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Mercade

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[54] **RECOVERY OF SCHEELITE FROM ORES BY FLOTATION**

[75] Inventor: **Venancio V. Mercade,** Metuchen, N.J.

[73] Assignee: **Engelhard Minerals & Chemicals Corporation,** Menlo Park, Edison, N.J.

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[51] **Int. Cl.**[2] **B03B 1/04;** B02C 21/00

[58] **Field of Search** 209/11, 5, 166, 167; 241/20, 24

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Primary Examiner—Robert Halper
Attorney, Agent, or Firm—Melvin C. Flint; Inez L. Moselle

[57] **ABSTRACT**

A flotation process for recovering scheelite (calcium tungstate) from a low grade slimey ore containing other calcareous minerals such as calcite is described. The scheelite is selectively flocculated by conditioning the ore pulp at a high pH, using intense agitation, usually prolonged, in the presence of predetermined quantities of a deflocculating agent, a source of polyvalent cations to depress selectively calcite and other calcareous impurities, and a minimal amount of a fatty acid collector. The conditioned pulp containing the hydrophobic scheelite floccules is subjected to froth flotation, preferably in the presence of a frother having high wetting power, e.g., sodium dialkyl sulfosuccinate.

12 Claims, No Drawings

RECOVERY OF SCHEELITE FROM ORES BY FLOTATION

This is a division, of application Ser. No. 272,450 now abandoned, filed July 17, 1972.

BACKGROUND OF THE INVENTION

It is generally recognized that the selective flotation of slimey nonsulfide ore pulps presents some of the most difficult problems encountered in the ore flotation field. When the valuable mineral is a slimey nonsulfide material present in small amount, and the ore also includes an appreciable quantity of slimed nonsulfide gangue minerals having essentially the same flotation characteristics as the valuable mineral, the difficulties may be insuperable. It is rarely possible to obtain high recoveries of essentially pure valuable minerals under these circumstances.

Scheelite, a valuable tungsten-containing ore, frequently occurs in low grade (e.g., 0.2 percent to 2 percent WO_3) finely mineralized ore deposits in association with one or more other calcium-containing minerals such as calcite, apatite or fluorite. The various calcium minerals have remarkably similar flotation characteristics. Therefore, when an attempt is made to float the scheelite with an anionic collector, calcite, apatite and other calcareous minerals tend to float along with the scheelite, reducing the grade of the scheelite concentrate and in some cases impairing the recovery of the scheelite. In a typical operation with an ore assaying 0.8 percent WO_3, scheelite float products of 10 percent to 15 percent grade are obtained at a recovery of 65 percent using an oleic acid collector in an alkaline pulp containing sodium silicate as a gangue depressant. This represents rather modest concentration ratios of roughly 1:10 to 1:20 and flotation efficiencies of approximately 25 percent to 30 percent. The terms "concentration ratio" and "flotation efficiency" are defined hereinafter.

It is conventional to upgrade the scheelite flotation concentrates to a minimum of 65 percent WO_3 by leaching the carbonate and phosphate impurities with mineral acid, usually hydrochloric acid, or by reacting the concentrates with alkali to produce synthetic scheelite. Obviously large quantities of acid must be consumed when concentrates of 10 percent to 15 percent WO_3 grade are enriched to 65 percent WO_3 or above or when synthetic scheelite is produced by reaction of the low grade concentrates with alkalies. The reagent consumption involved in upgrading the flotation concentrates adds considerably to the recovery costs but has been considered to be essential because of the difficulty in preventing flotation of calcite and/or apatite or fluorite with flotation reagents which afford adequate recovery of the scheelite.

The economics of recovering the tungsten values from a low grade scheelite ore could be improved by either increasing the recovery of the scheelite without sacrifice in grade or by improving the grade without loss in recovery. The realization of appreciably higher grades at significantly increased recoveries would represent a marked advance in the art. The achievement of these goals has awaited the discovery of means for improving the depression of gangue, especially the calcareous gangue, without impairing the floatability of the scheelite. Another problem to be solved before achieving the improved grades and recoveries is the difficulty of obtaining adequate frothing in the strongly alkaline pulps which favor the recovery of scheelite by flotation with a fatty acid collector in the presence of sodium silicate.

PRIOR ART

Many investigators have attempted to improve the results obtained by fatty acid flotation of scheelite. They have studied the effects of pH, concentrations of soda ash, sodium silicate and oleic acid and have attempted to improve the depressing effect of sodium silicate. To the best of my knowledge, they have been unable to produce exceptionally high grade concentrates at outstanding recoveries when floating low grade scheelite ores with fatty acid collectors.

"FLOTATION TESTS ON KOREAN SCHEELITE ORE," W. Mitchell, Jr., C. L. Sollenberger and T. G. Kirkland, MINING ENGINEERING, January 1951, Transactions AIME, Vol. 190, pages 60 to 64, reports results of beneficiating a sheelite ore by flotation with emphasis on determining optimum conditions for obtaining maximum grade and recovery in the rougher concentrates. The most satisfactory reagent combination was found to be 1 lb./ton oleic acid, 2 lbs./sodium silicate, 1 lb./ton sodium carbonate, 1/10 lb./ton pine oil and a small amount of a wetting agent ("Pentasol 124" or "Aerosol OT"). A pH of 10 was recommended. Extended conditioning with an impeller revolving at 1725 r.p.m. was found to be deleterious to concentrate grade when using these reagents and conditioning period in excess of 5 minutes was found to be of no advantage. Concentrates containing about 10 percent WO_3 at close to a 90 percent recovery were obtained under the allegedly optimum conditions.

U.S. Pat. No. 2,373,305 to Gieseke discloses the use of anionic wetting agents, e.g., "Aerosol OT," to enhance flotation of scheelite from calcite and silica gangue with a fatty collector and quebracho to depress gangue. The pulps were floated at their natural pH values and conventional frothers were used. Maximum concentration ratio was 25:1 at a 65 percent WO_3 recovery. Flotation efficiency to obtain a concentrate of 6 percent grade was about 20 percent.

Russian investigators have studied the effect of the use of polyvalent metal salts with sodium silicate, added separately or simultaneously (in an undefined manner) on the floatability of scheelite, calcite, and apatite with oleic acid. Reference is made to the following:

"INTRODUCTION TO THE THEORY OF FLOTATION," V.I. Klassen and V. A. Mokrovsov, Butterworths, Inc. (1963), pages 329 to 335. This publication summarizes work reported by F. N. Belash, O. V. Pugina, Tsvetnye Metall, 1946, Vol. 19, No. 6, pages 22 to 27.

Belash and Pugina, concerned with the soap flotation of scheelite, studied the effect of using polyvalent metallic salts along with sodium silicate on the floatability of pure mineral systems containing either scheelite, calcite or apatite using about ¼ lb./ton oleic acid. Polyvalent metal salts were added separately and as "additions of a mixture". The publication does not explain how the mixtures of salt and silicate were prepared. On the basis of investigations with pulps containing individual minerals, not mineral mixtures, they demonstrated that certain metal salts, especially when used as mixtures with sodium silicate, enhanced the depressing effect of sodium silicate on all of the minerals when se-

lected proportions of silicate and salt were used. While improved depression of apatite by use of the salts was demonstrated by data for one scheelite ore, the grade of the resulting scheelite concentrate did not exceed 20 percent.

Another study of the effect of addition of metal salt on the selective and depressing action of sodium silicate during the flotation of scheelite from calcite and fluorite appears in a publication of N. A. Kozhemyakin and N. S. Dikinova, Tsvetnye Metall, 1970, Vol. No. 43, No. 8, 93 to 98. Separate addition of ferrous sulfate or ferric chloride to the sodium silicate was reported by these investigators to be better than simultaneous incorporation of the reagents.

The following patents disclose processes for floating scheelite from ores containing other calcium minerals wherein salts of heavy metals were used in conjunction with sodium silicate or sodium condensed phosphate dispersants to depress calcium carbonate and/or apatite minerals.

U.S. 2,040,187 - Rose et al.

U.S. 2,140,485 - Clemmer et al.

"FROTH FLOTATION AND AGGLOMERATE TABLING OF NONMETALLIC MINERALS," Oliver C. Ralston, Canadian Institute of Mining & Metallurgy, Transactions, Vol. XL, 1937, page 713.

The prior art workers who investigated various aspects of selective scheelite flotation failed to recognize the criticality of employing high energy conditioning with minimal amount of collector in the presence of an effective dispersant-depressant system. Insofar as can be ascertained, they also failed to appreciate the remarkable benefits which could be realized by using certain metal salts with sodium in a specific manner described hereinafter.

THE INVENTION

Accordingly, a general object of the ivention is to provide an improved method for selectively floating scheelite from low grade slimey ores which include calcium-containing gangue minerals.

A specific object is to selectively flocculate and float scheelite from a deflocculated slimey ore pulp in which minerals such as calcite, apatite and fluorite, alone or in combination, are depressed and deflocculated.

Briefly stated, the present invention resides in a method for recovering scheelite by froth flotation from a slimey low grade tungsten ore pulp containing at least one calcareous mineral other than scheelite, such as calcite, apatite, and fluorite, and siliceous gangue. The method comprises subjecting the slimey ore pulp to intense, and usually prolonged, agitation at a high pH in the presence of a predetermined optimum quantity of a reagent capable of deflocculating the constituents of the ore pulp, a source of polyvalent cations to depress calcareous minerals other than scheelite, and a minimal predetermined amount of a fatty acid collector, whereby the scheelite is selectively flocculated in the deflocculated pulp, and sujecting the pulp thus conditioned to froth flotation, preferably using a synthetic organic wetting agent as the frother, to recover as a froth product a concentrate of the flocculated scheelite.

In a preferred embodiment of the present invention, the ore pulp is deflocculated and the calcareous and siliceous gangue minerals are selectively depressed by adding a predetermined quantity of a previously prepared stable hydrosol obtained by mixing a dilute alkaline silicate solution with a dilute solution of a polyvalent metal salt, the hydrosol containing less than 2 percent SiO_2.

DESCRIPTION OF THE INVENTION

The method of the invention is applicable to beneficiating finely mineralized scheelite ores containing as gangue minerals silica and/or silicates as well as one or more other calcareous minerals, especially calcite (or other forms of calcium carbonate), apatite and fluorite. The ores may assay from a fraction of a percent Wo_3, e.g., 0.1 percent WO_3, up to 10 percent WO_3 or above. The invention is of especial importance and benefit in processing ores or ore fractions containing less than 3 percent WO_3.

The term "scheelite" encompasses pure calcium tungstate minerals as well as calcium tungstate in which molybdenum proxies for some of the calcium, e.g., the molybdenum-bearing scheelite variety of mineral.

Flotation and table tailings maybe processed. Alternatively, crushed, ground ore may be employed. The ground ore or tailings should be finer than 65 mesh (Tyler) and may be 200 mesh or finer.

When sulfides are present with the ore or ore tailings, they should be removed by flotation with a suitable sulfide collector prior to floating the scheelite. In many cases it is preferable to alkalize the pulp with soda ash to a pH of about 10 and then deflocculate the pulp prior to carrying out the sulfide flotation, as described in the illustrative examples. Improved scheelite recovery may be realized by such practice. When molybdenum sulfide is present, it may be recovered by addition of a neutral oil collector after deflocculation and prior to flotation of other sulfides with a conventional xanthate collector.

Conventional low energy conditioning for short times, e.g., 5 minutes, may be used in floating sulfides.

The preferred deflocculating (dispersing) agent is an alkali metal (especially sodium) silicate and it is preferably added to the alkalized ore pulp as a preformed stable metal salt-alkali metal silicate hydrosol. These hydrosols are fluid liquids containing less than 2 percent SiO_2 by weight and produced by mixing a dilute aqueous solution of an alkali metal silicate with a dilute aqueous solution of a suitable metallic salt. The salts which are useful are those acid-forming salts which produce very finely divided and stable colloids when mixed as dilute solutions with dilute solutions of alkali metal silicates to form compositions containing less thaw 2 percent SiO_2. The most satisfactory salts produce sols which appear to be true solutions when viewed with the naked eye. However, investigation of these sols with a light scattering microscope will reveal the presence of very small individual particles uniformly distributed throughout the composition without aggregates being present. Examples of salts which produce such hydrosols include mineral acid salt (nitrate, sulfate, chloride) of iron (ferrous and ferric), cobalt and beryllium. These hydrosols have a strong depressing effect on calcite.

Cobalt salts are outstandingly effective in depressing apatite which may be present in the ore. Beryllium salts result in hydrosols which are remarkably effective in depressing calcite but may not be as effective as other salts in depressing apatite. Aluminum salts, which form

sols containing some aggregates, may be used although such hydrosols may be less effective with some ores than hydrosols produced with other salts which form hydrosols with more finely divided suspended solids. On the other hand, salts, e.g., copper sulfate, which produce coarse precipitates when mixed with alkaline sodium silicate solutions containing less than 2 percent SiO_2 are unsuitable. The resulting sols may actually activate the flotation of calcite and/or apatite.

For reasons of economy, sodium silicate solutions are the preferred alkali metal silicates used in preparing the hydrosols. Sodium silicate solutions having Na_2O/SiO_2 mole ratios within the range of 1:1.60 to 1:3.75 are commercially available. "O", which analyzes (wt.) 9.16 percent Na_2O; 29.5 percent SiO_2 and the balance water, is an example of a suitable starting material after dilution with water to a SiO_2 content below 2 percent by weight. The pH of an alkali metal silicate solution after dilution to below 2 percent SiO_2 is generally within the range of 10 to 12. "O" diluted to 5 percent (SiO_2 concentration of 0.45 percent) has a pH of about 11.1.

To produce the hydrosols, the metal salt is dissolved in water and the solution is mixed to uniformity with the prediluted alkali metal silicate solution, preferably by adding the salt solution to the alkaline silicate solutions. Generally, salt is used in amount within the range of about 5 to 20 parts by weight (anhydrous basis) to 100 parts by weight alkali metal silicate (anhydrous basis). In a typical hydrosol prepared by mixing a 1 percent aqueous solution of $FeSO_4.7H_2O$ with "O" diluted to 0.45 percent SiO_2, the weight ratio of sodium silicate (anhydrous) to salt (hydrated) will be about 8/1. The pH of the hydrosols is slightly less than that of the dilute sodium silicate solution used in preparing the hydrosol. For example, a stable hydrosol obtained by adding a suitable amount of a dilute solution of ferrous sulfate to "O" diluted to 5 percent (0.45 percent SiO_2) may have a pH of about 10.6.

To obtain the full benefits of employing the hydrosol, i.e., adequate deflocculation of the initial ore pulp and optimum selective depression of calcite, apatite and other gangue, a predetermined quantity of hydrosol must be employed. Such optimum proportion varies from ore to ore, principally with the quantity of calcite or other calcium gangue that is present. As the amount of calcite or other calcium gangue increases, an increased amount of hydrosol is generally required to obtain optimum results. Example IV illustrates the effect of variation of the quantity of hydrosol on the selective flotation of scheelite from calcite and provides a model upon which to base simple tests to determine an optimum proportion of dispersant.

The use of a freshly prepared hydrosol is recommended.

The hydrosol is a fluid material, readily incorporated with conventional metering devices, and may be mixed with the alkalized ore pulp using mild mixing for a short time, e.g., 1 to 5 minutes' conditioning.

While alkali metal silicate is the preferred deflocculant and it is preferably employed as a preformed hydrosol containing the metallic salt as a cooperative depressant, it may be possible with some ores to use other deflocculants, e.g., sodium condensed phosphates or lignosulfonates, and/or to add the metallic salt to the pulp after incorporating the deflocculating agent. The results of such separate addition of salt and deflocculating agent are usually markedly inferior to those obtained when a hydrosol is employed but may be superior to results carried out without using a salt additive.

Oleic acid is a preferred anionic collector and it must be employed in minimal or starvation amount in order to minimize flotation of calcite and other calcium minerals after addition of the hydrosol. With low grade ores, e.g., ores containing 0.1 percent to 1 percent WO_3, the predetermined quantity of collector is within the range of from about 0.05 to 0.2 lb./ton. Tall oil acids may be used, preferably in combination with an emulsifying agent such as an oil-soluble petroleum sulfonate.

Intensive agitation is required when conditioning the deflocculated ore pulp with the fatty acid collector. When the ore is high in calcite, the intensive agitation usually should be prolonged. The intensive agitation is necessary in order to form floated scheelite floccules which are sufficiently strong and coherent to endure subsequent cleaner flotation without losses of scheelite occurring. Prolonged intensive agitation apparently minimizes calcite flotation. It will be apparent to those skilled in the art that commercial froth flotation processes in which the concentration ratios are very high invariably necessitate one or more cleaner flotation steps. Losses of mineral values in middlings, such as occurs in conventional scheelite flotation processes, is very undesirable, adding a recirculating load.

The deflocculated pulp is conditioned with the fatty acid collector in equipment containing an impeller system capable of rotating at high speed and aerating the pulp. A Fagergren flotation machine is a specific example of commercially available equipment that may be used in the conditioning step. Reference is made to Perry's "CHEMICAL ENGINEERS' HANDBOOK," pages 21 to 73, Fourth Edition, published by McGraw Hill Book Company, for a diagram and a description of the operation of a suitable model of a Fagergren machine which provides mechanical agitation and aeration by a rotating impeller on an upright shaft, the rotor being surrounded by a stationary cage (stator) fitting closely around the rotor and providing a shearing action. Rotors operating at peripheral velocities within the range of about 1300 to 2000 ft./min. are recommended. The corresponding speed of rotation obviously varies with the size of the impeller. For example, a laboratory model Fagergren mixer (2.0 inch rotor and 3-7/9 inch stator) operates at a maximum speed of 2900 r.p.m., corresponding to a peripheral velocity of 1520 ft./min. A 7 inch impeller similar in design can be rotated at 930 r.p.m. whereby tip speed is about 1700 ft./min.

Generally, the energy input during the conditioning step is within the range of 25 to 100 hp. hr./ton.

The conditioning time using the intensive agitation varies for any given flotation pulp with the volume of the conditioning equipment and the power input rate in a large conditioning unit is lower than in a laboratory unit because of the limitation as to rotor top speed. Thus, as the impeller diameter and liquid volume increase, conditioning times become longer because power scale-up is not proportional to slurry volume. Optimum conditioning time varies from ore to ore and is readily determined by simple experiment for any given size equipment and slurry volume. This is demonstrated in an illustrative example.

A frother must be incorporated into the conditioned pulp to float the scheelite. In most cases, conventional frothers (e.g., pine oils or conventional alcohol frothers) will not produce satisfactory froths. In some cases, essentially no froth is obtainable with these conventional frothers because of the highly hydrophobic nature of the flocculated scheelite. In order to produce a froth, an anionic wetting agent, preferably an alkali metal dialkyl sulfosuccinate such as Aerosol OT (or a fatty acid alkanolamide such as "Monamid 150 ADD") may be used.

The preparation of fatty acid alkanolamides, including those of the type employed in carrying out the present invention, is described in U.S. Pat. No. 2,094,609 to Wolf Kritchevsky; U.S. Pat. No. 2,173,909, also to Kritchevsky, deals with the use of fatty acid alkanolamides in ore flotation.

The rougher scheelite concentrate is cleaned one or more times by reflotation with stagewise addition of frother if necessary. The cleaner flotations necessitate dilution with water and thus pH will decrease during cleaning. For example, the pH may be 10 during rougher flotation and decrease to 9.5 in the second cleaner. Contrary to expectations, it was found that the addition of alkali (caustic soda) during cleaning to maintain pH at 10 did not aid in depressing calcite. In fact, calcite was activated. Low shear agitation is recommended for cleaning the rougher scheelite concentrate.

In carrying out the flotation process of the invention, concentration ratios over 1:2000 may be realized by flotation.

Residual calcite and apatite in the cleaned scheelite flotation concentrates may be reduced by leaching with a mineral acid. Concentrated hydrochloric or nitric acids are usually employed. One procedure for acid leaching is described in the illustrative examples. Other procedures may be employed.

Alternatively, the scheelite concentrate may be dissolved in alkali, e.g., soda ash, and synthetic scheelite crystallized in known manner from the solution.

The following examples are given for illustrative purposes.

The samples of tungsten ore used in the examples were run-of-mine scheelite ores from King Island, Australia. Typical ore from this mine is high in andradite (an iron silicate mineral) and contains substantial amounts of calcite with lesser amounts of siliceous minerals such as pyroxene, epidote, sphene and feldspar. Sulfide minerals include pyrite, arseno-pyrite, molybdenite and pyrrhotite.

An assay of a representative composite sample of the ore is as follows:

	Wt. %
Tungsten (WO_3)	0.77
Iron (Fe_2O_3)	8.34
Total Sulfur (S)	1.12
Free SiO_2	6.72
CO_2	2.95

BASIC TEST PROCEDURE

The basic test procedure used in all examples was as follows. A 500 gram portion of the ore sample was crushed to minus 10 mesh (Tyler) and ground in a stainless steel rod mill for 20 minutes at 60 r.p.m. at 50 percent solids. The ground charge (minus 200 mesh) was transferred to a 500 gram capacity Denver Sub-A flotation cell and was diluted to 25 percent solids. The pulp was then treated with the equivalent of 10 pounds of soda ash per ton of ore and conditioned for 5 minutes at 1200 r.p.m. In all tests (except those in which dispersant was added at a subsequent point of the process), the incorporation of soda ash was followed by addition of a dispersing agent (described in the examples) and the pulp was then conditioned for another 5 minutes at 1200 r.p.m.

Before carrying out sulfide flotation, molybdenite was recovered by conditioning for 5 minutes with 0.5 lb./ton "Eureka" oil as a collector. A molybdenite froth product was taken after addition of "Dowfroth 250" and flotation for 5 minutes at 1200 r.p.m.

To float the sulfides, the tailings of the molybdenite flotation were conditioned for 5 minutes with 0.5 lb./ton of a xanthate collector ("Z-6") which is potassium amyl xanthate, or "Z-5" which is potassium secondary-amyl xanthate. The sulfide flotation was repeated in a second stage and the sulfide froth products were combined, flocculated, filtered and dried.

The tailings from the sulfide flotation were then processed for flotation of the scheelite. In order to condition the pulp with a high energy input, the tailings were transferred to a 7-½ inch plastic container capable of handling a one gallon charge and equipped with a Fagergren mixer (2 inch rotor and 3-⅞ inch stator) impeller. Oleic acid was added in amount of 0.18 lb./ton (except where otherwise indicated) and the pulp was conditioned for 5, 15, 30 or 45 minutes, depending on the test, with the impeller operating at 2700 r.p.m., corresponding to a peripheral velocity of about 1400 ft./min. In a typical operation of this impeller with a 30 percent solids slurry, energy input is 28 hp. hr./ton for a 15 minute conditioning period. In a control test, carried out to demonstrate the necessity for high energy conditioning, conditioning with the oleic acid was in the Denver machine at 1200 r.p.m. for 5 minutes. All conditioned pulps were transferred to a 500 gram Denver Sub-A flotation cell for flotation of scheelite and a rougher float was taken at 1200 r.p.m. after addition of a given frother. The rougher flotation lasted 5 minutes. The rougher flotation concentrate was cleaned three times in a 250 gram Denver flotation cell in which the impeller operated at 900 r.p.m. In all of the cleaner operations, flotation time was 5 minutes. The cleaned float products and tailings were flocculated with alum, filtered, dried at 100°C. and weighed.

In some cases the scheelite concentrates were upgraded by treatment with hydrochloric acid to remove calcium carbonate and apatite when present. Leaching was carried out with 5 percent hydrochloric acid in increments until effervescence stopped (pH of about 1.5), followed by agitation for 20 minutes at room temperature, filtering, washing and drying.

The term "concentration ratio" is the ratio of the WO_3 assay of the feed to the WO_3 grade of the flotation concentrate. "Flotation efficiency" is a value obtained in accordance with the following equation:

$$\text{Flotation efficiency} = 100 \times \frac{\text{grade} \times \text{recovery}}{\text{grade} \times \text{recovery of perfect separation}}$$

EXAMPLE I

A. This example, Part A., illustrates an especially preferred embodiment of the invention wherein a low grade tungsten ore pulp was dispersed with a freshly prepared iron-silicate (Fe^{+2}) hydrosol and, after differential sulfide flotation in which 75.3 percent of the molybdenite was recovered, the pulp was conditioned with a starvation quantity of oleic acid, using prolonged high intensity agitation, and floated with a fatty acid alkanolamide frother, followed by two cleanings, to recover 87.7 percent of the tungsten (based on a head assay of 0.93 percent WO_3) in the form of a concentrate of 66.6 percent grade.

The hydrosol was prepared by diluting "O" sodium silicate solution to 5 percent by addition of water and adding, with mixing, a 1 percent aqueous solution of $FeSO_4.7H_2O$.

The reagents used in the test were as follows:

	Lb./ton
Dispersion (before sulfide flotations)	
Na_2CO_3	10.0
"O" Na_2SiO_3	0.30
$FeSO_4.7H_2O$	0.38
Molybdenite Flotation	
"Eureka" oil	0.5
"Dowfroth" 250	
Sulfide Flotation	
"Z-5"	0.5
Sheelite Flotation	
Oleic acid	0.18
Monamide 150-ADD	0.38

The material balance and assays were as follows:

	Wt. %	WO_3, %	% WO_3 Dist.	MoS_2, %
Molybdenite concentrate	1.8	0.40	0.8	57.71
Molybdenite cleaner tails 1–2	1.0	1.34	1.4	—
Sulfide froth product	2.0	0.59	1.3	—
Sulfide rougher tails	89.8	0.070	6.8	—
Sulfide cleaner tails 1–3	4.2	0.44	2.0	—
Scheelite concentrate	1.22	66.6	87.7	—
Heads	—	0.93	—	1.38

The data show that 87.7 percent of the scheelite of 66.6 percent WO_3 grade was recovered from a minus 200 mesh scheelite ore containing less than 1 percent WO_3. Concentration ratio was about 1:65 and flotation efficiency was 85.1 percent.

B. To demonstrate the desirability of employing prolonged high intensity conditioning before scheelite flotation, the procedures of Part A were repeated in detail except that the pulp was conditioned with oleic acid for flotation of the scheelite for only 5 minutes with the Fagergren impeller operated at 2700 r.p.m. The recovery of scheelite was essentially the same as it was with the prolonged conditioning with the Fagergren impeller at 2700 r.p.m. but the grade of scheelite in the concentrate was only 42.22 percent as compared to 66.6 percent with the prolonged conditioning. Thus, the use of prolonged high energy conditioning resulted in an increase of almost 50 percent in the grade of the scheelite concentrate, representing an increase in concentration ratio from 1:47 to 1:65 and an increase in flotation efficiency from about 70 percent to over 85 percent.

EXAMPLE II

This example illustrates the than of using the sodium silicate dispersant in the form of a preformed hydrosol (iron-silicate hydrosol in this case), rather than unmodified sodium silicate. The example also shows the benefits of adding the salt-silicate mixture as a preformed hydrosol rather thana by sequential addition of the salt and the silicate to the pulp.

The head sample used assayed: 0.90 percent WO_3 (corresponding to 1.12 percent $CaWO_4$); 2.95 percent CO_2 (corresponding to 6.7 percent $CaCO_3$ and 0.85 percent P_2O_5 (corresponding to 2.98 percent $Ca_5F(PO_4)_3$.

In all of the tests the sodium silicate or sodium silicate-iron sulfate combinations were incorporated into the pulp after addition of soda ash (10 lb./ton) and before addition of Ereka oil and sulfide flotation. With the exception of variations in dispersant, the same reagents employed in Example I were employed. In all cases the sodium silicate was employed in amount corresponding to 5 lb./ton "O" and salt, when employed, was added in amount corresponding to 0.5 lb./ton $FeSO_4.7H_20$. All dispersed pulps were conditioned with 0.18 lb./ton oleic acid with Fagergren impeller at 2700 r.p.m. for 15 minutes after addition of the collector.

In test A, the dispersant was a 5 percent solution of "O" sodium silicate; no salt was used with the "O". In test B, the iron-silicate hydrosol was prepared as in Example I by adding a 1 percent solution of $FeSO_4.7H_2O$ to "O", previously diluted to 5 percent. A freshly prepared hydrosol was employed in test B. In test C, the hydrosol was prepared by adding the diluted "O" to the 1 percent solution of the ferrous sulfate and the hydrosol was used shortly after it had been prepared. In test D, the "O" was diluted to 5 percent and then added to the pulp, followed by mixing for 1 minute; after addition of the diluted "O", a 1 percent solution of $FeSO_4.7H_2O$ was incorporated, followed by mixing for 1 minute. In test E, the 1 percent ferrous sulfate solution was added to the pulp, followed by mixing for 1 minute and then the 5 percent solution of "O" was added, followed by mixing for 1 minute.

TABLE I

EFFECT OF USING SODIUM SILICATE ALONE OR IN COMBINATION WITH FERROUS SULFATE SALT ON THE FLOTATION OF SCHEELITE

Test	Dispersant System	Scheelite Flotation Concentrate Wt. %	WO_3, %	Recovery, %	Flotation Efficiency, %
A	Silicate without salt	4.80	16.7	89.3	43.1
B	Hydrosol - (salt added to silicate)	1.32	63.2	92.7	85.2
C	Hydrosol - (silicate added to salt)	1.83	69.9	76.9	81.6
D	Silicate first, followed by salt	5.88	15.4	97.6	43.2
E	Salt first, followed by silicate	5.50	14.1	86.2	38.8

A comparison of the metallugical results in Table I for tests A and B shows that the use of sodium silicate in the form of a hydrosol obtained by adding iron sulfate to diluted sodium silicate increased dramatically the grade of the scheelite concentrate from 16.7 percent to 63.2 percent with a slight increase in recovery. The fact that the weight of the flotation concentrate was reduced from 4.80 percent to 1.32 percent with this significant increase in grade shows that the effect of the iron salt when added in hydrosol form in test A was to depress minerals which would otherwise float with the scheelite without depressing the scheelite.

Similar results were obtained in test C, in which the hydrosol was prepared by adding the silicate solution to the salt solution, However, in this case, the flotation concentrate was richer in WO_3 than in test B and recovery of WO_3 values was less. The weight of the concentrate was greater than in test B but less than in test A. These results indicate that a hydrosol prepared by adding sodium silicate solution to salt solution was somewhat effective in depressing minerals other than scheelite but that more scheelite was depressed than in test B. The 69.9 percent grade of the concentrate in test C was markedly superior to the 16.7 percent grade in test A at a lower, but still good, recovery.

In contrast to tests A and B in which the use of an iron salt effected an outstanding increase in WO_3 grade with a modest increase in recovery (test B) or with the modest loss in recovery (test C), data for separate additions of ferrous sulfate and sodium silicate (tests D and E) with results for test A, sodium silicate alone show that these benefits were not obtained by using the ferrous sulfate with the sodium silicate when they were added separately. When the ferrous sulfate solution was added to the pulp before the sodium silicate was added (test E) grade and recovery were slightly lower than when no iron salt was used. On the other hand, when the ferrous sulfate solution was added after the sodium silicate, recovery was improved but grade was reduced slightly.

EXAMPLE III

Tests were carried out to demonstrate the necessity for controlling the amount of oleic acid collector in order to selectively flocculate and float scheelite while maintaining calcite depressed by using an optimum predetermined quantity of hydrosol to disperse the pulp.

The sample of tungsten ore used in the test assayed 1.37 percent WO_3 and 4.14 percent CO_2 (corresponding to 9.41 percent $CaCO_3$).

The procedure of Example I was followed using a freshly prepared hydrosol obtained by adding 1 percent ferrous sulfate solution to "O" diluted to 5 percent. The hydrosol was used in amount equivalent to 5 lbs./ton "O" and 0.62 lb./ton $FeSO_4.7H_2O$ and it was added to the pulp after incorporating soda ash, 10 lbs./ton. Oleic acid collector was used in amounts of 0.09, 0.18 and 0.27 lb./ton and high energy conditioning (15 minutes in the Fagergren at 2700 r.p.m.) was used to condition the pulp. The frother used in the scheelite flotation was the alkanolamide of Example I.

Using a minimal quantity of oleic acid (0.09 lb./ton), flotation efficiency of scheelite was 76.2 percent and only 15.5 percent for calcite. Thus, the flotation was highly selective to scheelite and calcite was effectively depressed.

On the other hand, when the amount of oleic acid collector was increased to 0.18 lb./ton, the flotation efficiency of scheelite decreased to 61.3 percent and the flotation efficiency of calcite increased to 32.7 percent. Thus, by doubling the amount of oleic acid, sufficient collector was present to float calcite and also to reduce the recovery of scheelite.

The effect of adding excessive collector was even more striking when the amount of oleic collector was tripled — to 0.27 lb./ton. In this case, flotation efficiency of scheelite was only 51.6 percent, as compared to the 76.2 percent efficiency when only 0.09 lb./ton oleic acid was used. The efficiency of calcite flotation undesirably increased to 46.6 percent, approximately triple the efficiency of 15.5. percent when 0.09 lb./ton oleic acid was used. Thus, by using only 33 percent of this amount of collector, flotation efficiency of scheelite was increased by about 50 percent and flotation efficiency of calcite was decreased by about 300 percent. These results demonstrate the criticality of restricting the quantity of fatty acid collector when conditioning the slimey deflocculated pulp with a high energy input.

EXAMPLE IV

Tests were carried out to determine the effect of varying the amount of hydrosol used to disperse a tungsten ore pulp and to depress calcite on the relative floatability of scheelite and calcite in the ore.

The ore used was a sample of the same ore used in Example III (1.37 percent WO_3). In all cases, a freshly prepared ferrous sulfate-sodium silicate hydrosol (Example II) was used (8 parts by weight "O" to 1 part by weight $FeSO_4.7H_2O$). The quantity of hydrosol used in the tests varied in amounts corresponding to 3, 11 and 14 lbs./ton "O". All of the procedures and reagents of Example II were used. In all cases the collector was oleic acid (0.18 lb./ton).

It was found that the flotation efficiency of scheelite improved gradually as the quantity of hydrosol increased from the equivalent of 3.0 lb./ton "O" (0.37 lb./ton $FeSO_4.7H_2O$) to 11.0 lb./ton "O" (1.37 lb./ton $FeSO_4.7H_2O$) and decreased slightly as the amount of hydrosol increased to 14.0 percent "O". Thus, flotation efficiency of scheelite was only 39.9 percent with 3 lb./ton "O" whereas efficiency exceeded 60 percent at 11 lb./ton "O". Efficiency was 54.0 percent at 14 lb./ton "O".

In contrast to the flotation efficiency of scheelite which was increased by increasing the amount of hydrosol up to an optimum value of 11 lb./ton "O", the flotation efficiency of calcite decreased sharply as the amount of hydrosol was varied within this range. When hydrosol was used in amount equivalent to 3 lb./ton "O", flotation efficiency of calcite was 82.5 percent, but with 11.0 lb./ton "O", the value was only 32.7 percent. With the equivalent of 14 lb./ton "O", the flotation efficiency of calcite increased to 42.5 percent.

In other words, using 0.18 lb./ton oleic acid, scheelite was preferentially floated with the equivalent of 11.0 lb./ton "O" but the flotation was undesirably preferential to calcite when the amount of hydrosol was reduced to the equivalent of 3 lbs./ton "O". When excessive hydrosol was used (14 lb./ton "O" for this ore pulp), the flotation became less selective to scheelite.

EXAMPLE V

Tests were carried out with the scheelite ore of Example II to demonstrate how variation in the cation of the salt used with sodium silicate to produce the hydrosol dispersant affects the relative flotation efficiencies of scheelite, calcite and apatite in a low grade tungsten

ore when using high energy conditioning with a minimal amount of oleic acid collector and to show that selective flocculation and flotation of the scheelite with effective dispersion and depression of both calcite and apatite requires the use of a stable hydrosol free from coarse precipitate.

To produce the hydrosols, a 1 percent solution of a metal salt was added with mixing to a solution of "O" sodium silicate previously diluted to 5 percent, as in Example I. The salts used were: $FeSO_4.7H_2O$; $CoSO_4.7H_2O$; $CuSO_4.5H_2O$; $Pb(NO_3)_2$; $Be(NO_3)_2.3H_2O$; $Al_2(SO_4)_3.18H_2O$. All hydrosols were used within an hour after preparation. In a control test a salt was not added to the diluted "O" brand. It will be noted that copper and lead salts has been suggested in the Clemmer patent (supra) as an agent for conditioning a tungsten ore before addition of sodium silicate to improve the selectivity of a fatty acid collector for scheelite in ores containing calcite and apatite.

All hydrosols were prepared with an equivalent weight of metal cation.

Portions of the ore were alkalized with soda ash and dispersed with hydrosols described in Table II before undergoing sulfide flotation and scheelite flotation as in Example II. Concentrates were cleaned as in Example II. In the scheelite flotation, conditioning was in the Fagergren at 2700 r.p.m. for 15 minutes. The concentrates from the scheelite flotation step were analyzed for WO_3, CO_2 and P_2O_5. Recoveries of WO_3, CO_2 and P_2O_5 were computed from these analyses and assays made on the head samples. Flotation efficiencies for scheelite, apatite and calcite then were computed using the formula described above, with an appropriate value for the grade of perfect separation for each constituent. Overall scheelite flotation efficiency was then computed for each test from the following equation:

$$\text{Overall efficiency} = \frac{\text{F. E. scheelite} + (100 - \text{F. E. apatite}) + (100 - \text{F.E. calcite})}{3}$$

wherein "F. E." represents flotation efficiency.

Data in Table II show that all of the hydrosols were more efficient in floating scheelite than sodium silicate was but that only the transition metal salts which produced extremely stable fine hydrosols (salts of iron, cobalt) were superior to sodium silicate in depressing the flotation of both calcite and apatite. The beryllium salt improved the depression of calcite significantly but not the apatite. It is interesting to note that two metal salts suggested in the prior art for use with sodium silicate in selectively floating scheelite from calcite and apatite improved the flotation of scheelite but both also improved the flotation of calcite and apatite and were therefore less effective than sodium silicate alone when used in my high energy conditioning process using a trace quantity of oleic acid collector.

In order to demonstrate the economic advantage of using stable hydrosols in the flotation of scheelite, as compared to sodium silicate or unstable hydrosols, the mineralogical constituents of the concentrates of Example V (Table II) were computed from the assays and the theoretical grades of the concentrates after leaching with hydrochloric acid, assuming 100 percent removal of calcite and apatite could be achieved. The quantity of concentrated hydrochloric acid (100 percent) required to leach calcite and apatite were calculated. The results appear in Table III.

TABLE III

EFFECT OF HYDROSOL COMPOSITION ON THEORETICAL GRADE OF SCHEELITE CONCENTRATES AFTER ACID LEACHING AND AMOUNT OF ACID REQUIRED

Hydrosol Composition Salt Used	Theoretical Upgrading of Concentrates After HCl Leach, WO_3 Percent	HCl Theoretically Required to Leach, lb./ton		
		Calcite	Apatite	Total
None (control)	55.3	122	12	134
$FeSO_4$	70.3	1	4	5
$CoSO_4$	71.3	1	2	3
$Be(NO_3)$	71.1	6	8	14
$CuSO_4$	60.3	106	16	122
$Pb(NO_3)_2$	67.8	140	20	160

Data in Table III indicate that less than 1/10 of the acid would be required to leach all calcite and apatite from the scheelite concentrates when using hydrosols of iron, cobalt or beryllium rather than sodium silicate to depress calcite and apatite and that, using such hydrosols, the products would be at least 15 percent higher in grade. While the grades of the leached concentrates would be from about 3 percent to 10 percent higher using hydrosols of copper and lead instead of straight sodium silicate, the grades would be lower than those obtainable with hydrosols of iron, cobalt or beryllium; furthermore vastly more acid would be required with hydrosols of copper or lead. For example, using a hydrosol of iron instead of a hydrosol of lead, only 1/32

TABLE II

EFFECT OF COMPOSITION OF HYDROSOL DISPERSANT ON RELATIVE FLOTATION EFFICIENCIES OF SCHEELITE, CALCITE AND APATITE IN LOW GRADE TUNGSTEN ORE AND OVERALL EFFICIENCY OF SCHEELITE FLOTATION

Hydrosol Composition			Flotation Efficiency, %			Overall Scheelite Flotation Efficiency, %
Salt Used	Salt, lb./ton	"O", lb./ton	Scheelite	Apatite	Calcite	
(Control)	0	5.0	43.1	8.1	43.1	64.0
$FeSO_4.5H_2O$	0.63	5.0	85.2	5.4	1.3	89.5
$CoSO_4.7H_2O$	0.62	5.0	84.4	2.5	1.3	93.5
$Be(NO_3)_2.3H_2O$	0.42	5.0	81.8	9.2	4.6	89.3
$Al_2(SO_4)_3.18H_2O$	0.50	5.0	70.8	9.9	*	80.5
$CuSO_4.5H_2O$	0.55	5.0	48.7	10.9	72.2	55.2
$Pb(NO_3)_2$	0.60	5.0	45.9	12.0	58.5	58.5

*CO_2 not assayed in this concentrate

the amount of acid would be required. The use of 5 lb./ton HCl with the iron hydrosol would represent, under current prices, a savings of $2.5/ton of concentrate over that acid required with straight sodium silicate.

EXAMPLE VII

The outstanding efectiveness of a hydrosol obtained by adding a dilute ferric chloride to sodium silicate is demonstrated in this example.

The hydrosol was prepared by adding a 1 percent solution of $FeCl_3.6H_2O$ to "O" diluted to 5 percent. The stable five-grained hydrosol was used in amount equivalent to 11 lb./ton "O" and 1.39 lbs./ton $FeCl_3.6H_2O$ with 0.09 lb./ton oleic acid collector to float scheelite from the ore of Example III (1.37 percent WO_3 and 4.14 percent CO_2).

The procedure of Example III was followed and the results compared with those of a similar test in which the same amount of oleic acid was used with a hydrosol equivalent to 11.0 lb./ton "O" and 1.39 lbs./ton $FeCl_3.6H_2O$.

Using the hydrosol prepared with the ferric salt, flotation efficiencies of scheelite was 79.3 percent (69.5 percent grade at a recovery of 84.3 percent). When the hydrosol was produced with the ferrous salt, flotation efficiency was 76.2 percent (57.7 percent grade at a recovery of 81.2 percent).

I claim:

1. A method for recovering scheelite by froth flotation from a slimey low grade tungsten ore pulp containing calcareous minerals other than scheelite, such as calcite, apatite or fluorite, and siliceous gangue which comprises agitating said ore pulp at a strongly alkaline pH for at least 5 minutes with an energy input of at least 25 hp. hr./ton in the presence of a predetermined amount of a reagent capable of deflocculating the constituents of the ore pulp, a predetermined amount of a source of polyvalent cations to depress calcareous minerals other than scheelite, and from 0.05 to 0.2 lb./ton of a fatty acid collector, said amount of fatty acid collector being insufficient to produce a froth adequate for flotation, whereby the scheelite is selectively flocculated in the deflocculated pulp, adding a synthetic organic frother having strong wetting power, and subjecting a pulp thus conditioned to froth flotation to recover as a froth product a concentrate of the flocculated scheelite.

2. The method of claim **1** wherein the frother is a fatty acid alkanolamide.

3. A method for floating scheelite from a slimey low grade tungsten ore pulp containing calcareous minerals other than scheelite, including a substantial amount of calcite, and siliceous gangue which comprises: alkalizing said pulp with soda ash, deflocculating the alkalized pulp by adding a predetermined quantity of a stable preformed hydrosol obtained by mixing a dilute aqueous solution of an alkaline silicate with a dilute aqueous solution of salt containing polyvalent metal cations having the ability to depress calcite, selectively flocculating the scheelite by agitating said ore pulp at a pH of about 10 for at least 5 minutes with an energy input of at least 25 hp. hr./ton with from 0.05 to 0.2lb./ton of a fatty acid collector, said amount of fatty acid being insufficient to produce a froth adequate for flotation, and subjecting the resulting ore pulp to froth flotation in the presence of a synthetic organic frother having strong wetting power so as to produce a froth product which is a concentrate of scheelite and a tailing product.

4. The method of claim **3** wherein the salt used in making the hydrosol is a ferrous salt.

5. The method of claim **3** wherein the salt used in making the hydrosol is a ferric salt.

6. The method of claim **3** wherein the salt used in making the hydrosol is a cobalt salt.

7. The method of claim **3** wherein the ore pulp contains sulfides which are floated from the pulp with a xanthate collector before the pulp is conditioned for flotation of the scheelite.

8. The method of claim **7** wherein the ore pulp is deflocculated with said hydrosol before sulfides are floated.

9. The method of claim **3** wherein the fatty acid is oleic acid and the frother is a fatty acid alkanolamide.

10. A method for recovering scheelite from a low grade finely mineralized tungsten ore containing as gangue appreciable amounts of calcite, siliceous minerals and sulfide minerals which comprise: grinding said ore to at least minus 6, mesh to liberate the scheelite, forming the ground ore into a pulp, adding soda ash to increase the pH of the pulp, deflocculating said pulp by incorporating therein a predetermined quantity of a preformed stable hydrosol prepared by mixing a dilute solution of alkaline sodium silicate with a dilute solution of a salt of a metal selected from the group consisting of ferrous, ferric, cobalt and baryllium, the beryllium, containing less than 2 percent SiO_2 by weight, floating sulfides from the pulp in the presence of a xanthate collector, conditioning the tailings of the sulfide flotation with a predetermined amount of oleic acid within the range of 0.05 to 0.2 lb./ton for a time in excess of 5 minutes with an energy input of at least 25 hp. hr./ton of ore in the pulp, and subjecting the conditioned ore to froth flotation at a pH of about 10 in the presence of a fatty acid alkanolamide frother.

11. The method of claim **10** wherein the salt used in making the hydrosol is a ferric salt.

12. The method of claim **10** wherein the salt used in making the hydrosol is a ferrous salt.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,915,391
DATED : October 28, 1975
INVENTOR(S) : Venancio V. Mercade

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7 - line 31, should read -- ratios over 1:200 --.

Column 9 - line 23, should read -- "O"Na_2SiO_3 3.0 --;
line 26, should read -- "Dowfroth" 250 0.084 --.

Column 10 - line 8, should read -- illustrates the advantage of using --;
line 23, should read -- Eureka oil --.

Column 16 - line 41, should read -- cobalt and beryllium, the hydrosol containing --.

Signed and Sealed this

seventeenth Day of *February 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks