

CONCLUSIONS

Gravity Separation Methods

Heavy-media separation does not seem feasible. The prime object of this method is to discard a large amount of material as a low-grade tailing. Fine dissemination of the valuable mineral eliminates this possibility; the amount of tungsten mineral in a commercially valuable ore may be so small that the total specific gravity of the ore is affected only in the order of hundredths of a unit.

Tabling is an expedient way to produce a saleable concentrate. However, the recovery obtained in the laboratory leaves much to be desired; a middling split, with re-circulation and re-grinding (preferably by rolls, for reasons presented earlier) might increase recovery several per cent without lowering grade, but would doubtless result in greater slime losses.

Flotation Technology

The objectives of this investigation have been, first, a high recovery of tungsten mineral, and, second, the production of a reasonably good grade of rougher concentrate for a subsequent recleaning operation. These objectives have been achieved. It is noted that flotation at an elevated temperature yielded the higher recovery.

Although it has been proved that an adequate recovery can be made on medium- or high-grade material at ambient temperatures, the increased recovery gained through elevated temperature might prove a critical factor in the recovery of mineral from a low-grade ore.

A conventional recleaning process might prove hazardous, rather than beneficial, to the concentrate grade, because of the tenacious adherence of the collector film to all minerals in the rougher concentrate. A possible method of recleaning might be to destroy the oleic film by an acid wash, and, since quartz is the minor constituent in the concentrate, use, for example, a long-chain amine for the selective flotation of the quartz.

Rod-milling, with its selective action on the larger particles, minimizes the production of slimes and reduces the feed to flotation size in a short time; this contrasts with the pebble mill, which produces large quantities of fines and grinds slowly by comparison.

Flotation Theory

The "ionic theory" of flotation, proposed by Wark⁵ and Gaudin⁶, holds that a collector is ionized and that the ions are adsorbed, or exchange with other adsorbed ions, to form a hydrophobic layer at the solid-solution interface. More recent work by Wark and others⁷ states:

"Since neutral salts, acids, and alkalis in sufficient concentrations cause micelle formation at greatly reduced concentrations of the paraffin chain salts, they greatly influence flotation by the latter."

"Acids and alkalis may influence flotation by paraffin chain compounds in two different ways: (1) they may prevent adsorption of the collector, the quantitative relationship between these ions and the collector being complex; (2) they may affect the solution and its surface in the same way as do neutral salts."

With reference to Fig. 1, it may be seen that both concentrate grade and recovery fell with an increase in pH. Since an alkali salt (Na_2CO_3) was the chief pH regulator, a possible correlation might be drawn between the results shown in the figure and the effect of alkali-metal ions, as above cited.

Cook and Nixon⁸ now propose that neutral heteropolar molecules, rather than the corresponding ions, are, in general, responsible for hydrophobic films on the surfaces of solids that are treated with aqueous solutions of heteropolar electrolytes. Fig. 2 shows a successively smaller recovery with stage additions of oleic acid, whereas Fig. 3 shows a drop in concentrate grade (increase in non-selectivity) with successively greater total oleic acid additions. Cook and Nixon say:

"The 'collector' action in long-chain compounds is complicated by physical adsorption which leads to the production of double layers (with the polar end extending away from the solid surface in the second layer) with excess 'collector', and generally to non-selectivity".

This theory, though at odds with that of Gaudin, et al.,

seems to be borne out by the results plotted in Figs. 2 and 3.

The basis for flotation studies at elevated temperatures was obtained from a paper by Cook⁹, who says:

"In flotation studies, one finds that salts of even such strong acids as the alkyl sulfonic and sulfuric acids undergo sufficient hydrolysis in solutions of pH 7-9 to act as collectors for non-metallic and metallic minerals. That is, we consider that the free acids and bases, not the ions, are the collectors."

"A significant factor . . . is the very much greater tendency for free acid than for neutral soap micelle formation. This is emphasized in the fact that the equilibrium constant for free acid condensation is somewhere around 10^6 times greater than that for neutral soap."

A suitable concentration of sodium oleate for experimental purposes was obtained from a curve showing degree of hydrolysis against soap concentration (after Cook, from Powney and Jordan). According to the curve, the degree of hydrolysis is proportional to both concentration and to temperature. A 10^{-3} molar concentration of sodium oleate showed maximum hydrolysis of about 14% at 60 C, which would correspond to the formation of about 0.25 lb of oleic acid per ore-ton. Concentrate grade and recovery rose rapidly to a maximum at pH of 9.2 to 9.6 (Fig. 4) and then declined. Since hydrolysis is also a function of pH, we may consider (correlating with Cook's theory cited above) that the optimum collector action was obtained at the above pH range, or that, possibly, the optimum amount of

collector was formed by hydrolysis of the sodium oleate.

RECOMMENDATIONS

Ore Dressing Plant

Although testwork is by no means complete, sufficient data has been gathered so that the following preliminary recommendations can be made:

1. A minimum-cost plant could consist of primary (jaw) and secondary (roll) crushers, screens, and tables, with provision for recirculation of middling. This plant would doubtless prepare a high-grade saleable concentrate, but at the expense of a comparatively low total recovery. The expense of many laboratory assays would be minimized; pan assays, with the common miner's pan, would provide, in experienced hands, good plant control.
2. A high-recovery plant, with considerably higher initial cost than the gravity plant described above, would include crushing equipment followed by a rod-mill-classifier circuit and flotation. Tabling of both tailing and concentrate from the flotation circuit might prove advantageous; on the other hand, if elevated temperature conditions were applied in the flotation cells, and a reclean were made as suggested previously, recovery and grade might leave little to be desired. It must be borne in mind that flotation requires reagent feeders, thickener and filter equipment, and careful laboratory control as prerequisites to successful operation. However, recoveries in this type of plant may even surpass laboratory results.

Further Testwork

It is recommended that further flotation tests be made. The results obtained in this investigation indicate that additional temperature studies might provide further correlation with Cook's theory, and, in addition, determine a lower limiting point for maximum recovery. However, selectivity (and, consequently, concentrate grade) still depends

on the elimination of the remaining gangue, whether by depression in the rougher circuit or by its flotation away from the huebnerite, whereas recovery may require little further improvement.

It should be noted that the use of amines or of other reagents as cleaners is a possibility which, in itself, must be the subject of a thorough investigation.

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APPENDIX

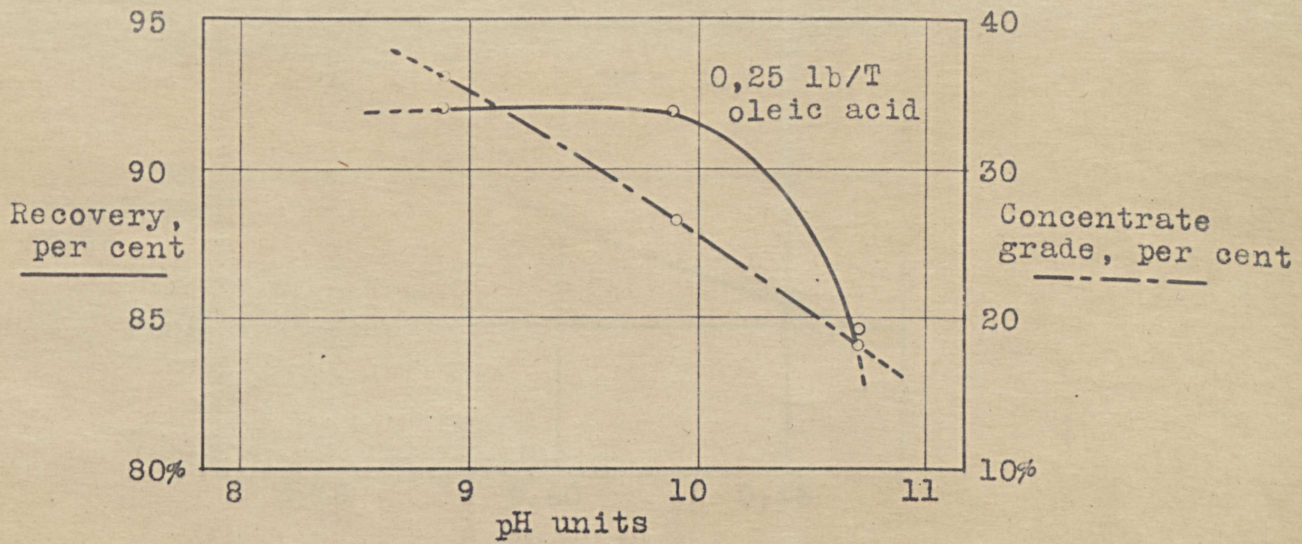


Fig. 1. Recovery and concentrate grade vs. pH.

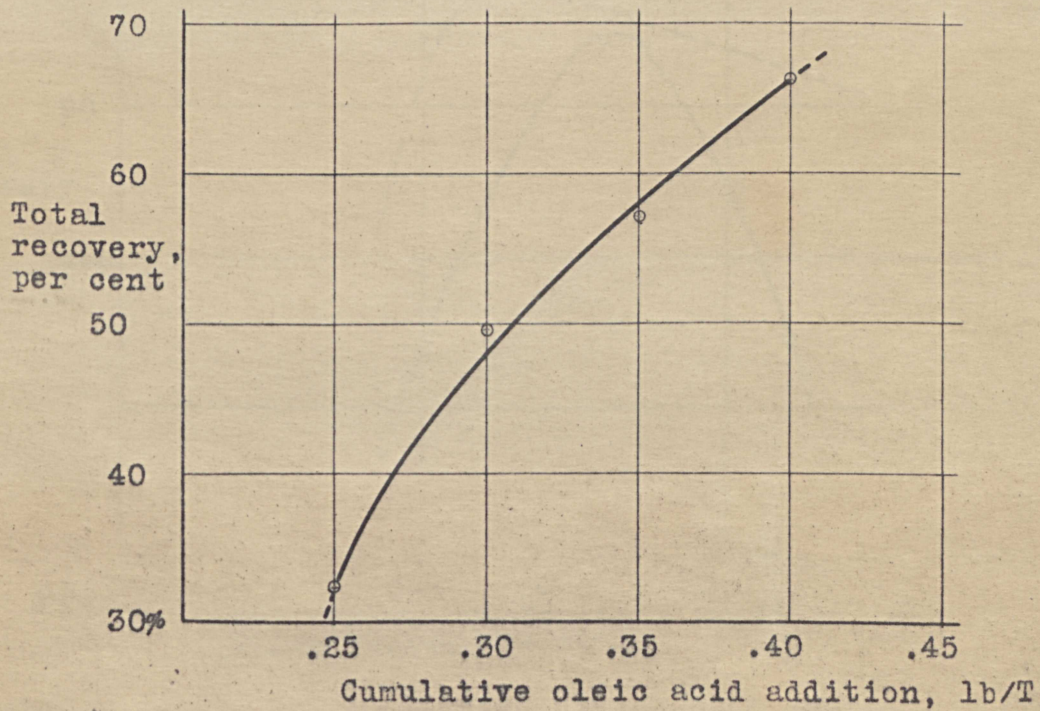


Fig. 2. Stage addition of oleic acid vs. total recovery.

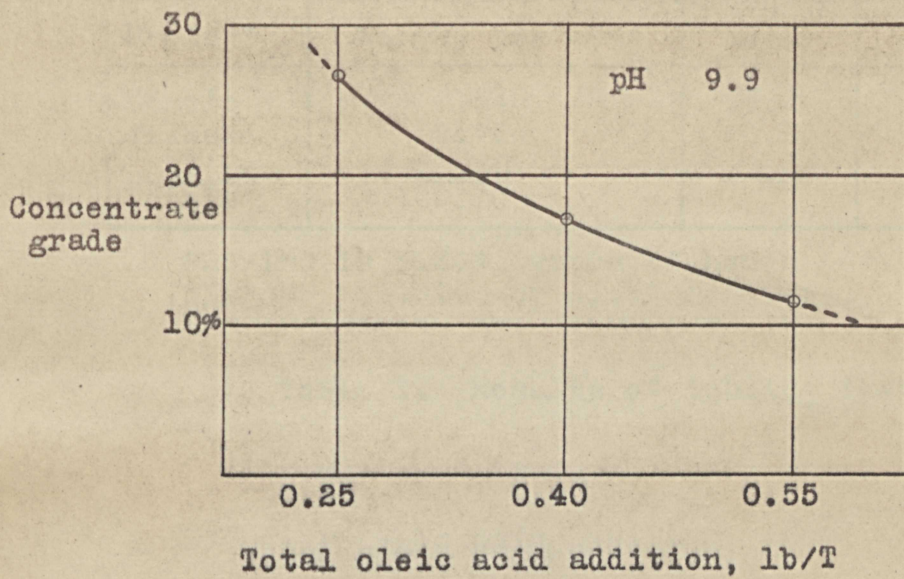


Fig. 3. Concentrate grade vs. total oleic acid

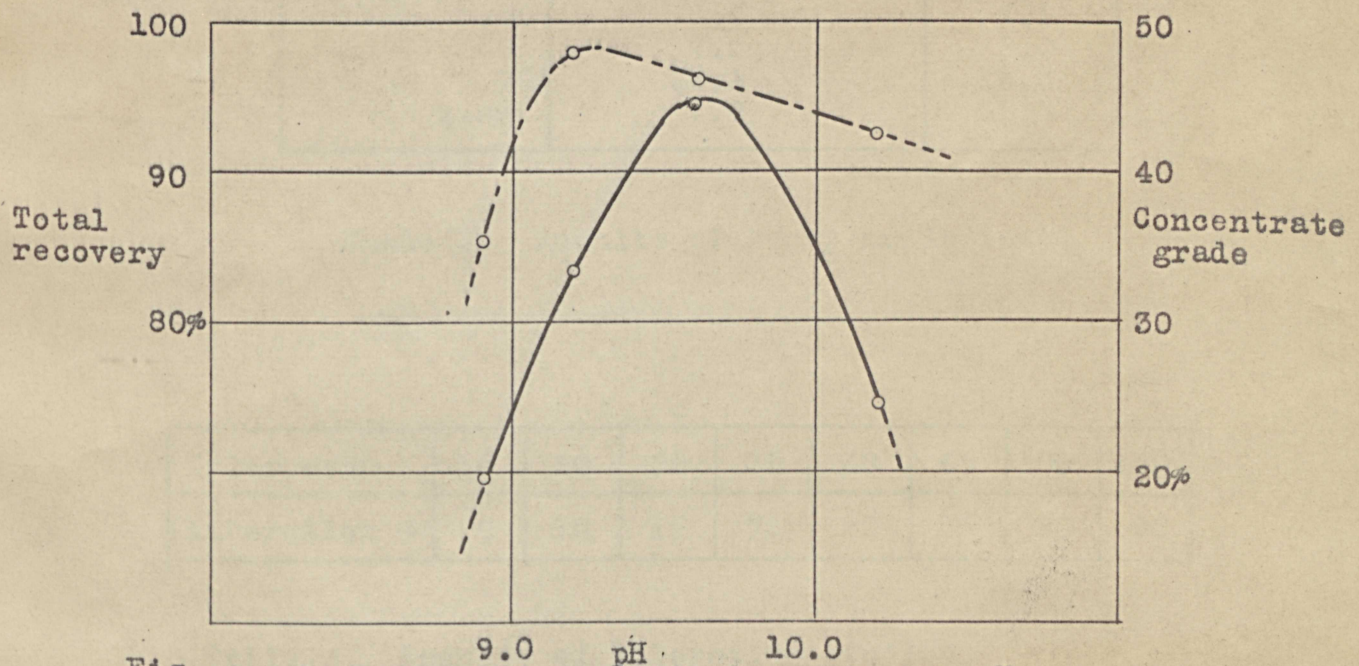


Fig. 4. Recovery and concentrate grade vs. pH. (Froth removed at 60 C.)

Product	Weight per cent	Assay	Product (x)
Conc't	8.54	60.3	515
Slimes	9.76	6.0	59
Tailing	<u>81.80</u>	<u>3.2</u>	<u>262</u>
Totals	100.00		836

836/100 is 8.36%, grade of heads (original sample)
515/836 is .616, or 61.6% recovery.

Table 1. Results of tabling test.

Product	Weight per cent	Assay
Float 2.75	33.7	4.9
Sink 2.75	8.9	5.4
Sink 2.80	9.7	7.1
Sink 2.85	7.5	9.0
Sink 2.90	32.3	16.5
-10 mesh	7.9	12.2

Table 2. Results of heavy-media test.

Tyler mesh	14	20	28	35	48	65	100	150
Liberation %	0	10	15	75	80	85	90	95

Table 3. Results of liberation studies.

No.	Reagents (lb/T)			pH	Recovery	Conc. grade
	Na ₂ CO ₃	Metso	Oleic			
1	1.0	0.5	0.25	8.9	92.0	36.2
2	2.0	1.5	0.25	9.9	91.8	26.6
3	2.5	1.5	0.25	10.7	84.0	18.2
4	2.0	1.5	0.40	9.9	91.4	16.8
5	2.0	1.5	0.55	9.9	95.7	11.6
6	1.5	1.5	0.20*	9.6	70.1	30.4
7	1.5	1.0	0.40	9.0	92.0	40.0

*Added during conditioning in the cell. This sample ground with 0.25 lb/T oleic acid. Note poor recovery.

Table 4. Summary of selected flotation tests.
(Ambient temperature)

No.	Reagents (lb/T)			pH	Recovery	Conc. Grade
	Na ₂ CO ₃	Metso	Oleic			
T1	1.0	1.0	2.0	8.8	85.5	19.9
T2	1.25	1.0	2.0	9.2	97.8	31.4
T3	1.5	1.0	2.0	9.6	96.2	44.5
T4	1.75	1.0	2.0	10.2	93.3	25.0

Table 5. Summary of flotation tests at 60 C.