

[54] FLOTATION OF COPPER ORES

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[63] Continuation of Ser. No. 37,679, May 15, 1970, abandoned, which is a continuation-in-part of Ser. No. 874,026, Nov. 3, 1969.

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[51] Int. Cl.B03b 1/04, B03d 1/02

[58] Field of Search.....209/166, 167, 5, 209/164; 241/20, 24

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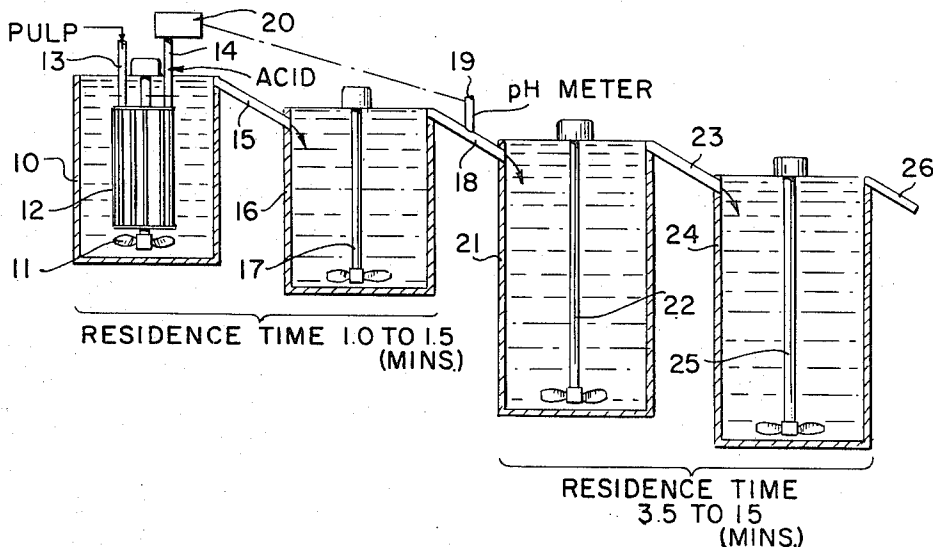
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[57] ABSTRACT

A process for the flotation of copper minerals employing sulfhydryl anionic collectors wherein the copper minerals are conditioned in at least one stage at a pH below 5.5 for a predetermined period followed by at least one further stage of conditioning for a predetermined period at a pH beginning above 9.0 in the presence of the collector, and the resulting pulp is subsequently subjected to froth flotation.

36 Claims, 5 Drawing Figures



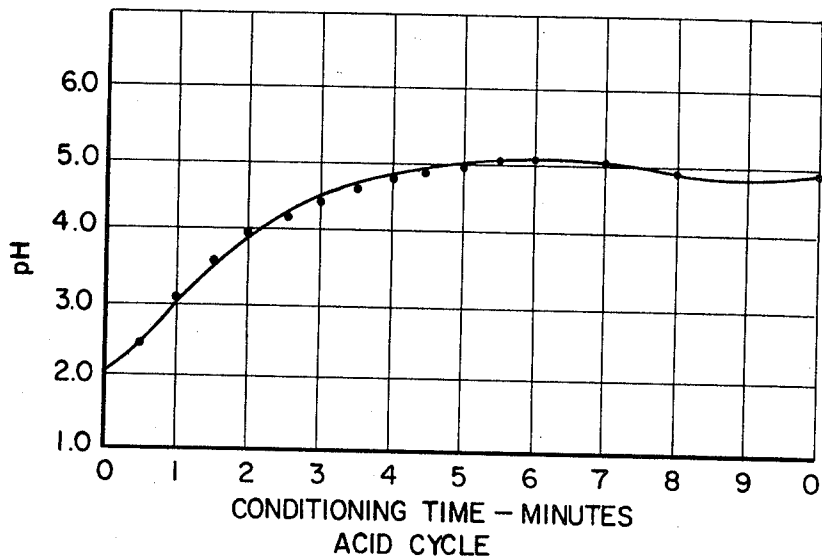


Fig. 1.

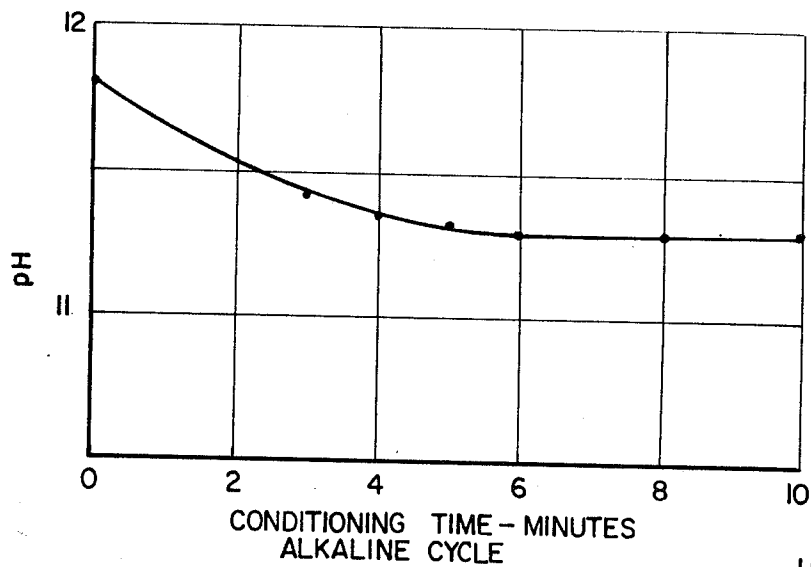
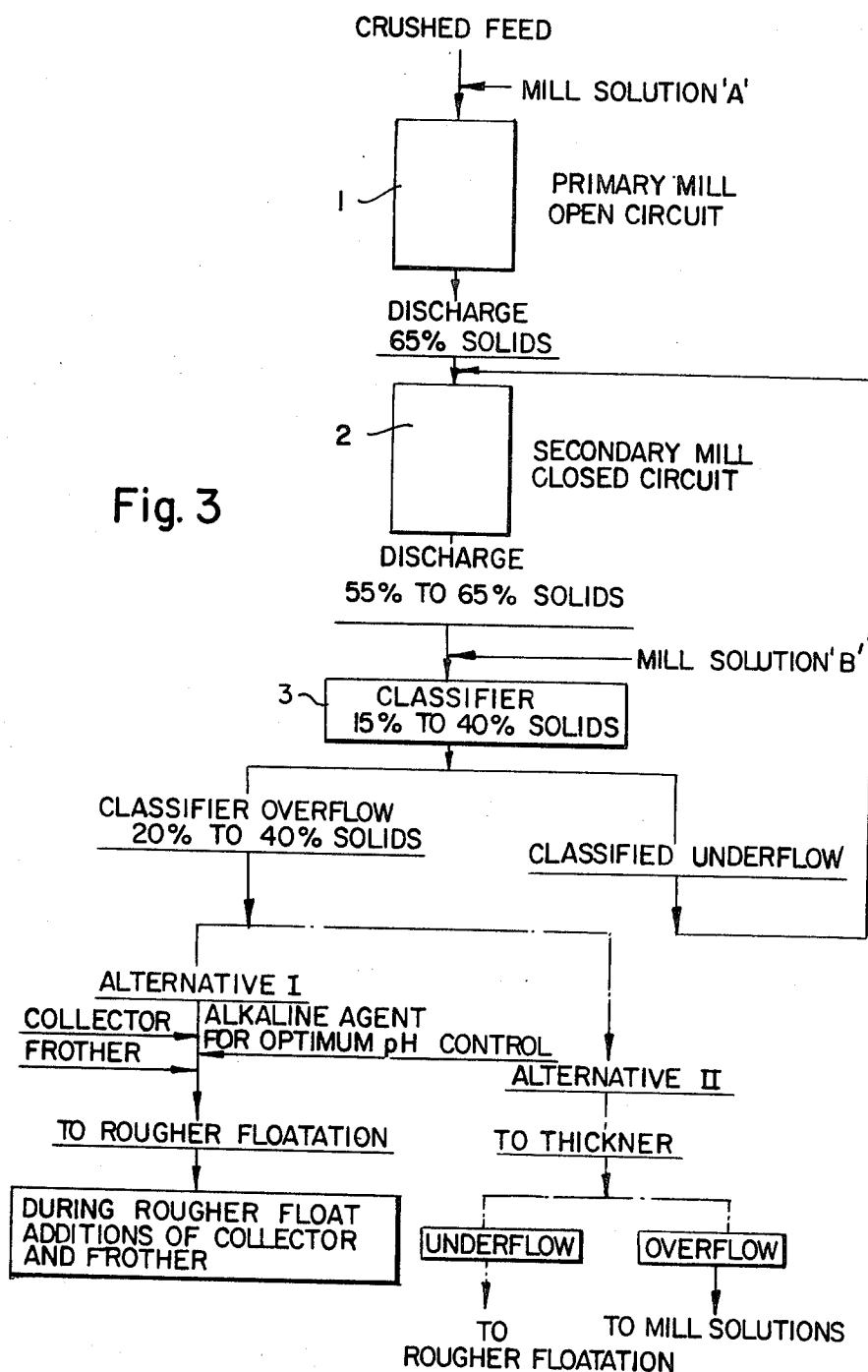


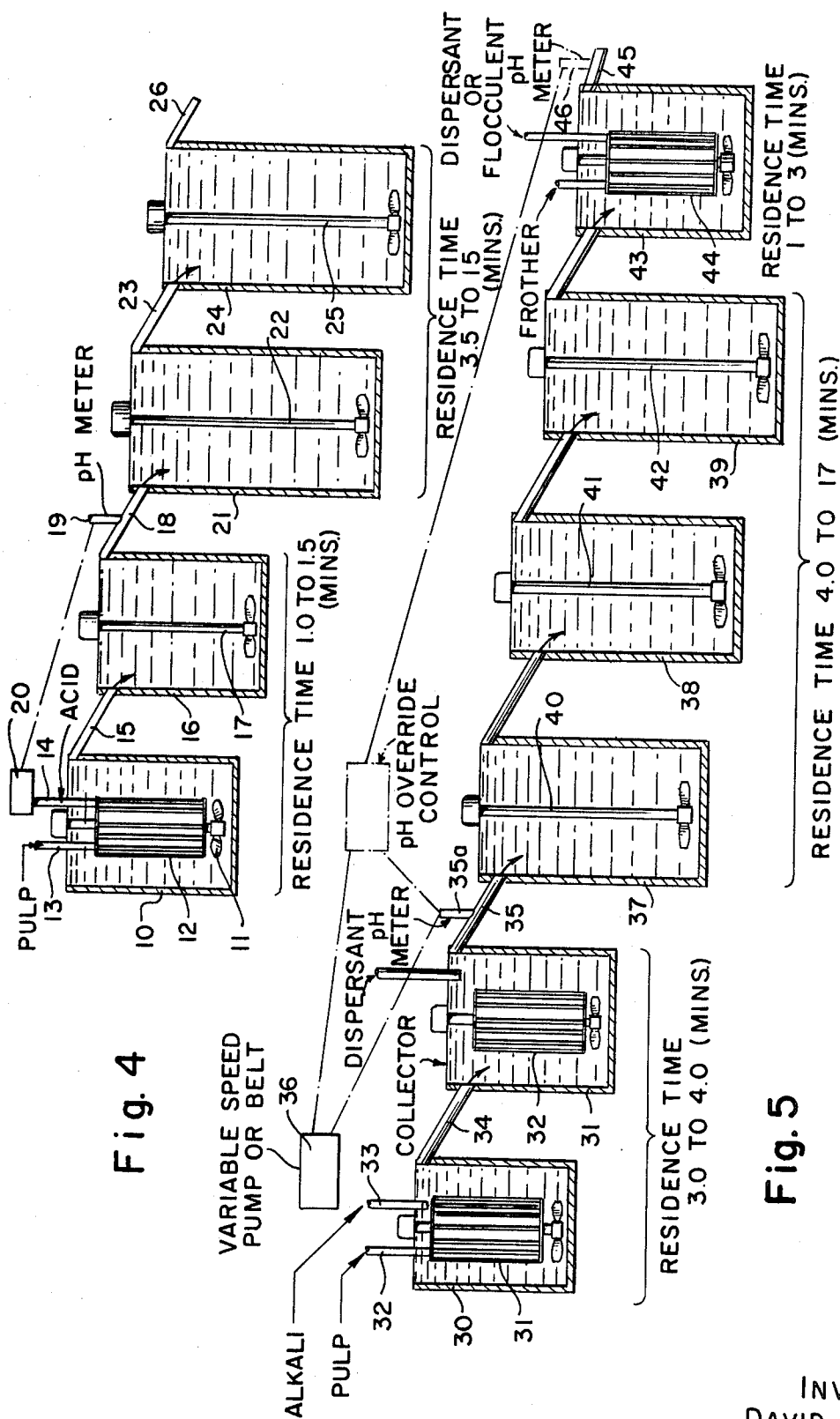
Fig. 2.

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FLOTATION OF COPPER ORES

This is a continuation of application Ser. No. 37,679, now abandoned filed May 15, 1970, which in turn is a continuation-in-part of Ser. No. 874,026 filed Nov. 3, 1969.

BACKGROUND OF THE INVENTION

This invention relates to the flotation of copper minerals in which sulfhydryl anionic collectors are used as the collecting agent.

In accordance with conventional practice the selection of a collector, or combination of collectors, will be determined by the particular mineral, or combination of minerals, present in the ore being treated. It is well known that sulphides are collect by a wide group of compounds containing the sulfhydryl group such as mercaptans, thiocarbonates (xanthates), thioureas, dithiocarbamates and dithiophosphates. A variety of such compounds are commercially available as collectors and many others are available as experimental reagents which are potentially available commercial. The sulfhydryl anionic collectors are discussed and classified in "Flotation," Second Edition, A. M. Gaudin, McGraw Book Company Inc., Toronto, 1957, page 182. They vary widely in their collecting power for particular sulphide minerals and thus it is usual when the treatment of a particular ore is in contemplation, to ascertain by laboratory experiment the most effective collector both from a metallurgical point of view and from an economic point of view. In many cases where the ore contains more than one mineral the selection of the collector may be affected by the fact that the different minerals are collected most effectively by a particular collector within what is usually a relatively narrow range of pHs and it may be desirable to find a collector which will effectively float one mineral within a range of pHs where the other minerals will remain depressed or alternatively, to seek a collector which, within a given pH range, will float a number or all of the valuable minerals. In each case the selection of the most effective collector is a routine experiment even though it is often time consuming, particularly with the more complex ores.

The present invention is not generally dependent upon the particular collector employed but rather is directed to the preparation of pulps containing sulphide minerals for froth flotation using sulfhydryl anionic collectors (all of which have a similar collecting action on sulphide minerals) in such a manner that mineral collection and host rock rejection are optimized. Thus when in the present application I use the expression "sulfhydryl anionic collectors" I intend the term to include any sulphur-connected anionic collector or combination of collectors which has been selected for the flotation at hand by the conventional procedures outlined above.

One of the problems in the flotation of copper minerals has been the inability of prior processes to achieve satisfactory activation of the copper minerals present and the tendency in some cases of certain copper minerals to remain substantially inert to activation and collection with sulfhydryl anionic collecting agents such as the xanthates, unless such ores are treated with a sulphidizing agent such as sodium sulphide. Even where such ores have been so treated the loss of copper values in tailings has been higher than would be desirable. Sulphidizing procedures are known to require very sensi-

tive control and to increase recovery at the expense of a certain lowering of the grade of concentrate. Further, sulphidizing agents produce an adverse influence on the froth making the froth flotation difficult to control.

The present invention has as its principal object the provision of procedures whereby without the use of sulphidizing agents the recovery of copper minerals from the ores may be accomplished to produce concentrates of at least as high grade and with higher recoveries than has been previously possible, even with the use of sulphidizing agents. Further, it will float at least one of the members of the family of copper silicates, which normally do not respond to even sulphidizing agents.

It is a further object of the invention to provide integrated plant circuits whereby these procedures may be effectively and economically carried out.

SUMMARY OF THE INVENTION

According to my invention the ore to be treated is prepared by forming a suitable pulp which is subjected to a period of conditioning in an acid circuit at a pH of below 5.5 and which may involve periods during which the pH may be as low as 0.5, as will hereinafter be explained. Following the conditioning in the acid circuit the pulp is subsequently made alkaline and is conditioned for a predetermined period or periods in the presence of a sulfhydryl anionic collector, for example a xanthate, the final stage of conditioning being carried out at a pH of about 9 and which may be as high as about 12 depending upon the particular constituents present in the ore.

In preparing the pulp the acid conditioning of the ore may be carried out in the grinding circuit or in a separate conditioning stage subsequent to grinding, or partly during grinding and partly in a subsequent conditioning stage.

The acid circuit conditioning exerts a profound effect upon the copper minerals resulting in a portion of the acid soluble minerals going into solution. When a pulp is subsequently treated in the alkaline circuit the copper in solution precipitates and the combined effects of the two circuits appears to be to activate the soluble copper minerals and to enhance the activation of the more readily activated copper sulphides so as to enable the effective recovery by flotation of sulphuric acid soluble and copper sulphide minerals in the flotation circuit.

A valuable factor of the present invention is that by acid treating the tailings from the flotation circuit and recirculating a portion of the thus obtained tailings liquor to the acid stage of conditioning, acid consumption may be reduced and worthwhile recovery of the sulphuric acid soluble copper reporting in the flotation tailings may be made, since any copper contained in the tailings liquor which is recirculated is precipitated when the pulp made up from the tailings liquor passes from the acid conditioning circuit into the alkaline conditioning circuit.

Consumption of acid may also be reduced by the presence in the initial pulp of ferric sulphate which may be added to the acid conditioning circuit either as a separate reagent or be allowed to build up in the circuit as a result of the action of the acid on the iron particles produced during grinding and the action of the acid on the liners and grinding media of the milling units if grinding is carried out in an acid circuit.

This last mentioned feature makes the invention of special value to copper producers who have previously maintained copper leach dumps in addition to the normal flotation plant who recover acid soluble copper from such dumps or tailings by acid leaching and precipitation on iron, or by other means such as electrolytically. The present invention makes possible the direct recovery of soluble copper from such leaching dumps by employing leachant from such dumps or tailings as make-up solution for the pulp in the acid conditioning circuit.

In the case of copper bearing ores which contain high proportions of talcy and clayey slimes, the present invention may be combined with that disclosed in my co-pending application Ser. No. 874,026, wherein a final conditioning in the presence of a dispersing agent or a flocculating agent is used to maintain these slime materials depressed. However, I have found that where such talcy and clayey slimes are not present to an extent which would normally interfere with flotation of copper minerals, the addition of dispersing agents to the alkaline conditioning circuit may have an adverse effect upon recovery.

It is characteristic of the pulps prepared according to my invention that the copper minerals are much more highly activated than is the case using conventional processes. This manifests itself in the fact that effective flotation can be carried out on a broad range of copper minerals and that these can be floated with high recovery at a single pH. Furthermore, the rougher concentrate can be subjected to a considerable variety of conditions during cleaning, e.g., for depression of pyrite, without any substantial loss of copper values. Thus, for instance, if molybdenite is present in the ore to be treated the conditioning in the alkaline stage of my process may involve a predetermined period at a pH in excess of 12 before flotation is carried out at a pH of about 11.5, resulting in the flotation with good recoveries of both the molybdenite and the copper values. In the case of ores containing substantial quantities of pyrite the cleaner floats may be conducted at pHs in excess of 12 with concentrations of cyanide for pyrite depression which would, in conventional processes, lead to depression of both the copper minerals and the pyrite.

BRIEF DESCRIPTION OF THE DRAWINGS

The description of the invention will proceed with reference to the accompanying drawings wherein

FIG. 1 is a graph of pH versus time in respect of acid conditioning during the acid conditioning circuit.

FIG. 2 is a graph of pH versus time in the alkaline conditioning circuit.

FIG. 3 is a flow sheet of a typical conventional wet grinding circuit supplying feed for a flotation plant.

FIG. 4 is a schematic drawing of an acid conditioning circuit according to the invention, and

FIG. 5 is a schematic drawing of an alkaline conditioning circuit according to the invention.

Referring particularly to FIG. 1 which represents pH versus time, when the acid is added all at once it is observed that the pH rises rapidly from a low value occurring at the time of addition of the acid to a natural constant pH determined by the acid consuming constituents in the pulp. Thus the pH of the pulp remains substantially constant after a period of 5 minutes from the addition of the acid. This suggests that the principal ac-

tion of the acid conditioning circuit takes place within the first 5 minutes, although, in fact, I have observed that minor improvements and recovery may take place after conditioning of up to 15 minutes. The most surprising aspect of the acid addition is that the minimum pH achieved in the first few seconds of the acid conditioning stage has a profound effect upon the final copper recovery. Thus, if the same quantity of acid is added in stage additions over say 5 minutes, rather than adding it all at once at the beginning of the cycle, the recovery drops off markedly. Surprisingly, however, where there is a predetermined amount of ferric sulphate in the pulp comparable or improved recoveries to those achieved in the case of all-at-once addition of the acid have been shown to occur while using lesser amounts of sulphuric acid.

Referring particularly to FIG. 2, it is seen that the pH in the alkaline conditioning circuit drops markedly from a peak value corresponding with the time that the alkaline agent is added and that the curve levels out to a relatively constant value after about 5 minutes of conditioning, which value corresponds to the alkaline consuming ingredients in the pulp. The shape of this curve suggests that periods of greater than 5 minutes conditioning in the alkaline circuit will be required to produce optimum effects.

The following examples illustrate the invention and indicate comparative results on certain of the same ores as between the process of the present invention, conventional flotation practice and conventional sulphidizing flotation processes.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

EXAMPLE I

The ore in which this work was carried out was a copper ore in which the main sulphide mineral was reported to be chalcocite with a minor amount of chalcocite as the sulphides. The oxide copper mineral was reported to be mainly malachite. The head analysis was 0.96 percent total copper and 0.38 percent sulphuric acid soluble copper. In all of the following tests 600 grams of the ore were ground in a laboratory rod mill for the same period of time with tap water at a pH of approximately 7.0. The percent solids of the pulp was 55 and the product produced was approximately 95 percent minus 100 mesh. The pH of the pulp after grinding was 6.3 to 6.

The pulp, after grinding, was transferred to a Denver laboratory flotation cell with a 500-gram bowl and the conditioning and rougher flotation was carried out at approximately 27 percent solids. In all of the tests reported in Series I to VI the circuit used following grinding was the addition of sulphuric acid for a conditioning period of 9 minutes followed by raising of the pH with lime to in excess of 9.0 and the addition of potassium amylxanthate with the pulp conditioned for a period of 20 minutes. Rougher flotation was carried out using either pine oil or Dow Froth as a frother and floated for a period of 8 minutes with the addition of a small amount of potassium amylxanthate at 4 minutes. These conditions were standard for all of the series unless otherwise noted.

Series I

Effect of Dispersing Agent to Rougher Flotation Tailings

The following two tests were identical with the exception that in the second test 0.7 lbs. of sodium silicate per ton of ore was added at the end of the alkaline circuit.

No. 1 Stage

Added 10 lbs. sulphuric acid (H_2SO_4) per ton ore and conditioned pulp for 9 minutes.

pH begin 2.2.

pH end 4.7

No. 2 Stage

Raised pH with lime (CaO) to 11.85, and added 0.23 lbs potassium amyl xanthate (Z6) per ton and conditioned for 20 minutes.

Flotation

In first case added frother which was pine oil and floated for period of 8 minutes with addition of 0.07 lbs. Z6 per ton.

In second case, following No. 2 Stage, added 0.7 lbs. Na_2SiO_3 per ton, conditioned for 2 minutes, and then repeated the flotation procedure as in the first case.

In the first case the tailings rejection was 94 percent by weight analyzing 0.208 percent total copper as compared to the test using sodium silicate of 93.5 percent by weight analyzing 0.220 percent total copper.

It is seen that on this type of copper ore the use of sodium silicate as the dispersant gave no additional tailings weight rejection and further indicated a higher copper tailings loss with its use, even in comparatively low quantities.

SERIES II

Effect of time of Addition of Same Amount of Acid Agent

Test No.	lbs./ton	Controlled Initial pH	Length of time Acid Addition	Rougher Tailings % Wt.	Total Cu %
2028	12.0	2.1	All at once	92.6	0.176
2033	12.0	3.0-3.5	1' 32''s	92.8	0.193
2034	12.0	3.5-4.5	6' 10''s	94.5	0.247

In this series of tests the acid conditioning stage was 9 minutes and the alkaline conditioning stage 16 minutes. The flotation period for all tests was 14 minutes with a small amount of xanthate added during the flotation stage. The final pH at the beginning of the alkaline stage in all cases was approximately 11.8 and at the end of the conditioning stage 11.2.

FIG. 1 shows the effect of adding all of the acid at once. It will be observed that where all of the acid was added at once, (Test 2028), the pH dropped to 2.1 and rose to a pH of 3.1 in 1 minute. In Test 2033 the acid was added over a period of 1 minute and 32 seconds to control the pH within the range of 3.0 to 3.5. In test 2034 the acid was added to control the pH within the range of 3.5 to 4.5 and took a period of 6 minutes and 10 seconds. In Test 2034 the acid conditioning cycle was increased to 12 minutes from 9 minutes as used in Tests 2028 and 2033, due to the lengthened time of acid addition. Although the same amount of acid was used in all tests, the comparative tailings copper losses in the varied initial pH ranges is quite startling. In Test 2028 where the pulp was at a pH of less than 2.5 for approximately 30 seconds, the tailings loss was 0.176 copper as against 0.193 copper, where in Test 2033 the pH was controlled between 3.0 and 3.5. In Test 2034 the tailings loss of 0.247 is even more startling where the lowest pH that the pulp was allowed to drop to was 3.5.

From a practical plant operating point of view, where such a circuit is used two small conditioners with a total retention time of less than 90 seconds would precede the main conditioning time in the acid circuit. Although impressive results have been shown for conditioning periods in this acid cycle of up to 15 minutes, FIG. 1 shows that in an ore of this type the major consumption of the sulphuric acid takes place in approximately 5 minutes. From the point of view of the lowest alkaline agent consumption this would be the shortest conditioning cycle indicated in not requiring any excess alkaline agent to neutralize the sulphuric acid that had not been chemically reacted with any acid consuming pulp constituents.

FIG. 2 shows the effect of initially raising the pH to in excess of 9 and the consumption of part of the alkali in this circuit. It will be noted that the initial pH in this test was 11.8 and at the end of 5 minutes had dropped to a pH of approximately 11.3, whereas at the end of 16 minutes the pH was still 11.3, indicating that the minimum period for alkaline stability on this ore is approximately 5 minutes.

Series III

The following series of tests shows the method by which, in using this invention, the optimum amount of sulphuric acid may be arrived at. All test conditions in these tests were identical, with the sulphuric acid added all at once following the grinding stage, the lowest pH reached recorded, and the alkaline stage raised to approximately 11.8.

Obtaining Optimum Amount Acid Agent in Acid Cycle

Test No.	H_2SO_4 lbs./ton	Rougher Tailings % Wt.	% Total Cu	Minimum pH
(a)	7.3	94.2	0.216	2.1
(b)	8.7	94.2	0.214	2.1
(c)	10.0	92.7	0.208	1.9
(d)	12.0	93.0	0.182	1.9
(e)	14.0	92.4	0.184	1.6
(f)	16.0	91.4	0.188	1.4

It will be noted that the optimum amount of sulphuric acid for this ore and under conditions of the test was approximately 12 lbs. per ton and whereas an excess of sulphuric acid showed only a slight rise in tailings loss, when insufficient sulphuric acid was added the tailings loss was quite markedly higher.

Series IV

In this series the standard circuit which I previously described was used, the only change being the addition of an iron salt, in this case ferric sulphate. It will be noted that the ferric sulphate, using the same amount of sulphuric acid, gave a marked improvement in tailings loss. This surprising effect of the iron salt on further activation and increased recovery of the copper minerals is not understood.

Effect of Using Iron Salt in Acid Cycle

Test No.	H_2SO_4 lbs./ton	Ferric Sulphate lbs./ton	Rougher Tailings % Wt.	% Total Cu
(a)	10.0	None	92.7	0.208
(b)	10.0	0.30	91.6	0.179
(c)	10.0	1.0	91.9	0.171

Series V

This series of tests were conducted to study the effect of the total amount of copper in solution at the end of

the acid cycle. It will be noted that in the maximum amount of sulphuric acid used, that is, 10 lbs. per ton, there was only 1.2 percent of the total copper in solution. This is an amazingly small amount to account for the excellent activation of the copper minerals in the final rougher float. As 12 lbs. of sulphuric acid per ton was the optimum indicated for this ore, the maximum amount of copper in solution that would be required for optimum final activation of the copper minerals is indicated at less than 2 percent of the total copper.

EFFECT OF AMOUNT OF ACID ON THE TOTAL COPPER IN SOLUTION AT THE END OF THE ACID CYCLE

Test number	H ₂ SO ₄ , lbs./ton	pH acid cycle		Cu in solution		Rougher tailings, percent	
		Begin	End	Mgs./L.	Percent of total Cu	Wt.	Total Cu
(a)-----	7.3	2.1	4.95	14.4	0.35	94.2	0.216
(b)-----	8.7	2.1	4.9	39.6	1.1	94.2	0.214
(c)-----	10.0	1.9	4.8	43.6	1.2	92.7	0.208

Series VI

The following summary of comparative metallurgical data was obtained on the same ore that was used in Series I to V. The standard circuit was using the conventional xanthate flotation circuit wherein the ore was ground in an alkaline circuit, the pH adjusted to the optimum and the xanthate added in stages throughout the rougher flotation circuit. The results reported are considered to be the optimum using the conventional circuit.

Similarly, on the comparative circuit too, the results with sulphidizing using sodium sulphide were optimized. The third test referred to is a Weston Circuit. Following the grinding stage, using tap water wherein the pH at the end of the grinding was 6.3, 12 lbs. of sulphuric acid per ton was added to the Denver Flotation Cell and conditioned for 9 minutes. The pH at the beginning of this cycle was 2.0 and at the end, 5.0. At the beginning of the next cycle lime was added to bring the pH up to 11.8, and 0.27 lbs. per ton of potassium amyl xanthate was added and conditioned for 16 minutes. The pH at the end of the 16 minutes was 11.3 and followed by a rougher flotation for 14 minutes using Dow Froth as the frother and the addition of 0.03 lbs. of xanthate at the 7-minute period during the rougher flotation. It will be noted that not only was there a major decrease in the oxide copper reporting in the tailings using the Weston Circuit, but also there was a major decrease in the loss of the sulphide copper, illustrating the effect of the Weston Circuit on the excellent metallurgy obtained on the sulphide copper minerals in addition to that of the copper oxide minerals.

Table I

Test Description	Concentrate % Cu		Analysis of Cu Tailings		Sulphide Cu (Calc.)
	% Cu	Recovery	Total Cu	Oxide Cu	
Standard Circuit	29.60	48.1	0.68	0.57	0.11
Sulphidizing	27.9	71.3	0.38	0.32	0.06
Weston Circuit	29.2	78.2	0.176	0.172	0.004

Note: The "Standard Circuit" and "Sulphidizing Circuit" are closed circuited results. The "Weston Circuit" comparison is in open circuit wherein the 78.2 percent copper recovery figure does not take into con-

sideration any further copper recovery that may be obtained in closed-circuiting the cleaner tailings. The percent of the total copper in the cleaner tailings was 4.3 and if taken into the total tailings would raise the tailings figure from 0.176% Cu to 0.196% Cu.

Series VII

Effect of pH in Final Alkaline Conditioning Stage

The head analysis of the ore used in this series was 0.56 percent total Cu and 0.10 percent acid soluble copper. The acid soluble copper referred to in all series is copper soluble in H₂SO₄ in a standard solution and period of time.

The following tests were identical with the exception of the alkaline cycle wherein the pH at the beginning was varied.

The ore was initially ground in a laboratory rod mill to approximately 95 percent minus 100 mesh, using tap water and a density of 55 percent solids. The pulp was transferred to a Denver laboratory flotation machine 500 gram cell and conditioned and floated at approximately 27 percent solids. In the first stage 12.7 lbs. H₂SO₄ was added all at once lowering the pH to approximately 2.0, conditioned for 9 minutes, and the pH at the end rose to approximately 5.0.

In the second stage the pH was raised to various alkaline levels above 9.0 with lime, the collector potassium amyl xanthate added, and the pulp conditioned for 16 minutes, after which Dow Froth, the frother, was added and the rougher float carried out for 14 minutes.

The following were the comparative results:

Test number	pH alkaline stage		Rougher tailings, percent			
	Begin	End	Wt.	Total Cu	Oxide Cu	S Cu
3004-----	11.8	11.5	89.4	0.092	0.062	0.03
3006-----	10.75	9.95	91.3	0.068	0.046	0.022
3008-----	10.05	9.0	91.3	0.086	0.072	0.014

It will be noted that wherein the principal copper sulphide mineral is chalcopyrite, in this case the sulphide copper tailings are dropping as the pH at the end of the alkaline cycle approaches 9.0, and the oxide copper tailings are at their lowest at a pH of 10.75.

With chalcopyrite as the principal sulphide copper mineral the results indicate that the final pH of the alkaline stage, for optimum chalcopyrite recovery, could be lower than a pH of 9.0 and can be expected to lie in the region of about 8.5.

Suitable acid reagents for use in the acid conditioning circuit of the invention are sulphuric acid and sulphurous acid, or sulphur dioxide. These may be used in commercial reagent form to achieve the appropriate acid conditions herein described or alternatively, where all or part of the grinding circuit is to operate under acid conditions, use may be made of solutions of these acid reagents derived from acid leach copper mineral dumps, acid treated tailings, acid treated or naturally acid mine water, or solutions of such acid reagents which happen to be available from any other extraneous source and which do not contain dissolved materials which are deleterious to flotation. These solutions will usually contain a quantity of copper in solution and an advantage in their use, according to the invention, is that following the acid conditioning circuit of the present invention the copper in solution precipi-

tates in the alkaline conditioning circuit and reports in good recovery in the subsequently obtained flotation concentrate.

No upper limit has as yet been established for the concentration of dissolved copper in such solution which can be recovered in the foregoing manner without adverse effect upon the metallurgy of the process of the invention, but it is to be expected that there is an upper limit in any given case to the amount of copper in solution which can be tolerated without adversely affecting metallurgy. The examples herein indicate that useful quantities of copper can be recovered in this manner and that the beneficial effect of dissolved copper in activating the sulphuric acid soluble copper minerals and in enhancing the activation of the copper sulphide minerals is realized with very low concentrations of dissolved copper in the acid conditioning circuit.

When the acid is added to the final plant tailings lowering the pH of the solution to the point where any copper that may go into solution is held in solution by keeping the pH at a level below 5.5, this solution is circulated back to the grinding circuit, or alternately, following the grinding circuit to the pulp either leaving the grinding circuit or following the thickener and prior to the flotation circuit. In such a case I would prefer to split the final plant tailings into two parts, as the amount of solution required to feed to the head of the grinding circuit would be appreciably smaller than the solution in the total plant tailings. Further, as the flotation circuit tailings will normally be at a pH in excess of approximately 9, I would prefer to recover the second part of the tailings solution at this pH and use it as mill solution in the flotation circuit or at the end of the grinding circuit, in order to keep the alkaline agent costs at a minimum. If all of the plant tailings are acidified, it would mean that that part of the solution returned to flotation would, of necessity, have to be raised to a pH in excess of 9 and thus require higher alkaline agent.

In considering the application of all or part of the acidified plant tailings to the grinding circuit reference is particularly made to FIG. 3 of the drawings. This figure illustrates a conventional wet grinding circuit for preparing flotation plant feed which consists of a primary open circuit mill ¹ which may be a rod mill or primary ball mill which receives crushed feed material from a crusher plant. The discharge of the primary mill 1 is fed to a secondary mill 2 which discharges into a classifier 3, the underflow of which is close-circuited with the secondary mill 2. The classifier overflow may go directly to the flotation plant according to Alternative I where, if the acid conditioning circuit of the process of the invention is integrated with the milling circuit, it will be fed to the alkaline circuit of the present invention and subsequently to rougher flotation, further conditioning and such further cleaning stages of flotation as are required. In Alternative II, which is indicated in interrupted lines, the classifier overflow is fed to a thickener, the overflow of which is discharged to mill solution and the underflow of which is discharged to the flotation plant.

The acid solution can be fed into the grinding circuit in a number of ways. If we consider the use of a conventional crusher rod mill-ball mill circuit wherein the feed density in the rod mill will be approximately 65 percent solids, part of the acid solution can be fed to the head of the rod mill at point A on FIG. 3 which is normally

in open circuit. If, from an operator's point of view, they do not wish to have the rod mill operating in too low a pH acid circuit, part of the alkaline solution can also be added for adjustment, although I would prefer to have this circuit operated below a pH of 5.5. If a major drop in pH is required in the grinding circuit to achieve the optimum results, I would prefer to add the acid to the second stage of grinding, that is, the ball mill, wherein the ball mill is operating in closed circuit with a classifier. In such a case my preferred circuit is to add either acid solution from the plant tailings or fresh acid or a combination of the two to the discharge of the ball mill which would normally be at 55-65 percent solids at point B on FIG. 3. Leaving the ball mill the pulp is normally diluted to 15-40 percent solids and at this point I would prefer to add my acid solution together, if necessary, with fresh acid or fresh acid alone, dropping the pH to the optimum level for the predetermined period of time required for optimum metallurgical results. The acidified pulp would be further conditioned to allow it to rise to the level of its acid consuming constituents, as shown in FIG. 1. On the type of ore on which the graph was obtained, the conditioning period prior to the acidified pulp going to the classifier would be approximately 5 minutes. This would be applicable whether the classifiers were of the mechanical type such as the rake or spiral type, or cyclone classifiers. The overflow from the classifiers would then go to an additional acid conditioning period, or alternately, to an intermediate cycle that is between a pH of 5 to 8 where part or all of the xanthate type collector may be added, or alternately, directly to the alkaline conditioning cycle where the pH is raised to in excess of 9.0, followed by rougher flotation wherein only a minor amount of the collector would be added. If only a part of the collector is added in the intermediate conditioning stage, that is, between a pH of 5 to 8, the remaining collector that would normally be added to the conditioning stage or stages prior to rougher flotation would be added to the alkaline cycle in which the pH is in excess of 8.5. During this final alkaline stage of conditioning my preferred pH range at the beginning of the conditioning using soda ash is 8.5 to 10, and in using lime a pH range of 10 to 12.5.

It will be seen that in the application of the inventor's process to plant practice, there may be more than one acid stage and more than one alkaline stage. However, it is necessary to have at least one acid stage wherein the pH is reduced to below 5.5 with sulphuric acid, or sulphurous acid, to below a pH of 5.5 for a minimum predetermined period, and at least one alkaline stage wherein the pH of a conditioning step prior to flotation is in excess of a pH of 8.5.

For carrying out my process externally of the grinding circuit a suitable conditioning circuit is illustrated in FIG. 4 of the drawings. The first conditioning tank 10 is equipped with a Wallace type agitator (Denver Equipment Company) having an impeller 11 superposed by a mantle 12 into which the pulp feed line 13 and the acid feed line 14 discharge. The overflow 15 from the tank 10 discharges into tank 16 which is equipped with the impeller type agitator 17. In the overflow 18 of tank 16 there is mounted the pH meter 19 which controls variable speed pump 20 which pumps acid into the acid supply line 14. Normally there would be two acid supply lines, one with a constant speed pump designed to supply the major portion of the

acid and one with a variable speed pump controlled by the pH meter 19 and designed to increase or decrease its speed responsively to the pH meter in order to maintain the pH in the discharge of tank 16 at its desired value. The conditioning tanks 10 and 16 between the have a capacity designed to provide a total residence time of from about 1 to about 1 1/2 minutes and the setting of the pH meter will be made with reference to the pH-time curve corresponding to that shown in FIG. 1 which will have been derived in optimizing the process of the invention for treatment of the particular ore concerned. Thus, if the total residence time in conditioning tanks 10 and 16 is 1 minute and the ore being treated were the same as that for which FIG. 1 was derived, the pH meter 19 would be set to maintain a pH in the overflow 18 from tank 16 of 3.1. The discharge of tank 16 goes into conditioning tank 21 equipped with the impeller type agitator 22 which conditioning tank discharges through overflow 23 into conditioning tank 24 also equipped with an impeller type agitator 25. The conditioning tank 24 discharges through overflow 26 into the first conditioner of the alkaline conditioning circuit or into a further cycle of the acid conditioning circuit if a further cycle is employed. The conditioning tanks 21 and 24 have a capacity designed to produce a total residence time of between about 3.5 minutes to about 15 minutes, the actual time for any given plant design depending upon the experimentally determined optimum time for the acid conditioning circuit. Having regard to the saving of alkaline consumption in the alkaline conditioning circuit to follow, their total residence time would be designed to ensure that the discharge from conditioning tank 24 was at a pH lying on the flat of the pH versus time curve. For example, if the ore being treated were the same ore as that for which the pH versus time curve illustrated in FIG. 1 was derived, the total time in the acid conditioning circuit would be greater than about 5 minutes and taking into account the residence time in conditioning tanks 10 and 16 which we have arbitrarily selected as one minute in the foregoing explanation, the total residence time in conditioning tanks 21 and 24 would not be less than 4 minutes.

Where the acid conditioning circuit is integrated with the grinding circuit, as previously discussed, the acid reagent, which may in this case be introduced in an acid make-up solution derived from one of a number of sources, may be introduced at either point A in advance of the primary mill, or at point B in advance of the secondary mill classifier. In the former case the time of residence within the grinding circuit will generally be sufficient to ensure that the pH of the classifier overflow will lie on the flat of the pH versus time curve for the ore concerned and that the acid conditioning cycle at a pH of below 5.5 has been completed. Where such is the case the grinding circuit, including the classifier, may be regarded as corresponding to the acid conditioning circuit illustrated in FIG. 4 and the classifier overflow will be fed either directly to the first stage of the alkaline conditioning circuit or to a further cycle in the acid conditioning circuit, if such further cycle is being employed.

In cases where the acid is fed to the primary mill the primary mill can be considered as corresponding to tanks 10 and 16 in the circuit illustrated in FIG. 4 and pH control is achieved by means of a pH meter at the primary mill discharge controlling the addition of acid

reagent to the acid solution feed line to the primary mill though a variable speed pump in the same manner as described in connection with the circuit illustrated in FIG. 4.

- 5 Where the acid reagent is added to the secondary mill discharge either as fresh reagent or as acid make-up solution from some extraneous source, two small conditioning tanks similar to tanks 10 and 16 in the circuit illustrated in FIG. 4 will be interposed between the
- 10 secondary mill and the classifier. These two conditioning tanks function in precisely the same manner and are controlled in the same manner as the conditioning tanks 10 and 16 and the discharge from the second tank is fed to the classifier which may be regarded in
- 15 whole or in part as performing the same function as tank 21 or tank 24 in the circuits illustrated in FIG. 4. Usually, however, it will be necessary to pass the classifier overflow into a series of conditioning tanks like tanks 21 and 24 in order to allow the acid conditioning
- 20 at a pH below 5.5 to reach completion. Alternately, following the two conditioning tanks, additional tanks may follow to complete the acid cycle prior to classification.

As has been pointed out, the presence of ferric sulphate in the pulp raises the minimum pH which is necessary in the conditioning cycle at a pH of less than 5.5 to produce optimum results. It is contemplated that where grinding is carried out in a wet circuit, sufficient fine particles of iron will be produced in the grinding to provide for the formation of sufficient ferric sulphate in the acid conditioning cycle to make the addition of ferric sulphate unnecessary to produce optimum results at the higher minimum pH. This, of course, will be particularly so where the grinding is carried out in an acid circuit as above described. There may be, however, cases during mill start-up and in the case of ores having a high proportion of acid consuming ingredients where provision needs to be made for the addition of ferric sulphate in order to obtain the benefit of the achievement of optimum results with the minimum pH in the higher ranges below 5.5. In such cases controlled amounts of ferric sulphate solution will be added to the circuit at the same point as the first point of addition of acid. It is contemplated however, that in the normal case sufficient ferric sulphate will build up in the circuit to eliminate the need for such provision.

A suitable alkaline conditioning circuit for purposes of the invention is illustrated in FIG. 5 of the drawings. The pulp discharged from the acid conditioning circuit enters tank 30, which is equipped with a Wallace type agitator 31, through supply line 32. An alkaline agent is added through the alkaline supply line 33 where the agent is in solution. Alternatively, the alkaline agent may be added in dry form by means of a variable speed conveyor discharging at the same point as the alkaline supply line 33. The overflow 34 from the alkaline conditioning tank 30 discharges into the alkaline conditioning tank 31 which is likewise equipped with a Wallace type agitator 32 and with means for introducing controlled amounts of collector and, if the circuit calls for it, dispersant. The capacity of alkaline conditioning tanks 30 and 32 is so designed as to provide a total residence time for the two tanks of from about 3 to about

4 minutes and a pH meter 35a on the overflow 35 of tanks 31 controls the variable speed pump 36 which supplies alkaline agent in solution to alkali supply line 33, or alternatively, the pH meter 35a controls the speed

of the variable speed belt (not shown) which supplies alkaline agent in dry form. The pH meter 35a is set to control the addition of the alkaline agent to produce a pH above 9 which has been selected as the optimum for the treatment of the particular ore being treated. The overflow from tank 31 discharges into tank 37 which discharges into tank 38 which discharges into tank 39, each of which tanks is equipped with an impeller type agitator 40, 41 and 42 respectively. The total capacity of the tanks 37, 38 and 39 is so designed as to produce a residence time of about 4 to about 17 minutes, corresponding with the optimum which has been established by experiment on the particular ore for this cycle of conditioning. The conditioning tank 39 discharges into conditioning tank 43 which is equipped with a Wallace type agitator 44 and which is provided with means for introduction of controlled quantities of frother and controlled quantities of dispersant or flocculent, if such are to be used. The tank 43 has a capacity designed to provide for residence time of about 1 to about 3 minutes and it discharges to the rougher flotation circuit through the discharge 45 in which is mounted pH meter 46 which is set to maintain a pH which is optimum for the flotation of the minerals concerned. The pH meter 46 exerts its influence on the variable speed pump or belt 36 through the override control 47 in which its signal is compared with the signal of pH meter 35a and the difference is applied as a correction to increase or decrease the amount of alkali introduced through supply line 33. It will readily be seen that as the change in pH caused by the override control begins to be reflected at pH meter 35a the difference between the signals from pH meter 46 and pH meter 35a will diminish. In order to avoid a hunting condition in the override control from developing the control will include a delay feature limiting the magnitude of adjustment which can be made to the variable speed pump or belt 36 within any time increment represented by the residence time of tanks 30 and 31.

A more detailed understanding of the invention may be had by reference to the following examples of laboratory testing on three different types of ores occurring in the same major copper deposit in the United States of America. These ores are identified as follows:

Lot 128 — High Clay Content

Cu (Total)	0.95%
Cu (Acid-Soluble)	0.23%
Fe	5.45%
S	4.22%
SiO ₂	60.0%
CaO	0.25%
MgO	0.35%
Al ₂ O ₃	15.7%

Lot 126 — Similar to 128 but higher in pyrite content

Cu	1.23%
Cu (Acid-Soluble)	0.17%
Fe	7.95%
S	10.1%

Lot 130 — This sample was a composite of daily concentrator feed samples, and could be described as medium in its clay and talc composition.

Cu (Total)	1.09%
Cu (Acid-Soluble)	0.36%
Fe	7.55%
S	3.23%

The ore body from which these samples were taken is that of a major copper producer in the United States and the producer's standard laboratory tests gave the

following metallurgy. All three samples contain varying amounts of talc and/or clay.

Lot 128	
Concentrate — % Cu	13.2%
% of Total Cu in Concentrate	75.8%
Rougher Tailings — % Cu	0.24%

Lot 126	
Concentrate — % Cu	8.85%
% of Total Cu in Concentrate	74.93%
Rougher Tailings — % Cu	0.35%

Lot 130	
Concentrate — % Cu	15.3%
% of Total Cu in Concentrate	76.56%
Rougher Tailings — % Cu	0.27%

The foregoing may be considered as indicative of the best metallurgy obtainable on these ores in accordance with the established practice of this operator and the recoveries indicated were accepted as the maximum possible recovery for these ores at the concentrate grades obtained.

A surprising thing concerning the process of the present invention is that it produces both an increase in grade and an increase in recovery.

In the examples, in all cases but one grinding was carried out on 800 gram charges in a laboratory rod-mill to a screen analysis of approximately 100 mesh, and at a pulp density of 50 percent solids. The pulp was transferred directly from the rod mill to a 600 gram laboratory Fagergren cell, and all conditioning and flotation was carried out in this cell. No desliming stage was used.

All cleaning steps were carried out in a Denver 500 gram cell.

Except where noted in the specific tests the rougher flotation time was 7 minutes, and in the cleaners the float was continued in each case to final clean-up with no set time. The average cleaner float time was about 4 minutes. The rougher float time is exceptionally low, as with this class of mineral, for any degree of recovery in a conventional circuit, a minimum float time of 15 minutes would be required.

With an 800 gram charge to a 600 gram Fagergren cell, the density of the pulp was approximately 30 percent solids. This is an unusual feature of the invention in view of the talc and clay contents of the ores treated. On normal ores, without talc or clay minerals present, the flotation density in current plant practice is approximately 25 percent solids. At this lower density, for the same flotation time, more cells would be required not only raising capital plant costs but also operating costs in power and maintenance.

In the following series of tests the rougher tailings and first cleaner tailings are shown only for comparative metallurgical reasons, and where the ratio of concentration at this point in the circuit is in the range of about 10 — 12 to 1. In all cases, on the three samples, complete circuits are described illustrating the production of concentrate grades in excess of 20 percent copper.

The copper analysis was done by the current standard atomic absorption method with a number of the testing programme samples check analyzed by the supplier of the various ore samples. Where the term "corrected" is used, this indicates application of the correction factor necessary to relate the laboratory analysis to the check analyses of the supplier. To the combined rougher and first cleaner tailing, to correct to the sup-

plier's analysis, the rule of thumb correction factor is plus 0.01 percent copper.

In Examples 2 to 7 inclusive, there was an average of 2 ½ percent of the total copper in solution. Except in the tests showing the solution analysis, all analyses are on the solids only.

EXAMPLE 2

A series of tests was run which included an acid conditioning cycle prior to the activation of the copper minerals with the collector.

In each case, after the acid cycle, the pH was increased with lime to give a pH of approximately 11.6 in the activation cycle with xanthate.

The lime cycle was 2 minutes, followed by 19 minutes conditioning with 0.22 lbs. per ton Z6 stage added, and this cycle was followed with the addition of 7.5 lbs. per ton of sodium silicate for 5 minutes with three drops of pine oil added in the last 2 minutes. The rougher float was 7 minutes with the addition of 0.025 lbs. Z6 per ton and one drop of pine oil.

The first cleaner was identical in all cases as to reagent balance and time of conditioning.

The following table shows the comparative results.

Test number	Grinding circuit		First cycle			Rougher plus 1st cleaner tailings analysis, percent	
	Reagents added, lbs./ton	pH, end	Reagents added, lbs./ton	pH		Wt.	Cu
				Begin	End		
1.....	Soda ash, 0.625 lbs....	7.7	H ₂ SO ₄ , 2.5 lbs....	4.7	5.4	90.1	0.057
2.....	Lime, 0.20 lbs.....	8.0	H ₂ SO ₄ , 2.5 lbs....	4.6	5.5	90.8	0.095
	H ₂ SO ₄ , 2.5 lbs.....	5.5	Nil.....	5.5	5.5	90.0	0.050

It will be noted that with the small amount of sulphuric acid added to the grinding stage there is a pronounced reduction in tailings loss. It was at first thought that this could be due to more acid soluble copper going into solution. However, later work did not substantiate the theory. It was a marked improvement in the floated copper minerals.

It will be noted in Test 3 that there was no change in pH from the beginning to the end of the acid conditioning cycle. With ores containing more acid soluble constituents the pH in the acid addition stage could rise to 7.0 or alkaline, depending on the amount of acid used and the natural pH of the pulp.

Lot 130

EXAMPLE 3

The third test in Example 2 using an acid stage in the grinding circuit with 10 minutes conditioning following the grinding stage of a pH of 5.5 resulted in a rougher plus first cleaner tailing rejection of 90.9 percent by weight analyzing 0.050% Cu. In this example, following the acid cycle, the pH was raised to the optimum, approximately 11.6, with lime and the dispersing agent was added at the same time followed by the xanthate activation cycle and then flotation. The tailings rejection was 91.25 percent by weight analyzing 0.062 percent Cu or a small increase in tailings loss compared to the circuit which added the dispersant following the xanthate activation cycle.

EXAMPLE 4

This example is a duplicate of the third test in Example 2 with the exception that following the conditioning

stage at a pH of 5.5 the pH was raised with lime to 7.7 and the pulp then dispersed with sodium silicate prior to the raising of the pH to 11.6, followed by activation of the copper minerals with xanthate. The tailings rejection in this test was 91.3 percent by weight analyzing 0.065 percent Cu as against the tailings loss in the comparative test of 0.050 percent Cu, again illustrating the effect of the use of a dispersing stage prior to the activation cycle with xanthate.

EXAMPLE 5 (TEST 64)

During the grinding stage of this example, 3 ½ lbs. per ton of sulphuric acid was added resulting in an end pH of approximately 5.1. Following the grinding stage the pulp was conditioned for ten minutes with no further reagent addition. There was no change of pH during this cycle. At the end of 10 minutes 2.0 lbs. of lime and 0.255 lbs. of Z6 per ton respectively were added to the pulp raising the pH to approximately 6.5. The pulp was conditioned for ten minutes and at the end of this period lime was added bringing the pH of the pulp up to 11.55 and the pulp was conditioned in this cycle for 19 minutes. The end pH was 11.45. Following this cycle 12.25 lbs. per ton of sodium silicate was added

together with three drops of pine oil for the last 2 minutes of the 5 minute conditioning cycle. When the sodium silicate addition was made the pH of the pulp immediately dropped from 11.45 to 11.15. The flotation stage was the same as that used in the previous examples. The tailings rejection was 89.4 percent by weight analyzing 0.048 percent total Cu and 0.013 percent acid soluble Cu. Samples of the total solution from the rougher and first cleaner tailings was analyzed for copper and contained 2.2 percent of the total copper (6.7 percent of the acid soluble copper). As the solid tailings contained 3.2 percent of the acid soluble copper the recovery of the acid soluble copper in the cleaner concentrate was 90.1 percent.

EXAMPLE 6 (TEST 65)

This example is a duplicate of the previous example with the exception that following the first acid conditioning stage the pH of the pulp was raised to 8.0 and it was conditioned with the xanthate at this point for 10 minutes. The tailings rejection was 90.5 percent by weight analyzing 0.051 percent total copper and 0.012 percent acid soluble copper. The acid soluble copper in solution is equal to 7.6 percent of the total acid soluble copper, and in the solids tailings is 3.0 percent for a total of 10.6 percent so that 89.4 percent of the acid soluble copper is in the cleaner concentrate product.

EXAMPLE 7 (TEST 63)

For this example Lot 128 ore was used and a 1,000 gram sample was ground for 12 minutes at 50 percent solids with 2 lbs. per ton of sulphuric acid. After 10 minutes of conditioning following grinding without the

addition of reagents the pH was 4.5. The pH was raised to 11.6 with the addition of 5.65 lbs. per ton of lime and 0.225 lbs. of Z6 were added for a 19 minute conditioning period at the end of which the pH was 11.45. 12.25 lbs. per ton of sodium silicate was added together with three drops of pine oil and the pH dropped to 11.10. A flotation cycle similar to that of Example 5, but carried out at approximately 33 percent solids, produced a combined rougher plus first cleaner tailings containing 88.4 percent by weight of the solids and analyzing only 0.042 percent of the total copper, which is most remarkable metallurgy for such a high pulp density.

As previously mentioned in the foregoing tests about 2 ½ percent of the total copper reported in the tailings solution. In order to filter the tailing it is helpful to flocculate them by making them acid with sulphuric acid. Surprisingly, although the total time involved from the acidulation of the flotation tailings in the flotation cell to the completion of filtration was 2 minutes or less, I have found that this copper actually goes into solution during that period. As the following tests will illustrate the tailings solution at the end of flotation in the alkaline circuit contains no dissolved copper at all.

By employing the tailings filtrate as make-up solution for the grinding of fresh feed material in the acid circuit it is possible to recover most of this sulphuric acid soluble copper by flotation since when the product of the wet grinding circuit is made alkaline the dissolved copper completely precipitates and floats with the copper sulphides and other copper minerals.

This phenomenon presents a simple and effective manner for rendering sulphuric acid soluble copper minerals amenable to sulphhydryl anionic collector flotation regardless of whether or not the ore contains clay or talc slimes rendering necessary the use of dispersants and flocculants in the manner already described.

It appears that for effective flotation of the combined acid soluble and sulphide copper minerals present in ores such as those to which reference has been made it is not necessary that all of the acid soluble copper minerals should be put into solution and precipitated. It is sufficient if only a small percentage of the acid soluble copper minerals go into solution and are precipitated.

EXAMPLE 8

Stage I

A 1,000 gram sample of the Lot 128 ore previously described was ground in a laboratory rod mill for 12 minutes at a pulp density of 50 percent solids with the addition of 2.0 lbs. per ton of H₂SO₄. Following grinding the pulp was transferred to a laboratory Fagergren cell where it was conditioned for 10 minutes without any further reagent addition. The pH at the beginning and end of this conditioning period was 5.0.

Stage II

13.0 lbs. per ton of Ca(OH)₂ was added and conditioned for 5 minutes. The beginning pH was 12.20 and the final pH was 12.25.

Stage III

2.2 lbs. per ton of H₂SO₄ and 0.18 lbs. per ton of Z6 were then added and the pulp was conditioned for 15 minutes. The beginning pH of this stage was 11.65 while that at the end was 11.40.

Stage IV

12.0 lbs. per ton of sodium silicate were then added as a dispersing agent together with 4 drops of pine oil and the pulp was conditioned for a further 5 minutes. Throughout this stage the pH was 11.10.

The rougher concentrate was then floated during a period of 7 minutes with the addition of 0.02 lbs. per ton of Z6 and one drop of pine oil. A small amount of sulphuric acid and "Separan" (a synthetic flocculant manufactured by Dow Chemical Co.) was added to the rougher tailings and the latter was filtered.

The rougher concentrate was resuspended in a Denver cell and conditioned for 3 minutes with the addition of 0.02 lbs. per ton of Z6 and 1.2 lbs. per ton of sodium silicate. The thus conditioned pulp was then floated to cleanup.

The tailings were treated in the same manner as the rougher tailings and in each case there was less than 2 minutes total contact time in the cell and the filter together.

The head sample of this ore was 0.95 percent total Cu and 0.23 percent acid soluble Cu.

The rougher plus first cleaner tailings analysis was as follows:

30	% Weight	87.7
	% Total Cu Analysis of solids	0.040
	% Acid Soluble Cu analysis of solids	0.019
	% of total Cu in the solutions from the rougher plus first cleaner tailings	3.0
35	% of original acid soluble copper in the solutions	12.5
	% of total Cu in the first cleaner concentrate	93.3

For this type of ore the recovery of 93.3 percent of the total copper in the first cleaner concentrate is an amazingly high recovery considering that only 3.7 percent of the total copper was in the solids tailings.

It will also be noted that even with one of the conditioning stages at a pH in excess of 12.0, it had no harmful effect on the final flotation results.

This may be particularly important where molybdenum sulphide minerals may occur in the same deposits as the copper minerals, producing relatively high recovery of the molybdenum

EXAMPLES 9, 10 AND 11

This series of tests used the same ore and circuitry as Example 8, to determine the effect of various alkali agents in combination with Ca(OH)₂, and also omitting the acid addition in Stage III.

Stage II in all tests was taken as closely as possible to the same pH, that is, 11.65.

The following table shows the comparative results and the alkali agents used in Stage II.

Example number	Alkali agents, lbs./ton				Rougher plus 1st cleaner tailings analysis, percent			
	CaO	Na ₂ CO ₃	NH ₄ OH	NaOH	Solids		Solutions	
					Wt.	Total Cu	A.S.* Cu	Total Cu
9.....	8.2	4.0			88.0	0.063	0.028	2.0
10.....	8.6		2.0		87.6	0.055	0.018	4.3
11.....	6.4			2.0	87.7	0.047	0.022	2.0

*A.S.=Acid soluble Cu.

It will be noted that all combinations are effective with the sodium hydroxide being outstanding.

EXAMPLE 12

In this example the same ore and circuitry was used as in Example 8. 3.2 lbs. per ton of H_2SO_4 was added to the grinding stage and 11.0 lbs. per ton of $Ca(OH)_2$ to Stage II.

The rougher and first cleaner tailings were settled with a flocculant only, no sulphuric acid being used. The solutions at all stages were sampled and analyzed for copper.

The following table shows the results obtained:

Stage No.	Description	pH		Copper in Sol'n Mgs./L	Total Ms
		Begin	End		
I	Grinding and conditioning	5.4	5.1	1.8 3.1 End	2.7 4.7
II	Lime addition	12.2	12.2	Nil	Nil
III	Collector addition	12.2	11.6	Nil	Nil
IV	Dispersant addition	11.25	11.2	Nil	Nil
	End of Rougher Flotation			Nil	Nil
	End of First Cleaner Float			Nil	Nil

The analysis of the rougher plus first cleaner tailings was 0.08 percent Total Cu, and 0.057 percent acid soluble Cu.

The combined tailings weight was 90.5 percent.

The recovery of the acid soluble copper in the first cleaner concentrate was 77.6 percent.

The surprisingly low amount of copper in solution in Stage I followed by the high percentage of acid soluble copper retained in the first cleaner concentrate were the outstanding features of this test, together with total precipitation of the copper in Stage II that was in solution in Stage I.

EXAMPLES 13, 14 AND 15

In this series of tests, the same ore and circuitry was used as in Example 8. In the test prior to Example 13, 10 lbs. per ton of H_2SO_4 was added to the rougher tailings, and 2.8 lbs. per ton of H_2SO_4 was added to the first cleaner tailings. Following filtering of these tailings, 1,000 cc's of the solution was recovered and added to the grinding stage of Example 13. The same procedure was followed with Examples 14 and 15, with the combined tailings solution from Example 13 used in the grinding stage of Example 14, and the combined tailings solution of Example 14 used in the grinding stage of Example 15.

The objects of these tests was to determine whether or not the copper dissolved in the tailings would precipitate and float with the solids copper in the flotation circuit.

The solutions were sampled in all of the stages of the three continuous tests.

The following were the results obtained:

Stage number	Example number										
	Average pH			Solutions Cu. mgs./L			Solids tailings analysis, percent				
							T Cu			A.S. Cu	
	13	14	15	13	14	15	13	14	15	13	14
I	5.3	5.3	5.2	8.9	7.8	5.7					
II	11.8	11.8	11.8	0.0	0.0	1.2					
III	11.7	11.65	11.65	0.0	0.0	0.0					
IV	11.3	11.3	11.25	0.0	0.0	0.0					
Rougher plus 1st cleaner tailings				144	135	140	0.060	0.057	0.0510	0.026	0.026

NOTE: The percent A.S. Cu in the rougher plus 1st cleaner tailings in Example 15 was 0.017.

The surprising phenomenon in the series of tests was the large precipitation of the copper dissolved in the tailings at a pH of 5.0 to 5.5 when re-circulated to the grinding circuit and transferred to the flotation cell.

The second surprising factor was the flotation of this copper following its precipitation with approximately 93 percent of the total acid soluble copper reporting in the first cleaner concentrate.

The third surprising factor was that with but an indicated 20 percent of the total acid soluble copper circulated to the grinding circuit from the tailings, approximately 93 percent of the total acid soluble copper reports in the first cleaner concentrate.

Further testing was carried out with pH's as low as 2.0 in Stage I, but gave no indication of improved results over the prior described circuit indicating the presence of sufficient ferric sulphate to enable optimum metallurgy with a minimum pH in Stage I in the upper part of the range of 0.5 to 5.5.

EXAMPLE 16 — Ore Lot 130 as previously described.

In this example sulphur dioxide has been used in Stage I to replace sulphuric acid, with approximately 60 percent of the SO_2 added to the grinding circuit and 40 percent to the conditioning cycle following grinding. The SO_2 was added as a near saturated solution, thus forming a mixture of sulphurous acid and SO_2 .

In Stage II the alkaline agent $Ca(OH)_2$ and the collector Z6 were added simultaneously.

In Stage III the dispersing agent, Na_2SiO_3 , was added together with the frother, followed by the rougher float.

The first cleaner float was preceded by a 3 minute conditioning cycle using 0.75 lbs. of Na_2SiO_3 per ton, and 0.025 lbs. of Z6 per ton.

The first cleaner was insufficient to depress a satisfactory percentage of the remaining slimes in the rougher concentrate, and a second stage of cleaning was required using a 2 minute pre-conditioning period with 0.5 lbs. per ton of Na_2SiO_3 .

This illustration may be considered as a three stage preconditioning circuit to the rougher float, and an additional two stage dispersion circuit in the cleaners, to obtain satisfactory copper recovery in a concentrate containing an acceptably low clay content.

The following is the data on this example:

Stage I

To grinding circuit — 8.1 lbs./ton of SO_2 — 12 minutes

To conditioning — 4.7 lbs./ton of SO_2 — 10 minutes

pH at end grinding — 5.9

pH begin and end conditioning — 4.8 and 5.4 respectively

Stage II

20 minutes conditioning with addition of 22 lbs./ton of $Ca(OH)_2$ and 0.225 lbs. Z6/ton.

pH begin and end conditioning — 11.7 and 11.5 respectively.

Stage III

4 minutes conditioning with addition of 12.5 lbs./ton of Na_2SiO_3 , and two drops of pine oil.

Rougher flotation.

The following results were obtained:

Rougher plus 1st Cleaner Tailings	
% Weight	87.5
% Total Cu analysis	0.068
% Acid Soluble Cu analysis	0.033
% Total Cu in 1st Cleaner concentrate	94.5%
% Acid Soluble Cu in 1st Cleaner concentrate	89.5%
% Soluble Cu in solutions	Nil
Rougher plus first plus second cleaner Tailings:	
% Weight	92.5
% Total Cu in second cleaner concentrate	93.7

This test illustrated the following:

- The satisfactory substitution of SO_2 for H_2SO_4 in my process.
- The simultaneous addition of the alkaline agent and the collector following the acid conditioning stage.
- The use of three stage circuit prior to rougher flotation and the necessity of two stages of dispersion following the rougher flotation.
- The complete precipitation of any acid soluble copper that had gone into solution in the acid cycle.
- The high degree of flotability of the precipitated copper in conjunction with the sulphides.

Although on this type of ore a mixture of sulphurous acid and sulphur dioxide gave satisfactory results, I prefer to use sulphuric acid as it eliminates handling problems, and further, on other types of copper ores sulphurous acid or sulphur dioxide may have unforeseeable detrimental metallurgical effects.

EXAMPLE 17 — Ore Lot 130 as previously described.

This example illustrates the use of a three stage conditioning circuit prior to rougher flotation, using SO_2 in place of H_2SO_4 .

The following is a description and data on the circuit used:

Grinding Circuit — 12 minutes

No reagents added

pH at end — 7.2

Stage I — 10 minutes

conditioning with addition of 12.8 lbs./ton SO_2 and

0.625 lbs./ton of dispersant, lignin sulphonate.

pH begin — 4.0, and end — 4.1.

Stage II — As in Example 16

Stage III — As in Example 16

Rougher float.

Two cleaners as in Example 16.

At the end of Stage I the copper in solution was less than 5 percent of the total acid soluble copper and was totally precipitated in Stages II and III.

The metallurgy was practically identical to Example 16.

This test illustrated the following:

- Using an acid circuit in the grinding stage could be eliminated, unless it was desirable from an operating point of view.
- A dispersant could be used in the acid cycle where necessary without detrimental effects to the copper recovery.

EXAMPLE 18 — Ore Lot 130 as previously described.

This example illustrates the use of a two-stage conditioning system wherein a single acid stage is used and a single alkaline stage is used, prior to rougher flotation.

Two cleaners were used with dispersal of the pulp between each cleaner.

Grinding circuit — 12 minutes,
no reagents added.

pH at end — 7.2

Stage I — 20 minutes conditioning,

added 12.5 lbs./ton H_2SO_4 and 0.625 lbs./ton disper-

sant, tetra sodium pyrophosphate.

pH begin — 1.8, end — 3.6.

Stage II — 20 minutes conditioning,

added 22.7 lbs./ton $\text{Ca}(\text{OH})_2$, 0.25 lbs./ton Na_2SiO_3 , and two drops of pine oil, at end prior to rougher

flotation.

pH begin — 11.9, end — 11.4.

Rougher flotation followed by two stages of cleaning as in Examples 15 and 16.

The rougher plus first cleaner tailings was 86.4 percent by weight analyzing 0.057 percent total Cu and 0.023 percent acid soluble Cu for a recovery in the first cleaner concentrate of 95.5 percent of the total copper and 94.5 percent of the acid soluble copper. There was no soluble copper in the tailings solutions.

This can be considered outstanding metallurgy for such a type of ore, particularly the flotation of the acid soluble copper.

The foregoing method of treating sulphuric acid soluble copper minerals whereby the copper in solution following an acid stage of the process is totally precipitated in a subsequent alkaline stage offers a very convenient and economic means of recovering sulphuric acid soluble copper contained in the tailings. It is possible of course to acidulate the tailings, putting the sulphuric acid soluble copper almost instantly into solution, filter, or thicken and employ the filtrate as make-up solution for an acid grinding stage at the head of my process. However, filtration is a relatively expensive operation and some mill operators prefer not to grind in decidedly acid circuits because of increased steel losses and possible scrap losses brought about by corrosion. Thus, an alternative is to pass the tailings to a tailings pond where they may be acidulated, and return the liquor overflow, which may contain dissolved copper and/or ferric sulphate to an acid stage of conditioning which follows what may be a neutral or slightly alkaline grinding circuit. This alternative has outstanding merit in the case of operators having existing tailings dams and who already are recovering soluble copper from these dams by passing the tailings liquor through a special precipitation plant.

As will be apparent from the foregoing description of the process of the invention, the process may be integrated with the grinding circuit and various alternatives are possible in each of the acid and alkaline conditioning circuits.

Alternatives in Acid Conditioning Circuit

In using the invention the acid stage may be applied in a number of different ways. Where it is applied in the grinding circuit, as previously described, acidified tailings solution or alternately, acidified leach dump solution, may be fed into the plant circuit.

In the use of a conventional two-stage grinding circuit, as shown in FIG. 3, this acidified solution may be fed as the make-up solution to the primary mill feed. Alternately, if the drop in pH effected in the primary mill would give problems in maintenance in the mill or in pulp handling, I would prefer to add the acidified solution to the discharge of the secondary mill or to the discharge of any other grinding unit which is in closed circuit with a classifier. The discharge from such a mill will normally be in a range of 55-65 percent solids and diluted to 15-40 percent solids prior to classification. As a dilutant, the acidified mill solution, with or without additional acid agent, may be added and I would prefer a conditioning cycle here wherein initially the first two conditioners have a residence time of between 60 to 90 seconds to assure the maximum pH drop for this initial period of conditioning (see FIG. 1). Following the 60 to 90 seconds retention time, the pulp will flow to one or more additional conditioners for a sufficient period of time for the pH to rise to its natural end point due to the acid consuming constituents of the pulp. This pH would normally be in the range of 4.5 to possibly as high as 7. Thus, prior to the classifier, the pulp pH will have risen to the point where its acid effect on maintenance of the equipment would be at a minimum. Leaving the classifier the pulp overflow would go to one or more additional stages of conditioning. The pulp underflow would be returned to the feed end of the grinding unit. Where acidified solution from either the tailings or other sources is fed to the circuit it may require the addition of further acid agent for optimum final metallurgical results. In the case where the acidified solution is added to the primary grinding mill there would normally be a gradual rise in pH from the discharge of the mill throughout the remaining part of the grinding circuit.

Summarizing the acid conditioning stage, the acid agents that may be used are sulphuric acid, sulphur dioxide or sulphurous acid, solution from acid treated tailings, solution from acid treated leach dumps, or any combination of the above as practical and economical.

Following the acid cycle in which the end pH will normally be in the range of 4.5 to 6.0 it may be beneficial to add part of the collector to a second conditioning stage at a pH of from about 5 to a pH of about 8. This is particularly so with copper ores containing pyrite and wherein part of the copper values are closely associated with the pyrite which may require final ultra fine grinding for their liberation, and I prefer to float this pyrite in my rougher float circuit. If the stage is omitted I prefer to go directly from the end of the acid cycle to a pH in excess of 8.5. For automatic pH control of this circuit I prefer to use two conditioners at the beginning of the alkaline circuit with a retention time of approximately 3 to 4 minutes, wherein the alkaline agent is all fed to the first conditioner and automatically controlled by a pH meter on the discharge of the second conditioner. This may be accomplished by the use of a variable speed reagent pump or a variable speed belt conveyor feeding the reagent in dry form. I prefer to add my collector to the second conditioner and in some cases, if required, also the dispersing agent. The frother would be added to the last conditioner at the end of this conditioning cycle. Also, if a flocculant is required, I prefer to add the flocculant to the last conditioner of this cycle.

What I claim as my invention is:

1. A process for the flotation recovery of copper values from ores containing copper values in the form of at least one sulphide copper mineral and at least one sulphuric acid soluble copper mineral using a sulphhydryl anionic collector comprising: subjecting a pulp of the ore to acid treatment by conditioning the pulp with addition of an acid agent, the acid agent being selected from the group consisting of sulphuric acid, sulphurous acid and sulphur dioxide, whereby the copper values of the ore are conditioned within an acidic pH range during at least part of said acid treatment for subsequent flotation at an alkaline pH; subsequently subjecting the thus conditioned pulp containing the copper sulphide values and sulphuric acid soluble copper values to alkaline treatment which includes at least one stage of alkaline agitation conditioning in the presence of at least one alkaline agent selected from the group consisting of lime, calcium hydroxide, sodium carbonate and combinations of lime or calcium hydroxide with sodium hydroxide, sodium carbonate or ammonium hydroxide in the pH range of from about 8.5 to about 12.3 in the presence of a sulphhydryl anionic collector to enable the effective recovery by flotation of copper sulphide values and sulphuric acid soluble copper values, such alkaline conditioning being carried out in the presence or absence of a suitable frother; and subsequently in the presence of a suitable frother subjecting the pulp to froth flotation in a pH range of from about 8.5 to about 12.0 to produce a concentrate of copper sulphide values and sulphuric acid soluble copper values.

2. A process according to claim 1 wherein the sulphhydryl anionic collector is a xanthate.

3. A process as claimed in claim 1 wherein the acid agent is in diluted form as acid agent diluted with water, acidified mill solution, solution from acid treated tailings, solution from acid treated leach dumps or any combination of any of the foregoing with any other or with additional acid agent.

4. A process as claimed in claim 1 wherein the acid treatment is carried out in a continuous circuit and the addition of an acid agent is made in a continuous manner in a predetermined amount per ton of dry solids in the pulp fed to said circuit at at least one point in said circuit.

5. A process as claimed in claim 1 wherein the acid treatment is carried out in a continuous circuit and the addition of acid agent is made in a continuous manner at one or more points in the circuit, the amount of acid agent added at each said point being the amount required to maintain the pH at a control point downstream of the point of addition of acid agent at a predetermined value.

6. A process as claimed in claim 1 wherein the acid treatment is carried out in a continuous circuit and the addition of acid agent is made in a continuous manner at at least two points in the circuit, partly in predetermined amount per ton of dry solids in the pulp fed to said circuit and partly in an amount required to maintain the pH at a control point in said circuit at a particular value.

7. A process as claimed in claim 1 wherein the acid agent is sulphuric acid.

8. A process as claimed in claim 4 wherein the acid agent is sulphuric acid, and the predetermined amount per ton of dry solids in the pulp fed to said circuit is

from about 2 to about 16 lbs. calculated on the basis of 100 percent sulphuric acid.

9. A process as claimed in claim 1 wherein the acid agent is sulphuric acid and said acidic pH range is from about 1.4 to about 5.5.

10. A process as claimed in claim 1 wherein the ore contains a relatively high amount of acid consuming constituents and during said acid treatment subsequent to the copper values of the ore being conditioned within an acidic pH range during part of said acid treatment, conditioning is continued as the pH is permitted to rise to 7 or slightly higher due to the presence of said acid consuming constituents.

11. A process as claimed in claim 1 wherein said alkaline treatment comprises one stage of agitation conditioning at a pH of from about 8.5 to about 10.5 in the presence of a sulfhydryl anionic collector and another stage of agitation conditioning at a pH of from about 10.5 to about 12.0 in the presence of a sulfhydryl anionic collector.

12. A process as claimed in claim 1 wherein a dispersing agent is present in said pulp during at least a final portion of said alkaline treatment.

13. A process as claimed in claim 1 wherein during the acid treatment the pulp density is from about 20 percent to about 55 percent solids, during the alkaline treatment is from about 20 to 55 percent solids, and at flotation the pulp density is from about 20 percent to about 40 percent solids.

14. A process as claimed in claim 1 wherein the alkaline treatment is carried on in a continuous circuit and the alkaline agent is added at at least one point in said circuit in an amount required to maintain a predetermined pH at a control location downstream of said point.

15. A process for the flotation recovery of copper values from ores containing copper values in the form of at least one sulphide copper mineral and at least one sulphuric acid soluble copper mineral using a sulfhydryl anionic collector comprising: preparing a pulp of the ore by grinding the ore to flotation feed size in a wet grinding circuit containing at least one stage of wet grinding; subsequently, subjecting the pulp of the ore to acid treatment by conditioning the pulp with addition of an acid agent, the acid agent being selected from the group consisting of sulphuric acid, sulphurous acid and sulphur dioxide, whereby the copper values of the ore are conditioned within an acidic pH range during at least part of said acid treatment for subsequent flotation at an alkaline pH; subsequently subjecting the thus conditioned pulp containing the copper sulphide values and sulphuric acid soluble copper values to alkaline treatment which includes at least one stage of alkaline agitation conditioning in the presence of at least one alkaline agent selected from the group consisting of lime, calcium hydroxide, sodium carbonate and combinations of lime or calcium hydroxide with sodium hydroxide, sodium carbonate or ammonium hydroxide in the pH range of from about 8.5 to about 12.3 in the presence of a sulfhydryl anionic collector to enable the effective recovery by flotation of copper sulphide values and sulphuric acid soluble copper values; said alkaline conditioning being carried out in the presence or absence of a suitable frother; and subsequently in the presence of a suitable frother subjecting the pulp to froth flotation in a pH range of from about 8.5 to

about 12.0 to produce a concentrate of copper sulphide values and sulphuric acid soluble copper values.

16. The process of claim 15 wherein subsequent to the wet grinding circuit, the density of the pulp is adjusted to a desired density at one or more points prior to and during the process by dilution, thickening, or thickening and dilution to a pulp density within the range of from about 20 to about 55 percent solids.

17. A process as claimed in claim 16 wherein during the acid treatment the pulp density is from about 20 percent to about 55 percent solids, during the alkaline treatment is from about 20 to 55 percent solids, and at flotation the pulp density is from about 20 percent to about 40 percent solids.

18. A process as claimed in claim 17 wherein the acid agent is in diluted form as acid agent diluted with water, acidified mill solution, solution from acid treated tailings, solution from acid treated leach dumps or any combination of any of the foregoing with any other or with additional acid agent.

19. A process as claimed in claim 15 wherein the acid treatment is carried out in a continuous circuit and the addition of an acid agent is made in a continuous manner in a predetermined amount per ton of dry solids in the pulp fed to said circuit at at least one point in said circuit.

20. A process as claimed in claim 15 wherein the acid treatment is carried out in a continuous circuit and the addition of acid agent is made in a continuous manner at one or more points in the circuit, the amount of acid agent added at each said point being the amount required to maintain the pH at a control point downstream of the point of addition of acid agent at a predetermined value.

21. A process as claimed in claim 15 wherein the acid treatment is carried out in a continuous circuit and the addition of acid agent is made in a continuous manner at at least two points in the circuit, partly in predetermined amount per ton of dry solids in the pulp fed to said circuit and partly in an amount required to maintain the pH at a control point in said circuit at a particular value.

22. A process as claimed in claim 15 wherein the alkaline treatment is carried on in a continuous circuit and the alkaline agent is added at at least one point in said circuit in an amount required to maintain a predetermined pH at a control location downstream of said point.

23. A process for the flotation recovery of copper values from ores containing copper values in the form of at least one sulphide copper mineral and at least one sulphuric acid soluble copper mineral using a sulfhydryl anionic collector comprising:

1. subjecting a pulp of the ore to acid treatment with sulphuric acid in the amount ranging from about 2.0 to 16.0 pounds of sulphuric acid based on 100 percent sulphuric acid per ton of solids in the pulp for a period of time ranging from at least about 4 minutes to about 20 minutes whereby the copper values of the ore are conditioned for subsequent flotation in an alkaline circuit;
2. adding lime to the pulp at the end of the acid conditioning treatment in an amount sufficient to raise the pH of the pulp to a pH ranging from about 8.5 to about 10.5 and adding a sulfhydryl anionic col-

lector to condition the pulp under conditions of agitation:

3. continuing such conditioning with agitation for a period of time ranging from about 3 to about 9 minutes;
4. adding additional lime at the end of the conditioning stage (3) in an amount sufficient to raise the pH of the pulp to a range from about 10.9 to about 11.9 with or without additional sulfhydryl collector and further conditioning with agitation for a period of at least 4 minutes up to about 20 minutes;
5. adding frother to the pulp under conditions of agitation during or after the conditioning stage (4) and subjecting the pulp to froth flotation in a pH range of from about 10.9 to about 11.9 to produce (a) a flotation concentrate enriched in copper sulphide values and sulphuric acid soluble copper values; and (b) a waste product impoverished in copper values.

24. A process for the recovery of copper values by flotation from ores containing copper values in the form of at least one sulphide copper mineral and at least one sulphuric acid soluble copper mineral using a sulfhydryl anionic collector, said process comprising: subjecting a pulp of the ore to be treated to conditioning in at least one acid conditioning stage wherein an acid agent selected from the group consisting of sulphuric acid, sulphurous acid and sulphur dioxide is added to the pulp for conditioning of the pulp within a pH range of about 1.4 to about 5.5 during at least a portion of such conditioning stage, whereby the copper values are conditioned for subsequent flotation in an alkaline circuit; subsequently subjecting the thus conditioned pulp containing the copper sulphide values and sulphuric acid soluble copper values to alkaline treatment in an alkaline conditioning circuit and adding to the pulp an agitation conditioning with at least one alkaline agent selected from the group consisting of lime, calcium hydroxide, sodium carbonate and combinations of lime or calcium hydroxide with sodium hydroxide, sodium carbonate or ammonium hydroxide in at least one alkaline agitation conditioning stage in the pH range of about 8.5 to about 12.3 in the presence of a sulfhydryl anionic collector to enable the effective recovery by flotation of copper sulphide values and sulphuric acid soluble copper values; and subsequently in the presence of a suitable frother subjecting the pulp to froth flotation in the pH range of about 8.5 to about 12.0 to produce a concentrate of copper sulphide values and sulphuric acid soluble copper values.

25. A process for the flotation recovery of copper values from ores containing copper values in the form of at least one sulphide copper mineral and at least one sulphuric acid soluble copper mineral using a sulfhydryl anionic collector comprising: preparing a pulp of the ore for subsequent flotation of the copper values by grinding the ore to flotation feed size in a wet grinding circuit containing at least one stage of wet grinding; in at least one of the said stages of wet grinding subjecting the pulp of the ore to acid treatment by the addition of an acid agent to said grinding stage, the acid agent being selected from the group consisting of sulphuric acid, sulphurous acid and sulphur dioxide, whereby the copper values of the ore are conditioned within an acidic pH range during at least part of said acid treatment for subsequent flotation at an alkaline pH; subsequently subjecting the thus conditioned pulp contain-

ing the copper sulphide values and sulphuric acid soluble copper values to alkaline treatment which includes at least one stage of alkaline agitation conditioning in the presence of at least one alkaline agent selected from the group consisting of lime, calcium hydroxide, sodium carbonate and combinations of lime or calcium hydroxide with sodium hydroxide, sodium carbonate or ammonium hydroxide in the pH range of from about 8.5 to about 12.3 in the presence of a sulfhydryl anionic collector to enable the effective recovery by flotation of copper sulphide values and sulphuric acid soluble copper values; said alkaline conditioning being carried out in the presence or absence of a suitable frother; and subsequently in the presence of a suitable frother subjecting the pulp to froth flotation in a pH range of from about 8.5 to about 12.0 to produce a concentrate of copper sulphide values and sulphuric acid soluble copper values.

26. A process as claimed in claim 25 wherein alkaline agent is added prior to the adjusting of the pulp density for subsequent conditioning.

27. A process as claimed in claim 25 wherein the acid agent is in diluted form as acid agent diluted with water, acidified mill solution, solution from acid treated tailings, solution from acid treated leach dumps or any combination of any of the foregoing with any other or with additional acid agent.

28. The process of claim 25 wherein subsequent to the wet grinding circuit, the density of the pulp is adjusted to a desired density at one or more points during the process by dilution, thickening, or thickening and dilution to a pulp density within the range of from about 20 to about 55 percent solids.

29. A process as claimed in claim 26 wherein the adjusting of the pulp density for subsequent conditioning includes addition of alkaline agent.

30. A process as claimed in claim 28 wherein during the acid treatment the pulp density is from about 15 percent to about 65 percent solids, during the alkaline treatment is from about 20 to 55 percent solids, and at flotation the pulp density is from about 20 percent to about 40 percent solids.

31. A process for the flotation recovery of copper values from ores containing copper values in the form of at least one sulphide copper mineral and at least one sulphuric acid soluble copper mineral using a sulfhydryl anionic collector comprising: preparing a pulp of the ore for subsequent flotation of the copper values by grinding the ore to flotation feed size in a wet grinding circuit containing at least one stage of wet grinding; in at least one of the said stages of wet grinding subjecting the pulp of the ore to acid treatment by the addition of an acid agent to said grinding stage; and continuing said acid treatment in at least one conditioning state subsequent to the grinding circuit with or without further addition of acid agent, the acid agent being selected from the group consisting of sulphuric acid, sulphurous acid and sulphur dioxide, whereby the copper values of the ore are conditioned within an acidic pH range during at least part of said acid treatment for subsequent flotation at an alkaline pH; subsequently subjecting the thus conditioned pulp containing the copper sulphide values and sulphuric acid soluble copper values to alkaline treatment which includes at least one stage of alkaline agitation conditioning in the presence of at least one alkaline agent selected from the group consisting of lime, calcium hydroxide, sodium carbonate and combi-

nations of lime or calcium hydroxide with sodium hydroxide, sodium carbonate or ammonium hydroxide, in the pH range of from about 8.5 to about 12.3 in the presence of a sulfhydryl anionic collector to enable the effective recovery by flotation of copper sulphide values and sulphuric acid soluble copper values, said alkaline conditioning being carried out in the presence or absence of a suitable frother; and subsequently in the presence of a suitable frother subjecting the pulp to froth flotation in a pH range of from about 8.5 to about 12.0 to produce a concentrate of copper sulphide values and sulphuric acid soluble copper values.

32. The process of claim 31 wherein subsequent to the wet grinding circuit, the density of the pulp is adjusted to a desired density at one or more points during the process by dilution, thickening, or thickening and dilution to a pulp density within the range of from about 20 to about 55 percent solids.

33. A process as claimed in claim 32 wherein during the acid treatment the pulp density is from about 15 percent to about 65 percent solids, during the alkaline treatment is from about 20 to 55 percent solids, and at flotation the pulp density is from about 20 percent to about 40 percent solids.

34. A process as claimed in claim 32 wherein the acid agent is in diluted form as acid agent diluted with water, acidified mill solution, solution from acid treated tailings, solution from acid treated leach dumps or any combination of any of the foregoing with any other or with additional acid agent.

35. A process for the recovery of copper values from ores containing copper sulphide minerals together with at least one of the sulphuric acid soluble copper minerals in at least one stage of conditioning wherein the pH

has been lowered to within the range of from about 1.8 to about 6.0 by the addition of sulphuric acid or sulphur dioxide, subsequently agitation conditioning the resulting thus conditioned pulp in at least one alkaline stage of conditioning in the presence of a sulfhydryl anionic collector wherein the pH is in the range of from about 7.7 to about 12.3 in the presence or absence of a suitable frother and then subjecting the resulting thus conditioned pulp containing both the copper sulphide values and the sulphuric acid soluble copper mineral values to froth flotation in the presence of a suitable frother at a pH in excess of 7.7 but less than 12 to produce a concentrate of said copper values.

36. A process for the recovery of copper values from ores containing copper sulphide minerals together with at least one of the sulphuric acid soluble copper minerals using a sulfhydryl anionic collector as the collecting agent said process comprising: preparing a suitable pulp of such ore wherein the liquid contains sulphuric acid soluble copper in solution; conditioning said pulp in at least one stage of conditioning wherein the pH is within the range of about 1.8 to about 6.0; subsequently agitation conditioning the resulting thus conditioned pulp containing both the copper sulphide values and the sulphuric acid soluble copper mineral values in at least one alkaline stage of conditioning in the presence of a sulfhydryl anionic collector wherein the pH is in the range of about 9.5 to about 12.3 in the presence or absence of a suitable frother and then subjecting the thus conditioned pulp to froth flotation in the presence or absence of a suitable frother at a pH in excess of 9.5 but less than 12 to produce a concentrate of said copper values and containing copper precipitated from said liquid.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,735,931

Dated May 29, 1973

Inventor(s) David Weston

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

Column 30, line 31 "presence or absence or" should
read -- presence of --.

Signed and sealed this 26th day of February 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents