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ORE FLOTATION

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This invention relates to the beneficiation of ores, and more particularly has reference to the flotation of tungsten. It will be seen, however, that the invention embraces the flotation of minerals other than tungsten from a gangue composed principally of calcite or other carbonate minerals.

The principal tungsten ores — scheelite ($\text{CaO} \cdot \text{WO}_3$), ferberite ($\text{FeO} \cdot \text{WO}_3$), wolframite ($\text{Fe} \cdot \text{MnO} \cdot \text{WO}_3$), and hubnerite ($\text{MnO} \cdot \text{WO}_3$)—are usually complex and contain a variety of associated minerals. The most common gangues are quartz, feldspar, garnet, mica, sulphides, arsenides, carbonates such as calcite, ankerite, etc., and phosphates such as apatite. Particularly to be noted in this connection is the fact that the contact-metamorphic scheelite ores, which are the most important, usually contain a large amount of calcite or other carbonate minerals.

Heretofore, tungsten ores have been beneficiated by hand-picking and gravity concentration processes, such as jigging and tabling. In order to achieve any semblance of success by gravity concentration processes, however, there are two conditions necessary. In the first place, there must be a pronounced difference between the specific gravity of the mineral and the specific gravity of the gangue, and in the second place, the mineral and the gangue cannot be too finely interlocked, but must be susceptible of separation by relatively coarse crushing. In the absence of these two conditions, the concentrates are low grade and must be retreated by expensive chemical or pyrometallurgical processes in order to produce marketable products. However, even when the two conditions are present, the concentrates, while of marketable grade, nevertheless account for a low recovery of the tungsten. Furthermore, no satisfactory method for handling the fines has heretofore been available.

At the present time, only the high grade and less complex ores are worked, and even in such case there are tailing dumps which contain large quantities of recoverable tungsten, provided a suitable method of beneficiation can be devised.

The market requirements for tungsten ore are relatively rigid. Concentrates are sold by the short ton unit of contained tungstic oxide (WO_3) and the base is usually taken at 60%. Higher grade concentrates bring a correspondingly higher price, and often a premium is given for exceptionally pure material. Concentrates of lower grade than 60% are difficult to sell and usually a penalty of several dollars a unit is imposed. In addition to the required tungsten content, a concentrate for the ferrotungstic market must not contain more than 0.05% of copper, bismuth, antimony, tin, arsenic, sulphur, or phosphorus. Although some of the impure concentrates are

used for chemicals, they have a relatively small market.

Thus it is apparent that a process such as flotation, which would successfully recover the fine mineral now wasted and enable high grade concentrates to be produced from the more difficult ores, would be of value in the concentration of tungsten ores. Flotation would serve as a useful adjunct to gravity concentration processes by making the milling circuit more flexible and permitting a higher recovery of an improved grade concentrate. By providing a suitable flotation process, the impurities could be more thoroughly rejected and it would be feasible to mill ores which it is now considered impossible to treat.

While attempts have heretofore been made to float tungsten, no process has yet been devised whereby a high grade and merchantable concentrate can be obtained. The difficulties in the past have resided, not so much in the inability to float the tungsten, as in effecting a separation between the minerals and the various gangues with which they are found.

As stated above, our invention also comprises the flotation of various minerals (particularly fluorspar, barite and scheelite) from calcite and other calcareous minerals. The separation of these minerals by flotation methods has heretofore been considered practically impossible. If it be a fact that flotation by a fatty acid or derivative thereof depends upon the formation of a relatively insoluble soap at the mineral surface, then, on account of the common calcium ion, fluorspar, scheelite and calcite should act the same in flotation, and barite should be similar in its flotative properties. This idea is supported by the results obtained by many investigators working on a variety of ores. Separation by flotation has been attempted by controlling the reactivity of the collector so that reaction proceeds with only one mineral; these attempts have been made by controlling the pH and also by using various fatty acids of relatively short hydrocarbon chains. However, all previous attempts to separate these minerals from calcite or other carbonate mineral by flotation, have failed.

To overcome the above mentioned difficulties is one of the objects of our invention.

Another object of our invention is to devise a process, or processes, for the flotation of tungsten.

Yet another object of our invention is to devise a flotation process for tungsten ores in which the concentrate is relatively free from impurities, and is of a high and merchantable grade.

Still another object of our invention is to devise a process for the flotation of certain minerals

from a gangue in which calcite, or other carbonate mineral, is an important constituent.

To accomplish the above, and other important objects, as will be hereinafter observed, our invention, in general, comprises the means and steps herein recited, it being distinctly understood, however, that various changes, and modifications, may be made therein without departing from the spirit of our invention or exceeding the scope of the appended claims.

The results herein set forth were obtained only after lengthy and numerous experiments, and the specific data submitted herewith is illustrative of the success we eventually obtained.

Scheelite ore

The first tungsten flotation tests made by us were on a scheelite ore from Nevada in which the gangue was predominantly quartz with a small amount of apatite. The early tests indicated that the scheelite was more floatable than the quartz, and we found that the use of a fatty acid or a fatty acid soap, alone or together with a frother, and an alkaline reagent, gave a satisfactory separation of scheelite. Any of the well known fatty acids or fatty acid soaps may be used, and the frother may be of conventional character, such as pine oil, cresylic acid, the alcohols, or any of the moderately soluble heteropolar organic compounds which lower the surface tension of water. Caustic soda, soda ash or sodium silicate may be used as the alkaline reagent.

In one typical test, such an ore, assaying 2.38% tungstic oxide, gave a concentrate of 62.72% WO₃, which constituted 89.7% of the total WO₃ content of the heads. The rougher concentrate was cleaned twice to give the final concentrate, and in commercial operation the middlings, which assayed 1.03% WO₃, would be returned to the flotation circuit, and the mineral would be recovered without a serious sacrifice in the grade of the final product.

The ore was ground to -100 mesh. As in the case of all the tests reported herein (with one exception, which will be referred to), the pulp contained 17% solids. Flotation was accomplished in a mechanically agitated machine of standard design. The reagents used per ton of crude ore were as follows:

	Rougher	Cleaner
Pine oil.....	0.12	-----
Oleic acid.....	.16	-----
Sodium oleate.....	.40	-----
Sodium carbonate.....	.75	.75
Sodium silicate.....	-----	.40

While the above mentioned test showed a satisfactory recovery of the tungsten in the concentrate, the phosphorus in the concentrate was 0.246%, considerably higher than the .05 limit already mentioned. This indicates that the phosphorus-bearing mineral, apatite, floats with the scheelite and is not completely depressed by the alkaline reagent.

After numerous experiments, we found that a low-phosphorus tungsten concentrate could be obtained by the use of a small amount of acid in the rougher or cleaner. The acids that can be used to depress the apatite may be the inorganic acids, such as hydrochloric, nitric, sulphuric or sulphurous, and the short-chained organic acids such as formic or acetic. A small amount of acid

suffices, merely enough to make the pulp neutral or slightly acid. In no case should the acid be added in an amount sufficient to dissolve the gangue.

A fatty acid or derivative, or both, may be used as the collector, and, as in certain other instances herein, a frother is not necessary under some circumstances. A small amount of a soluble silicate may be used to depress the quartz. The silicate may sometimes be omitted, however. The acid may be used either in the rougher or the cleaner, or both, but we have found that a slightly higher recovery of tungsten results when it is used in only the cleaner.

In a typical test on the Nevada scheelite ore having a gangue composed of quartz and apatite, and the heads assaying 3.16% WO₃ and 0.040% P, a high grade concentrate was produced assaying 77.06% WO₃, .036% P. and .03% S. This concentrate accounted for 87.6% of the total WO₃ and only 3.3% of the total P. A mechanically agitated flotation machine of standard design was used, and the heads were ground to 150 mesh.

The reagents used, and their respective amounts, were as follows:

	Rougher	Cleaners		
		1	2	3
Sodium silicate.....	0.40	.15	.15	-----
Oleic acid.....	.32	-----	-----	-----
Sodium oleate.....	0.2	-----	-----	-----
Formic acid.....	-----	-----	-----	.60

It will be observed that the concentrates produced by this process were of a high grade and that the phosphorus and sulphur contents are well within the limits prescribed by the industry. We found that the rougher concentrates cleaned well.

In neither of the preceding experiments did the ore contain any sulphide minerals. In view of the fact that the flotation reagents employed for sulphides sometimes have a deleterious effect on the subsequent flotation of oxides, we conducted a series of experiments on a sample of Montana scheelite ore, in which the scheelite was associated with gold, arsenopyrite, mica and quartz. This ore also contained 0.636% of phosphorus as apatite.

We first conditioned the ore and then proceeded to float the gold and arsenopyrite. Flotation of the sulphides was followed by flotation of the scheelite in a rougher and three cleaning stages. High grade tungsten concentrates which were low in phosphorus and arsenic, were obtained, while the arsenopyrite concentrates contained the gold and only a small amount of tungsten. The results of a typical test on this ore are as follows:

	Wt. per cent	Assay, percent			Percent of total WO ₃
		WO ₃	P	As	
Sulphide concentrates.....	5.2	1.44	-----	-----	2.0
Scheelite concentrates.....	4.2	77.91	0.032	0.056	89.8
Middlings.....	2.5	9.94	-----	-----	6.8
Tailings.....	88.1	.05	-----	-----	1.4
Composite.....	100.0	3.64	-----	-----	100.0
Heads.....	-----	3.62	0.636	-----	-----

This test indicates that selective flotation can be successfully applied to tungsten ores.

The ore was ground to 150 mesh and a me-

chanically agitated flotation machine was used. The ore was first conditioned by the use of sulphuric and lactic acids. Potassium amyl xanthate and hardwood creosote were employed for the flotation of the sulphides. We believe that under most conditions, other conventional sulphide flotation reagents might be substituted. An additional amount of lactic acid was added to the sulphide rougher to depress the mica and allow a clean sulphide concentrate to be produced.

After the flotation of the sulphides, the scheelite was floated with oleic acid and sodium oleate, and a small amount of silicate was added to retard the quartz. These rougher concentrates were cleaned with sodium silicate to depress the quartz and mica, and a final cleaner with formic acid depressed the remaining mica and apatite. It will of course be appreciated that suitable substitutions may be made for the above mentioned reagents, as occasion may warrant. The amounts of reagents were as follows:

	Sulphide		Scheelite			
	Cond.	Rougher	Rougher	Cl. 1	Cl. 2	Cl. 3
Sulphuric acid.....	1.00					
Lactic acid.....	.12	.08				
K amyl xanthate.....		.35				
Hardwood creosote.....		.20				
Oleic acid.....			.32			
Sodium oleate.....			.10			
Sodium silicate.....			.30	.15	.10	
Formic acid.....						0.40

We have found that the arsenopyrite readily floats in the acid circuit, and that the lactic acid is especially effective in depressing mica both in the sulphide flotation and in the flotation of scheelite. It is also effective in depressing apatite but to a lesser degree than the inorganic or short-chained organic acids.

As will be seen from the above, the tungsten concentrates in such a selective flotation process are of a high and marketable grade, and of a low phosphorus and arsenic content.

The three foregoing tests were made on scheelite ores containing a siliceous gangue, and show that the scheelite can be concentrated by using a fatty acid or a derivative soap, or both. When there is no phosphorus present in the ore, an alkaline circuit may be employed, but where phosphorus is present, an acid or non-alkaline circuit is necessary in order to secure low-phosphorus concentrates. All of these ores were free of the calcareous minerals which occur abundantly in the contact-metamorphic ores.

Contact-metamorphic scheelite ores

The presence of calcite or dolomite in scheelite ores has heretofore been considered as preventing the separation of scheelite by flotation. The reagents that have previously been used have not been effective in retarding or depressing the calcite and inasmuch as calcite, scheelite and apatite have about the same floatability, a separation between them has been considered impossible.

We have now devised a process by which scheelite can be successfully concentrated from ores containing a calcareous gangue, and we have been able to secure high grade concentrates, low in impurities. We have conducted our experiments on a large number of ores varying consid-

erably in grade. For instance, one ore contained over 25% calcite and only 0.37% tungstic oxide, whereas another contained only a trace of calcite and over 30% tungstic oxide. At the outset, it should be stated that the amount of reagents has to be varied to meet the need of the ore, and that ordinarily the proper amounts can only be determined by experimentation. As a general rule, however, a greater amount of calcareous gangue requires a greater amount of the metal salt-silicate referred to hereafter.

Referring to one specific experiment, carried out on a Nevada contact-metamorphic scheelite ore, the ore was ground to -65 mesh and was floated in a mechanically agitated flotation machine. Inasmuch as this ore contained pyrite and sphalerite, the sulphides were first separated by the use of potassium amyl xanthate and aerofloat, although any of the other conventional sulphide flotation reagents could be used. Inasmuch as it is necessary to thoroughly remove the sulphides in order to produce a subsequent tungsten concentrate sufficiently low in sulphur, a relatively large amount of reagent is required. We have found that the sulphides can be floated in an acid, neutral or alkaline pulp, without impairing the floatability of the tungsten.

After removal of the sulphides, the remaining ore is conditioned for a short time with a heavy metal salt, such as copper sulphate. We have found that the salts of other metals, such as silver, mercury, copper, lead, zinc, or manganese, which form relatively insoluble carbonates, can be employed. While in the specific test to which we refer, copper sulphate was used, other salts of copper such as copper nitrate, or copper ammonium hydroxide, are as effective. We have referred to introducing the metal salt in the conditioning stage, and prior to the flotation of the scheelite, but we have found that it may also be added to the sulphide conditioner or during the sulphide flotation, if the particular salt has no retarding effect on the sulphides. Of course, if it has such a retarding effect on the sulphides, it must be added after the sulphides have been floated.

After proper conditioning, a soluble silicate, such as sodium silicate, is added and thoroughly mixed in the pulp. After the silicate has been sufficiently mixed, a fatty acid or its derivative soap may be added to float the scheelite. The metal salt-silicate served to effectively retard the calcite and apatite, and the scheelite rougher concentrates obtained at this stage are of good grade.

The scheelite rougher concentrates are cleaned one or more times with a soluble silicate or an acidic constituent to depress the small amounts of calcite and apatite which are floated in the roughing operation. While in the specific test here set forth only silicate was employed, improved results have been obtained in other tests by using an acidic constituent such as acid dichromate, chromium nitrate, or any of the inorganic or short-chained organic acids. In general, we have found that in tests in which the proper amount of metal salt and soluble silicate have been used in the rougher, silicate alone will readily clean the rougher concentrate. If the proper amount of these reagents have not been used, however, then a final cleaning in a neutral or slightly acid pulp is necessary to depress the remaining calcareous material and apatite.

In the specific test referred to above, the fol-

lowing reagents were employed in the amounts indicated:

5	Reagents	Pounds per ton of crude ore				
		Sulphide	Conditioner	Rougher	Cleaner 1	Cleaner 2
10	K amyloxanthate.....	0.40	-----	-----	-----	-----
	Aerofloat.....	.32	-----	-----	-----	-----
	CuSO ₄	-----	.8	-----	-----	-----
	Sodium silicate.....	-----	-----	1.00	.25	.20
	Oleic acid.....	-----	-----	.96	-----	-----
	Sodium oleate.....	-----	-----	.20	-----	-----

As indicated above, the concentrates were of a high grade and were low in their phosphorus and sulphur contents. The results of this specific test were as follows:

20	Product	Wt. pct.	Assay, percent			Percent of total WO ₃
			WO ₃	P	S	
25	Sulphide concentrate.....	16.0	2.74	-----	-----	7.0
	Scheelite concentrate.....	7.8	74.10	0.022	0.06	68.2
	Middlings.....	11.8	14.64	-----	-----	20.3
	Tailings.....	64.4	.60	-----	-----	4.5
	Composite.....	100.0	8.49	-----	-----	100.0
	Heads.....	-----	8.54	0.137	5.27	-----

As will be seen, sodium silicate was the only alkaline reagent employed, and it was used in the scheelite rougher. We have found as a result of other tests, however, that the use in the rougher or cleaner of caustic soda or soda ash in addition to the silicate gives improved results. The recovery is increased without a serious sacrifice in the grade of concentrate. In a recent test, 86% of the mineral was recovered in a concentrate assaying 70% tungstic oxide.

We have also found that scheelite ores free of calcite, but containing considerable apatite may also be effectively concentrated by using the metal salt-silicate reagent combination in conjunction with the fatty acid. From such an ore, tungsten concentrates low in phosphorus can be produced by cleaning with a soluble silicate or an acidic reagent.

Ferberite ores

The flotation of ferberite has heretofore been considered impossible. Our investigations have shown that this was unwarranted, and, although ferberite is not as floatable as scheelite, we have devised a flotation process for the successful recovery of ferberite.

Most ferberite ores have a siliceous gangue with only small amounts of sulphides and apatite. While the ores which are liberated at coarse size may be readily concentrated by gravity processes, ferberite is, generally speaking, brittle; and crushing produces rich fines which are difficult to recover by any process other than flotation. Consequently, flotation serves as a useful adjunct to gravity processes. Certain of the ferberite ores contain an appreciable amount of hornstone composed of minute grains of ferberite disseminated in a matrix of chalcedonic quartz. Inasmuch as such ores require fine grinding for liberation, they can be successfully treated only by a process adapted to handle material of this size, and we have found that flotation of these ores gives a good recovery of mineral in a concentrate of marketable grade.

In a typical test, on a ferberite-quartz ore containing an appreciable amount of ankerite, and the heads of which assayed 10.24% WO₃, a con-

centrate was obtained having a WO₃ content of 59.54%, which accounted for 79.1% of the total WO₃.

This ore was ground to -200 mesh, and the flotation was carried out in a mechanically agitated flotation machine. The ore was passed through a rougher and three cleaners. The reagents used, and their amounts, were as follows:

10	Rougher	Cleaners		
		1	2	3
15	Cresylic acid.....	0.08	0.08	0.08
	Oleic acid.....	.32	-----	-----
	Sodium oleate.....	.40	-----	-----
	Sodium hydroxide.....	.50	.2	-----
	Sodium silicate.....	.2	-----	-----
	Sulphuric acid.....	-----	.08	.16

It will of course be appreciated that certain substitutions may be made in the reagents listed in this application without materially affecting the results obtained.

With respect to the sulphuric acid used in the final two cleaners, we found that the ankerite and siliceous gangue were effectively depressed. In other tests on ferberite ores, an acid was used in the rougher as well as the three cleaners, and we have found that acid dichromate is very effective in depressing the gangue and also the apatite. In one test, for instance, in which acid dichromate was used at the rate of .05 lb. per ton of crude ore in the rougher and .3 lb. per ton in each of the three cleaning stages, a concentrate of 63.94% WO₃ was recovered from a middling product from a mill treating a ferberite ore, which product had a composition of 31.16% WO₃. The concentrate accounted for 69.8% of the total WO₃, and had a phosphorus content of only .022% and .045% of sulphur. The other reagents used in this test were oleic acid, sodium oleate and butyl alcohol.

In certain ferberite ores, the mineral is particularly sensitive to depression by acid, and in such cases we have found that the introduction of a small amount of a metal salt renders the mineral less sensitive but does not impair the efficacy of the gangue-depressing property of the acid. Although not wishing to be bound by our explanation of the theory, we believe that the metal salt functions to form a comparatively insoluble metal oleate coating around the particles, and thus renders the particle less sensitive to depression by the acid. Regardless of the theory, however, the net result is a higher recovery of mineral in a concentrate of slightly better grade. This metal salt-acid combination also serves to effectively depress the apatite. It should be stated, however, that a precise control of the acid will give comparable results.

Ferberite seems to be best floated in an acid circuit, and, notwithstanding the fact that such ores are relatively free of carbonates, any apatite which may be present would be depressed by the slight acidity of the circuit.

During the course of the experimental work on the flotation of ferberite ore, some time was spent in the Boulder tungsten district of Colorado. Flotation of ferberite under mill conditions was attained. However, several difficulties had to be overcome which are rarely encountered in laboratory work. The low temperature (34° F.) of the water available made flotation difficult. The ground ore was so dispersed that although the coarse mineral was recovered by flotation in the

usual manner, the slime losses were too great. Further, the consumption of fatty acid or soap was greatly increased and flotation was slow. Coagulation of the pulp by customary settling reagents such as lime or sulphuric acid further increased the soap consumption and did not improve the flotation. It was found, however, that the use of an alkaline reagent, as soda ash, or a salt such as calcium sulphate, followed by a small amount of an acid gave selective coagulation of the mineral, whereas the fine gangue remained dispersed. The reverse order can also be used—acid followed by a base. The coagulated mineral was then readily floatable with the customary reagents and enabled a good separation to be obtained with low tailing losses. Emulsifying the fatty acid in the soap prior to flotation materially reduced the quantity of reagent necessary and gave normal flotation in spite of the cold temperature of the water.

Wolframite

Wolframite, the manganese-iron tungstate, is slightly more susceptible to flotation than ferberite, and the reagents used for ferberite act in a similar fashion on wolframite ores. For instance, on a Washington wolframite ore which assayed 28.69% WO_3 , 0.015% P and 0.002% S, a concentrate was obtained of 70.92% WO_3 , 0.015% P and 0.01% S. This concentrate accounted for 89.4% of the total WO_3 .

The ore was ground to -150 mesh, and floated in a mechanically agitated flotation machine. The reagents were as follows:

	Rougher	Cleaners		
		1	2	3
Oleic acid.....	.96			
Sodium oleate.....	.40			
Acid dichromate.....		.15	.15	
Butyl alcohol.....		.04		

It will be observed from the above that the rougher concentrates were cleaned once with no reagents. We found that the wolframite floated readily and that the dichromate effectively depressed the gangue.

Hubnerite

Due to the higher manganese content of hubnerite, this ore is even more floatable than wolframite, and the same reagents employed on ferberite or wolframite may be used for the flotation of hubnerite. A typical test on an Arizona hubnerite ore which assayed 4.20% WO_3 and 0.05% P resulted in the recovery of a concentrate assaying 71.56% WO_3 , .012% P and .043% S, accounting for 90.2% of the total WO_3 content of the ore.

This ore contained pyrite and chalcoppyrite, which were first floated by the use of 0.25 lb. of potassium amyl xanthate per ton of crude ore and .14 lb. of butyl alcohol as a frother. Sodium silicate at the rate of .65 lb. was used to prevent the tungsten from floating with the sulphides. We found that the use of these reagents did not impair the subsequent floatability of the hubnerite. We also found that butyl alcohol is preferable as a frothing agent, inasmuch as it secured an equally good recovery of sulphides but at the same time did not float as much tungsten as certain other frothers, such as pine oil.

In the hubnerite rougher, oleic acid at the rate of 0.40 lb. per ton of crude ore and sodium

oleate at the rate of .10 lb. was used, and here too the rougher concentrates were cleaned in the first cleaner without the addition of any reagents. In the second cleaner, butyl alcohol at the rate of .02 lb. per ton of crude ore was added, and .25 lb. per ton of crude ore of acid dichromate was used to depress the apatite and quartz.

In this test, the ore was ground to pass 150 mesh, and was floated in a mechanically agitated flotation machine. The pulp, in this case, contained 34% solids.

Complex ores

From the above, it will be noted that certain of the tungsten minerals are more floatable than others, and we have found that if they are arranged in their order of increasing floatability, such order would be: ferberite, wolframite, hubnerite and scheelite. We have found that scheelite can be successfully separated from wolframite, and, although this would not ordinarily be done, it might be necessary to effect such a separation in order to produce marketable grade products from an ore that contains some other additional mineral, such as fluorspar. In such event, fluorspar and scheelite could be concentrated into one product and the wolframite into another separate product. The separation of the fluorspar could be effected in a retreatment of the fluorspar-scheelite product. In the absence of such a procedure, and with the present state of the art, separation would be almost impossible if all three minerals were floated together.

Our experiments in this connection were conducted on an ore from the Springvale mining district of Washington which assayed 1.48% tungstic oxide and 0.009% phosphorus. Wolframite and scheelite constituted the tungsten and were associated with sulphides and gangue composed mainly of quartz and mica, and there were also present fluorspar, calcite, ankerite, apatite and tourmaline. The complex nature of the ore and the low tungsten content made testing difficult, but the results of several tests showed that the ore could be satisfactorily concentrated by flotation.

In a typical test, the results were as follows:

Product	Wgt. Pct.	Assay, per cent			Pct. of total WO_3
		WO_3	P	S	
Sulphide concentrate.....	1.9	2.09	-----	-----	2.7
Fluorspar concentrate.....	2.4	1.53	-----	-----	2.5
Scheelite concentrate.....	.5	59.85	-----	-----	20.2
Wolframite concentrate.....	.9	68.32	.020	.055	41.5
Composite middlings.....	5.6	8.44	-----	-----	32.0
Tailings.....	88.7	.02	-----	-----	1.1
Composite.....	100.0	1.48	-----	-----	100.0

The ore was ground to -150 mesh, and floated in a mechanically agitated flotation machine. The procedure was, first, to float the sulphides, and then to float the fluorspar, scheelite and calcareous materials in a second concentrate; and finally, a concentrate of the wolframite is secured. The sulphides were floated with xanthate and wood creosote, although other conventional sulphide reagents might be employed, and a sufficient quantity of a soluble silicate is included to temporarily depress the scheelite and wolframite.

The fluorspar, scheelite and calcareous materials were recovered in a concentrate that was relatively free of wolframite, and a small amount of oleic acid or oleate is all that is required for this step, if sufficient silicate is employed in

the sulphide rougher. If sufficient silicate is not used in the sulphide rougher, it may be necessary to use it in the scheelite-fluorspar rougher. In any event, a silicate is used in the first cleaner in order to depress any wolframite, quartz or mica. The middling product was combined with the wolframite rougher concentrate in order to recover the wolframite. The fluor-spar-scheelite concentrate was then recleaned with formic and hydrochloric acid in order to effectively depress the scheelite and yield a concentrate of fluorspar that is fairly free of scheelite. The middlings are enriched in scheelite and are of marketable grade with respect to the WO_3 content.

The tailings from the scheelite-fluorspar rougher stage are subjected to a flotation treatment in which oleic acid and a small amount of oleate are employed to float the wolframite. The concentrate thus obtained is a medium grade and is contaminated with mica, quartz and some ankerite. The wolframite rougher concentrates are cleaned by the use of manganese sulphate and sulphuric acid, as well as hydrochloric and lactic acids. While, of course, not wishing to be bound by the exact amounts used, the following represents quantities of reagents in the above mentioned test:

Reagents	Sulphide rougher	Scheelite rougher	Cleaners		Wolframite rougher	Cleaners		
			1	2		1	2	3
Amyl xanthate	0.30							
Cresosote	.10							
Sodium silicate	.20		35					
Oleic acid					0.12			
Sodium oleate		0.10			.03			
Formic acid				25				
Hydrochloric acid				10			10	15
Manganese sulphate							20	20
Sulphuric acid							20	20
Lactic acid							10	

As above stated, the final concentrates assayed well over 65% WO_3 , and were low in impurities. The results clearly show the feasibility of treating this type of ore by flotation.

The results of all the foregoing tests show conclusively that tungsten ores can be successfully treated by flotation methods to yield high grade concentrates that are low in impurities. Furthermore, if sulphides are present in these ores, they can be first floated by the customary reagents without affecting the subsequent flotation of the tungsten. When the tungsten ores are free of calcite and apatite, good concentrates are recovered by merely using an alkaline depressant for the siliceous gangue. When they are free of calcite, but contain apatite, the apatite may be depressed by an alkaline reagent in the rougher and an acid in the cleaner, or an acid reagent may be used in both the rougher and cleaner. The combination of a metal salt and soluble silicate in the rougher, and an alkaline or acid reagent in the cleaner, may be used on ores containing calcite or other carbonates, in order to effectively depress such constituents. It will be appreciated that our invention may be applied to complex ores which have readily floatable gangue minerals, and also that ores containing more than one tungsten mineral are amenable to our flotation processes.

Fluorspar

Reference has been made above to the fact that

heretofore the flotation of certain ores from calcite has been considered impossible. Specifically, the prior art is replete with statements to the effect that fluorspar and barite as well as scheelite could not be successfully separated from ores containing calcite.

It is true that on certain fluorspar ores, for instance, which contain small amounts of calcite, it has been possible to reject some of the calcite and produce fluorspar concentrates relatively free of this constituent. Usually, what success has been attained along this line has been due to the fact that the calcite was locked with the siliceous material and remained in the tailings or middling products. Furthermore, repeated cleaning of the rougher concentrates from an ore high in fluorspar but low in calcite does allow some of the calcite to drop back into the middling product as a result of a "starving out process". This simply means that the abundance of fluorspar crowds the calcite out of the froth. Even in such situations, however, much of the fluorspar remains in the middling products and consequently a low recovery is obtained.

When fluorspar ores contain an appreciable quantity of calcite there has heretofore been no method by which concentrates low in calcite could be obtained. We are well aware that a certain flotation process is claimed to effect a successful separation of fluorspar from calcite. In this process the slime is removed either by a preliminary de-sliming operation prior to flotation, or by frothing the pulp to remove the slime prior to floating the fluorspar. The sands are then floated in a warming pulp using cresylic acid and oleic acid and the rougher concentrates are cleaned four times. In this cleaning the calcite drops back in the middlings which are removed from the flotation circuit because their recirculation prevents high grade fluorspar concentrates from being produced. It is to be noted that in this prior process no actual depressant for calcite is used.

We have experimented with a large variety of fluorspar ores containing siliceous and calcareous gangue and numerous reagents have been tested. We have found several reagent combinations which will effect a successful separation.

For instance, we have found that sodium silicate and an acidic reagent such as acid dichromate are quite effective in depressing calcite. Acids other than the dichromate may be used in the flotation of these minerals. For instance, we have found that hydrochloric, nitric, sulphuric and formic acids specifically give equally good results. In using this combination on a fluorspar calcite ore assaying 73.60% fluorspar, 14.50% calcite and 12.25% quartz, which was ground to -65 mesh, and floated in a mechanically agitated flotation machine, a concentrate was obtained assaying 97.71% fluorspar, 1.38% calcite, and 0.89% quartz. This concentrate accounted for 82.6% of the total fluorspar content of the ore. The reagents used were as follows:

Reagents	Pounds per ton of crude ore					
	Rougher	Cleaners				
		1	2	3	4	5
Oleic acid	.96					
Sodium silicate	.40	.4	.6	1.00		
Acid dichromate					1.50	2.00

We found that a silicate followed by dichromate effectively depressed the calcite and siliceous materials, providing a minimum amount of collector is used in the rougher. Too much oleic acid, or other fatty acid or derivative, produces rougher concentrates which are impossible to clean. It will be observed in the above that this process produces fluorspar concentrates from ores containing considerable calcite without the necessity of a preliminary desliming or frothing operation, and that the calcite is actually depressed rather than merely "starved out".

We have found that the order in which the reagents are introduced is immaterial, and, for instance, dichromate may be used in the rougher and silicate in the cleaners. As an example of such a process, we secured a concentrate assaying 98.18% CaF_2 , 1.06% CaCO_3 , and 0.56% SiO_2 , which accounted for 71.6% of the total fluorspar. The crude ore contained 69.93% fluorspar, 18.02% calcite and 11.02% quartz. The tailings contained less fluorspar than in the test where silicate was used in the rougher. The rougher concentrate was cleaned first with dichromate and then with silicate. The calcite was depressed in the middling and high grade fluorspar concentrates were produced as above indicated. In this test the ore was ground to -65 mesh and a mechanically agitated flotation machine was used. The ground ore was first conditioned with dichromate before adding the oleic acid in the rougher. The amounts of reagents used were as follows:

Reagents	Pounds per ton of crude ore				
	Rougher	Cleaners			
		1	2	3	4
Acid dichromate.....	0.40	0.6			
Oleic acid.....	.80				
Sodium silicate.....		0.8	1.00	1.00	

We have found that another effective reagent combination consists in the use of copper sulfate, sodium silicate, oleic acid and acid dichromate. In this process the pulp was conditioned with copper sulphate for several minutes and then the silicate was added. After a thorough mixing the oleic acid was introduced for floating the fluorspar. The rougher concentrates were first cleaned with silicate and then with dichromate. The amounts of reagents employed were as follows:

Reagents	Pounds per ton of crude ore				
	Conditioner	Rougher	Cleaners		
			1	2	3
Copper sulphate.....	1.00				
Sodium silicate.....		0.40	0.40		
Oleic acid.....		.48			
Acid dichromate.....			0.40	1.00	

In using this reagent combination on an ore assaying 63.78% CaF_2 , 15.73% CaCO_3 , and 19.96% SiO_2 and which had been ground to -65 mesh, a concentrate assaying 98.25% CaF_2 , 0.86% CaCO_3 and 0.78% SiO_2 was recovered, which accounted for 85.6% of the total fluorspar in the ore.

We have found that when the proper amount of oleic acid and the metal salt-silicate combination is used, the silicate alone effectively depresses

the calcite to give a high grade fluorspar concentrate. The exact amount of reagent for best results depends on the character of the ore and must be determined by experimentation. Generally speaking, however, ores which contain considerable calcite or which require fine grinding for liberation require more metal salt and silicate for a separation.

While not wishing to be limited by the theory of the function of the metal salt-silicate combination, we believe that the metal salt, used in conditioning, reacts with the carbonate mineral to form a metal carbonate coating, and that the addition of silicate superimposes a coating of the metal silicate on the carbonate particle. Such coating may or may not be continuous, depending on the amount of reagent used and the time allowed for the reaction to proceed. The more complete the coating, the less tendency the particle has to float, and, in any event the silicate coated carbonate particle acts in flotation as a true silicate mineral. Inasmuch as the fluorspar does not take on the silicate coating, it is floated by the fatty acid and the same thing is true with respect to the scheelite above discussed and the barite which will be discussed later. If the calcite is insufficiently coated with the silicate, it will tend to float with the rougher concentrate, and in such event a cleaning with additional silicate depresses such calcite or siliceous material that may have floated either for this reason or because an excess amount of collector was used. A final cleaning with acid dichromate effectively depresses the remaining calcite and siliceous minerals.

The metal salt-silicate combination is effective on ores of any grade and the ores high in calcite are as amenable to treatment according to our invention as ores containing only small amounts of calcite. As an example, we conducted tests on a tailings product from a mill in the Kentucky-Illinois fluorspar district which assayed 17.28% fluorspar, 73.61% calcite and 8.05% quartz. The clean mineral, of course, had been removed without difficulty in a gravity mill. Inasmuch as fine grinding was necessary to liberate the fluorspar from the gangue which was composed of siliceous and calcareous minerals, concentration of such liberated fluorspar by gravity methods was impossible.

This Kentucky-Illinois ore contained some sulphides which were first removed by the conventional sulphide flotation reagents, sodium, aerofloat and aerofloat No. 25, and had no harmful effect on the subsequent fluorspar flotation. A fluorspar concentrate assaying 96.60% CaF_2 , 2.84% CaCO_3 and .01% SiO_2 was obtained which represented 48.6% of the total fluorspar. The flotation tailings assayed 7.57% CaF_2 , which represented 19.1% of the total fluorspar in the ore.

The reagents employed, and the amounts, were as follows:

Reagents	Pounds per ton of crude ore					
	Sulphide rougher	Rougher	Cleaners			
			1	2	3	4
Sodium aerofloat.....	0.15					
Aerofloat No. 25.....	.08					
Copper sulphate.....	1.00					
Sodium silicate.....		0.8	0.5	0.5		
Oleic acid.....		.64				
Acid dichromate.....					0.5	1.00

The pulp was conditioned with silicate before the oleic acid was added. As is apparent from the foregoing, good concentrates were obtained relatively free of sulphides, calcite and siliceous materials.

Barite

Our experiments have shown that barite can also be separated from calcite, in much the same way as fluorspar, the metal salt-silicate combination successfully retarding the calcite without affecting the barite.

In a typical test, the ore was ground to pass 150 mesh for liberation of the mineral and gangue, and the pulp was first conditioned with copper sulphate. The reagents used were as follows:

Reagents	Pounds per ton of crude ore				
	Conditioner	Rougher	Cleaners		
			1	2	3
Copper sulphate.....	1.00				
Sodium silicate.....		0.8	0.4	0.25	
Sodium oleate.....		.2			
Oleic acid.....		.8			
Acid dichromate.....					0.20

The concentrate recovered assayed 96.98% barite and 0.76% calcite, and accounted for 82.06% of the total barite in the feed. The bulk, 66.7%, of the calcite was depressed in the rougher.

Fluorspar-barite ores

During the course of our experiments, we found that the barite was sensitive to dichromate, and that slight excesses of this reagent depressed the barite. Such was not the case with fluorspar, which was hardly affected by even large amounts of acid dichromate in the cleaners. This indicated that there was a possibility of separating fluorspar from ores containing barite and calcite, and in order to verify this, we conducted a series of experiments.

We were able to effect such a separation, as is evidenced by a test in which a fluorspar-barite-calcite ore, assaying 41.82% fluorspar, 19.19% barite, and 33.80% calcite, gave a concentrate of 82.56% fluorspar, 13.24% barite and 1.49% calcite, and which accounted for 84.1% of the total fluorspar and 29.4% of the total barite. The first middling, constituting 10% of the heads, assayed 23.56% fluorspar, 34.48% barite and 37.52% calcite; and the second and third middlings, aggregating 10.4% of the heads, assayed 11.21% fluorspar, 73.01% barite and 9.86% calcite. The reagents used were as follows:

Reagents	Pounds per ton of crude ore				
	Conditioner	Rougher	Cleaners		
			1	2	3
Copper sulphate.....	0.80				
Sodium silicate.....		1.00	0.4		
Sodium oleate.....		.2			
Oleic acid.....		.96			
Acid dichromate.....				0.5	1.00

Mineral carbonates generally

As stated, it has heretofore been considered impossible to separate metal carbonates from calcite. Although the carbonates react differently

in soap flotation, a mixture of free carbonates appears to behave in a manner that is intermediate between the reactions of its individual constituents, and these constituents all float simultaneously rather than in succession. Our early experiments confirm the belief of the prior art.

Recent tests made by us, however, indicate that rhodochrosite and the manganese dioxides may be separated from calcite by using the above described metal salt-silicate combination, and a careful control of the oleic acid. As a matter of fact, we believe that a successful separation of metal carbonates from calcite or the alkaline earth carbonates generally is possible, and we have no doubt that fluorspar, barite and scheelite can be successfully floated from carbonates other than calcite.

It will be appreciated from all of the foregoing that we have devised a froth flotation process which is adapted to recover valuable constituents of ores that have heretofore been considered non-amenable to satisfactory flotation. Our invention is economical and easy to carry out. The concentrates recovered are of a high grade, and the materials are effectively depressed. The processes herein set forth should be applicable to large bodies of ore that up to the present time have been considered unrecoverable, and also to large quantities of tailings.

It will be apparent to any person skilled in the art that our invention is susceptible of a wide range of equivalencies, and that various modifications may be made in either the steps, the reagents, or the quantity of reagents, without departing from the spirit of our inventive concept. In certain instances we have specifically listed equivalent reagents, but it will be apparent in connection with practically every reagent, our range of equivalencies is not to be limited to such expressed instances. For instance, where we have used the term "fatty acid" in the specification or claims, it will be appreciated that this will include not only fatty acids per se but also fatty acid derivatives, such as soaps, or both.

We claim:

1. A method of floating minerals from calcite comprising introducing into the mineral containing calcite, a collector having a fatty acid radical, a frothing agent and a depressing agent for calcite consisting of a heavy metal salt which forms a relatively insoluble carbonate and an alkaline silicate, agitating and aerating the mixture, and then removing a concentrate relatively free from calcite.

2. A method of concentrating contact metamorphic scheelite ores comprising introducing into the mineral containing calcite, a collector having a fatty acid radical, and a depressing agent for calcite consisting of a heavy metal salt which forms a relatively insoluble carbonate and an alkaline silicate, agitating and aerating the mixture, and then removing a concentrate relatively free from calcite.

3. A method of floating minerals from calcite comprising introducing into the mineral containing calcite, a collector having a fatty acid radical and a depressing agent for calcite consisting of an inorganic acid and an alkaline silicate, agitating and aerating the mixture, and then removing a concentrate relatively free from calcite.

4. A method of concentrating fluorspar that also contains calcite comprising introducing into the mineral containing calcite, a collector having

a fatty acid radical and a depressing agent for the gangue and calcite which consists of a soluble silicate and acid dichromate, agitating and aerating the mixture, and then removing a concentrate relatively free from calcite.

5 5. A method of concentrating fluorspar ore containing calcareous and siliceous gangue comprising introducing into the mineral containing calcite acid dichromate as a conditioning agent, then floating the fluorspar ore by a fatty acid radical, depressing the gangue by a soluble silicate, agitating and aerating the mixture and then removing a concentrate relatively free from calcite.

10 6. A method of concentrating a fluorspar ore containing calcareous materials comprising introducing into the mineral containing calcite a metallic salt conditioning agent, a collector having a fatty acid radical and a depressing agent consisting of acid dichromate and a soluble silicate, agitating and aerating the mixture, and then removing a concentrate relatively free from calcite.

15 7. A method of floating barite ores containing calcite comprising introducing into the mineral containing calcite a metal sulfate, a soluble silicate, a collector having a fatty acid radical and a depressing agent consisting of acid dichromate, agitating and aerating the mixture, and then removing a concentrate relatively free from calcite.

8. A method of concentrating contact metamorphic scheelite ores comprising introducing into the mineral containing calcite, a conditioning agent of copper sulfate, then adding a soluble silicate to depress the calcite, introducing a collector having a fatty acid radical, agitating and aerating the mixture and then removing the concentrate relatively free from calcite.

5 9. A method of concentrating contact metamorphic scheelite ores comprising introducing into the mineral containing calcite a heavy metal salt which forms a relatively insoluble carbonate, then adding a soluble silicate and alkaline reagent to depress the calcite, introducing a collector having a fatty acid radical, agitating and aerating the mixture, and then removing a concentrate relatively free from calcite.

10 10. A method of concentrating contact metamorphic scheelite ores comprising introducing into the mineral containing calcite a heavy metal salt which forms a relatively insoluble carbonate, then adding a soluble silicate to depress the calcite, introducing a collector having a fatty acid radical, agitating and aerating the mixture, and subsequently cleaning the concentrate thus obtained by a soluble silicate and an alkaline reagent.

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