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TUNGSTEN ORE FLOTATION

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This invention relates to the concentration of tungsten ores, more particularly to the concentration of scheelite by froth flotation and to a novel reagent combination therefor.

Tungsten, although one of the most useful metals, has in the past been produced from domestic ores in relatively small quantities. This failure to make use of the domestic ores is accounted for by the fact that while these ores are widely distributed throughout the United States, their tungsten content is usually very low. The common tungsten-bearing minerals such as scheelite usually occur with a mixed gangue including sulfide minerals such as pyrites, carbonates such as calcite and the like and silicon-containing minerals such as quartz and garnet.

Past experience has shown that with the exception of a very few relatively high grade deposits, the domestic ores could not be effectively concentrated and refined on a commercially feasible basis by any known methods. Consequently the principal demand had to be supplied by refining imported ores of relatively higher grade. There existed, therefore, a real need for a method suitable for the concentration of the average low grade domestic ores.

It is, therefore, an object of the present invention to establish an improved froth flotation procedure adapted to concentrate low grade domestic ores. It is also an object of the present invention to provide the froth flotation reagent combination suitable for carrying out such a procedure.

In general, the objects of the present invention are accomplished by subjecting the ore to a preliminary froth flotation to remove the sulfide minerals and then collecting the tungsten concentrate by the aid of an anionic-type promoter, assisted by a suitable wetting agent. At the same time use is made of a suitable depressant for the carbonates and silicon-bearing constituents. In this manner a ratio of concentration of the tungsten mineral as high as 20 to 30:1 may be easily made while still maintaining a good recovery.

Since not all tungsten ores contain sulfide minerals as gangue, the initial flotation treatment to remove these materials is not always required. Therefore, the removal of sulfide gangue is not necessarily a part of the present invention. Where the sulfide materials must be removed a number of commercially available sulfide promoters may be used. For example, an excellent sulfide concentration may be made by conditioning a pulp of the ore with a suitable amount of sodium, potassium or ammonium diacetyl dithiophosphate and/or sodium secondary butyl

xanthate; adding a good frothing agent such as a higher aliphatic alcohol frother and then floating out and collecting the sulfide concentrate.

The tungsten concentration, with which the present invention is concerned, however, is fairly critical both as to the combination of reagents used and the manner in which they are added. Scheelite, for example, as a typical tungstate ore, may be concentrated from a pure mineral pulp with a good anionic reagent of the fatty acid type such as oleic acid, talloel, their sodium, potassium or ammonium soaps and the like. However, these same anionic agents are also fairly good collectors for certain of the gangue constituents usually found after the removal of the sulfide minerals in a typical tungsten ore. Calcite, garnet and apatite are typical illustrations. Therefore, the use of the anionic-type reagent alone is not sufficient to produce the necessary concentration.

A reagent capable of increasing the selectivity of the promoter is not only desirable but necessary. Unfortunately, most of the commonly used carbonate and silica depressants also tend to depress the flotation of scheelite and the like. Not only the nature of the depressant used but also the quantity required must be taken into consideration. In addition, the nature of the promoter must be considered since it is well known that many depressants used in froth flotation operations in addition to their effect on the mineral, may also either by their inherent nature or because of the quantity required, directly affect the collecting power of the frother and promoter.

Although the reason for their action is not fully understood, according to the present invention a few depressants have been found suitable for use with the activated promoter of the present invention. Among the materials which may be used successfully for this purpose are citric acid, tannic acid, tetrasodium or potassium pyrophosphate and quebracho. In the quantities required, the effect on the collecting power of the other reagents is not too great. Quebracho is perhaps preferable since it is slightly more effective in depressing the gangue without producing an appreciably adverse effect on the other reagents.

As was mentioned above, the concentrating power of the anionic reagent used as a promoter for the tungsten mineral may be enhanced by the addition of suitable quantities of an effective anionic-type wetting agent. Among the wetting agents suitable for use, excellent results may be obtained using substances such as Kemenol, a commercial alkyl aryl sulfonate, marketed by the Braun-Knecht-Heimann Company, and Aerosol

OT, a commercial wetting agent comprising sodium di-octyl sulfosuccinic acid. Of these Aerosol OT is preferable since it enables the recovery of as much as 50% more scheelite than any of the wetting agents tested. The invention, however, is not limited to the use of any particular wetting agent and other similar commercial products of like properties may be used if so desired. Care should be taken in selecting the wetting agent, however. The wetting agent must not because of its nature or the quantity required produce an adverse effect on the quality and collecting power of the froth.

Any desirable frother may be used in the present reagent combination. Excellent results were obtained, for example, using a higher aliphatic alcohol frother with an average carbon content of C₇ and C₈. The invention, however, is not intended to be limited to the use of any particular frother. Other frothers may be used if and when it is desirable to do so.

The particular quantities of promoter, depressant, activator and frother used will obviously vary with the exact materials being used. This is true both with regard to the particular ore which is being treated and the particular reagents selected. The optimum proportions of each of the reagents used, however, can be readily determined in accordance with the particular combination being used and the characteristics of the ore to be treated.

In addition to the naturally occurring low grade tungsten ores there is also available considerable amounts of discarded material from beneficiation processes which have been carried out on relatively high grade ores. These discards may take the form of table tailings or tailings from previous flotation processes. While these discards are very low in tungsten content, usually assaying less than 1/2 of 1% WO₃ they may represent as high as from 1/3 to 1/2 of the total tungsten content of the original ore. Since this discarded material represents a good proportion of the original content of tungsten in the ore it is desirable if possible to recover at least a portion of it.

Tungsten, itself, can be refined from these low grade materials by chemical processes. However, because the tungsten content is so low, tremendous capacity is required for even a very low production of final product. The necessity for maintaining this excessive capacity and the use of excessive amounts of chemicals makes the cost of processing the discarded material per se commercially unfeasible.

Not only is the process and reagent combination of the present invention capable of concentrating naturally occurring ores but its selectivity is great enough so that it may be advantageously applied even to these extremely low grade tailing piles. By making use of the process and reagents of the present invention which are capable of producing 20 to 30:1 the volume of material which must be treated can be cut down to a point at which the chemical refining process of the tailing piles becomes economically practical.

The nature of the invention as well as the relative effect of the different reagent components will be illustrated by the following examples showing the treatment of samples from low grade tailing piles such as those mentioned above. All parts are by weight unless otherwise noted.

EXAMPLE 1

A number of samples of a tungsten ore table tailings from a Nevada ore containing scheelite,

calcite, pyrite, quartz and garnet having an average assay of:

Tungsten ----- 0.30% WO₃
Carbonate (titration) ----- 21.61% carbonate
Insoluble ----- 78.09% insoluble

and a screen analysis of:

Table I

Mesh (Tyler)	Percent weight
+35-----	2.67
+48-----	6.23
+65-----	10.28
+100-----	12.67
+150-----	12.65
+200-----	11.12
-200-----	43.38

are given the following treatment. 600 parts of the feed was diluted to 22% solids with water and conditioned for 5 1/2 minutes without air in a Fagergren flotation machine using 0.074 #/ton of ammonium dicresyl dithiophosphate, 0.05 #/ton of sodium secondary butyl xanthate and 0.75 #/ton of soda ash. A lower aliphatic alcohol frother (C₇ to C₈) was then added in the ratio of 0.037 #/ton and the pulp further conditioned for 1/2 minute after which the sulfide minerals were floated for 6 minutes. Without being removed from the flotation machine, the samples were then given the treatments outlined in the following examples.

EXAMPLE 2

A sample treated as outlined above was further conditioned for 2 minutes after which, 0.03 #/ton of the same frother and 0.42 #/ton of oleic acid were added and a tungsten rougher flotation carried out for 6 minutes. The sulfide concentrate amounted to 4.34% of the total feed and the tungsten concentrate amounted to 23.54% of the weight of the feed assaying 0.88% WO₃ and 17.97% carbonate were obtained.

EXAMPLE 3

The procedure of Example 2 was repeated using 0.07 #/ton of Kemenol during the 2 minute conditioning period in addition to the other reagents listed. A sulfide concentrate amounting to 5.34% of the feed and a tungsten concentrate of 23.19% of the weight of the feed assaying 0.94% WO₃ and 18.47% carbonate were obtained.

EXAMPLE 4

Example 3 was repeated substituting an equal weight of Aerosol OT for the Kemenol. A sulfide concentrate of 4.93% and a tungsten concentrate of 31.4% of the weight of the feed assaying 0.85% WO₃ and 20.24% carbonate were obtained. It will be noted that whereas the substitution of Aerosol OT for the Kemenol reduced the grade from 0.94% to 0.85%, the recovery was raised from 23.19% to 31.14% of the ore by weight. The net tungsten recovery in the concentrate was increased by about 20% so as to produce a recovery of approximately 78% of the total WO₃ content of the flotation feed.

In each of Examples 2-4 inclusive, however, the tungsten concentrate also contained a high percentage of the carbonate and insoluble content of the flotation feed so that the grade, while improved in the ratio of about 2 to 3::1, is still too low for practical purposes.

EXAMPLE 5

The procedure of Example 2 was repeated using 0.037 #/ton of frother, 0.42 #/ton of oleic acid and 0.20 #/ton of quebracho present during the conditioning period and the tungsten concentrate was floated for 2 minutes. The results are shown in the following table:

Table II

Product	Percent wt.	Assays		Percent distribution	
		Percent WO ₃	Percent carbonate	WO ₃	Carbonate
Sulfide concentrate	5.34	0.20	15.37	3.28	4.97
Tungsten flotation	2.67	6.98	31.1	55.53	5.03
Tail	91.99	0.15	16.14	41.19	90.00
Feed	100.00	0.335	16.50	100.00	100.00

It will be noted that the use of quebracho has increased the grade from the 0.88% in Example 2 to 6.98%, a ratio of concentration of about 38:1. Quebracho is therefore effective in depressing the carbonate and insoluble gangue. However, the recovery is only about 55%.

EXAMPLE 6

The procedure of Example 5 was repeated with the addition, however, of 0.07 #/ton of Aerosol OT to the reagents during the conditioning period. The results are shown in the following table:

Table III

Product	Percent wt.	Assays		Percent distribution	
		Percent WO ₃	Percent carbonate	WO ₃	Carbonate
Sulfide concentrate	4.40	0.12	14.09	1.34	3.97
Tungsten concentrate	3.98	6.04	35.2	64.34	8.96
Tailing	91.62	0.14	14.86	34.32	87.07
Feed	100.00	0.373	15.63	100.00	100.00

It will be noted that the use of the depressant together with an anionic promoter assisted by the wetting agent produces a ratio of concentration of about 25:1 and enables recovery of about 65% of the WO₃ content even of the extremely low grade material which comprised the discard from previous beneficiation processes.

I claim:

1. In a method of concentrating tungstate minerals from ores containing carbonate and silicon-bearing gangue by means of froth flotation, the improvement which comprises carrying out the flotation step in the presence of a reagent combination of an anionic promoter, selected from the group consisting of the higher aliphatic fatty acids, talloel, and the sodium, potassium and ammonium soaps thereof, an alkali salt of a dialkyl sulfosuccinate and a gangue depressant selected from the group consisting of citric acid, tannic acid and quebracho.
2. In a method of concentrating tungstate minerals from ores containing carbonate and silicon-bearing gangue by means of froth flotation, the improvement which comprises carrying out the flotation step in the presence of a reagent combination of an anionic promoter, selected from the group consisting of the higher aliphatic fatty acids, talloel, and the sodium, potassium and ammonium soaps thereof, an alkali salt of a di-octyl sulfosuccinate and quebracho.
3. In a method of concentrating scheelite from ores containing carbonate and silicon-bearing gangue by means of froth flotation, the improvement which comprises carrying out the flotation step in the presence of an anionic promoter, selected from the group consisting of the higher aliphatic fatty acids, talloel, and the sodium, potassium, and ammonium soaps thereof, an alkali salt of a di-alkyl sulfosuccinate and quebracho.

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