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CONCENTRATION OF COPPER FROM COPPER ORES, CONCENTRATES AND SOLUTIONS

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No Drawing. Continuation of application Ser. No. 607,335, Nov. 2, 1966, which is a continuation of application Ser. No. 304,438, Aug. 26, 1963. This application Jan. 21, 1969, Ser. No. 792,760

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ABSTRACT OF THE DISCLOSURE

Copper is recovered from copper ore containing a mixture of oxidized copper minerals and copper sulfide minerals by leaching the ore with sulfuric acid, precipitating the copper by addition of acid soluble iron sulfide plus iron and separating the copper therefrom by froth flotation.

This is a continuation of my prior application Ser. No. 607,335, filed Nov. 2, 1966, now abandoned, which is in turn a continuation of my prior application Ser. No. 304,438, filed Aug. 26, 1963, now abandoned.

This invention is concerned with concentration of the copper content of copper ores and concentrates. More specifically, this invention is concerned with concentration of that fraction of the copper content of copper ores which generally is not extracted efficiently by conventional metallurgical processes.

Copper ores of commercial quality may generally be described as rock which contains a minor fraction of its weight in the form of copper minerals. Copper minerals, which are essentially chemical compounds of copper combined with sulfur, iron, oxygen, silica, etc., often are mixed with pyrite minerals and generally are present in copper ores as crystals dispersed throughout the mass of gangue minerals in the rock. The technical problem of recovering the copper content of copper ores, therefore, becomes the problem of separating a small quantity of copper or copper minerals from a large mass of diluent materials.

In the conventional metallurgy of copper, this separation is accomplished by methods which depend upon the properties of both the copper minerals and the gangue minerals in the ore. The copper minerals, when present in the rock primarily as copper sulfide compounds, generally are recovered by crushing and grinding the ore to "liberate" the copper minerals from the gangue minerals, and to produce a pulp in which the individual minerals are present as separate particles. The pulp then is treated with chemicals and blown with air to separate the copper minerals from the gangue minerals by the well-known process of froth flotation. The flotation process is the most important concentration procedure employed currently in the copper industry. The product of this process is copper concentrates, and is the normal feed material to conventional copper smelters.

The grinding and flotation process described above is highly efficient in separating small quantities of sulfide minerals from large quantities of gangue minerals. The process, however, generally fails to distinguish between the various sulfide minerals in the ore and generally extracts pyrite, or iron sulfide, from the pulp in addition to the copper sulfide minerals. For this reason, and because many copper ores contain far more pyrite than copper minerals, the separation of pyrite from the copper minerals in the flotation concentrate is a major technical problem. In attempting to solve the above problem, the current practice in the copper mining industry is to re-

grind and refloat the sulfide minerals in the flotation concentrate under conditions which discourage flotation, or "depress" the pyrite minerals. The process of regrinding and "recleaning" flotation concentrates is repeated until a final concentrate is obtained which is acceptable to copper smelters. The pyrite "tailings" from this process often contain a sizable fraction of the total copper in the ore, and these tailings are discarded as a waste product of the process. The recovery of copper from ores of the "pyritic" type, therefore, frequently is poor and the flotation process is both costly and inefficient when practiced on ores which contain reasonably large quantities of pyrite. The process is especially costly and inefficient when practiced on those "pyritic" ores in which the copper minerals are either mixed intimately with the pyrite minerals, of are present as a surface coating of copper minerals on the pyrite crystals.

Another important process for the commercial extraction and concentration of copper from copper ores, is known as the Acid Leaching Process. This process is employed when the available ores contain both acid soluble "oxidized" copper minerals and non-acid soluble gangue minerals, and involves the leaching of copper from the crushed rock with solutions of sulfuric acid. The leach solutions are separated from the solids and the copper is precipitated by either electrowinning or by cementation with scrap iron. The products from the process are copper cathodes and/or copper cement, both of which are marketable commercial products.

A third important process in the copper industry is known as the Leach-Precipitation-Float or the "L.P.F." process. This process, which is essentially a combination of the two processes previously described, generally is employed in the treatment of "mixed" copper ores, or those which contain both sulfide and "oxidized" copper minerals. The L.P.F. process, like the flotation process, requires grinding of the ore to "liberate" the sulfide minerals from the rock and, like the acid leaching process, requires the addition of sulfuric acid to dissolve the "oxidized" fraction of the copper from the gangue minerals in the pulp. Metallic iron then is added to the pulp to precipitate the soluble copper as metallic copper and both the metallic copper precipitate and the sulfide copper minerals from the ore are separated from the pulp by froth flotation. The product is a copper concentrate which is marketable as feed to copper smelters.

The precipitation procedure of the L.P.F. process requires the use of metallic iron in the ore pulp to precipitate the soluble copper from the leach solution. Low cost metallic iron, however, generally is available only in the form of "tin can" scrap or as other scrap iron of "massive" particle size.

Scrap iron of this character is mechanically difficult to contact with the solution in the ore pulp, and when contacted, often precipitates the copper either as film deposits attached to the surfaces of the scrap iron or in the form of metal aggregates of reasonably large particle size. Metallic copper, however, is more difficult to separate from the pulp by the flotation process than are sulfide minerals and when present as large particles, often remains in the pulp and is discarded with the tailings from the flotation process.

An additional problem of the L.P.F. process derives from the fact that air is employed in the flotation process to generate bubbles in the ore pulp. The air bubbles, however, saturate the solution with oxygen and the saturated solution is an excellent oxidizing agent and solvent for metallic copper. The solution chemically reacts with and dissolves the finely divided fraction of the copper precipitate in the ore pulp, thereby reducing the recovery of copper in the concentrate.

The copper industry, in attempting to solve the above

problems of the L.P.F. process, currently practices one or more of the following operating procedures:

(A) Employs iron metal powder in large excess quantities as the precipitant for soluble copper in the pulp; attempts to recover the excess iron from the pulp with wet magnetic separators prior to flotation, and attempts to achieve tolerable extraction of the copper precipitate from the pulp by careful adjustment of the reagents to the flotation procedure.

(B) Employs available scrap iron charged to acid resistant revolving horizontal drums, pumps the ore pulp through the drums, attempts to extract the surplus transported scrap iron from the pulp with wet magnetic separators, and attempts to achieve tolerable extraction of the copper precipitate from the pulp by adjustment of the reagents employed in the flotation procedure.

The above operating procedures are so costly, wasteful and inefficient, that the value of the copper recovered by the L.P.F. process often is exceeded by the operating cost of the L.P.F. plant. In practice then, the copper mining industry often abandons operation of their L.P.F. plants during periods of low copper prices and instead discards the oxide copper fraction of their ores with the waste rock from the sulfide flotation concentrator.

This invention relates to a process for treating copper ores containing oxidized copper minerals and broadly involves the addition of a calcine in which substantially all of the iron content is present as acid soluble iron sulfide and metallic iron, to the sulfuric acid leach pulp in which the oxidized copper minerals have been dissolved. The acid soluble iron and iron sulfide precipitates the copper in a form that can be recovered by conventional flotation procedures.

The invention includes a process for treating copper ores that contain oxidized copper minerals as well as copper ores that contain a mixture of oxidized copper minerals and sulfide copper minerals and that contain both large and small amounts of iron sulfide minerals.

The exact manner in which the process of this invention will be practiced therefore, will depend to a great extent upon the type of ore that is available, and also upon the by-products that are desired at the particular location at which the process is being practiced.

Because the process of this invention can be employed to recover copper from ores of many different mineral compositions, the flow diagram for this process shows several alternate procedures but the invention is not limited thereby. When the process is employed to recover copper from ores that are high in "oxidized" copper minerals, but are essentially free of both copper sulfide and iron sulfide minerals, the flow scheme may be described as follows:

Pyrite or other sulfide minerals containing iron sulfide are obtained from any convenient source other than the ore, and are employed as feed to step 1 of this process. The iron content of the imported minerals is converted to a calcine reagent which contains acid soluble iron sulfide and metallic iron, and is capable of precipitating copper from acid solutions.

The copper ore, is introduced to the crushing and grinding (step 2) of the process, as shown in the flow diagram. The acid soluble "oxidized" copper is leached from the ore in step 3 of the process by a suitable dilute acid, the leach solution is separated from the solids. The solution is reacted with the calcine and the resulting precipitated concentrate is collected as product, as is shown by the broken line from step 3 labeled as "Cu Conc." on the flow diagram.

Both the spent tailings from the above leach and the spent solution are discarded as waste, as is shown by the broken line from step 3 labeled "Tailings" on the flow diagram.

When the copper ore employed as feed to this process contains both acid soluble "oxidized" copper minerals and non-acid soluble sulfide copper minerals, but is essentially free of iron sulfide minerals, the flow scheme for the process of this invention, (also shown on the flow diagram) may be described as follows:

Step 1 is identical to that of the process previously described. Step 2 of the process requires grinding the ore to particle sizes which releases the sulfide copper minerals from the gangue rock. Step 3 of the process involves both leaching of the copper from the rock, and precipitation of the soluble copper by the calcine reagent added directly to the ore pulp.

The entire ore pulp is then discharged to the flotation step 4 of the process as is shown by the solid line on the flow diagram.

The copper flotation concentrate, containing both the precipitated copper and the copper sulfide minerals from the ore, is recovered as product, as is indicated by the broken line from step 4 labeled as "Cu Conc." on the flow diagram.

The tailings from the flotation procedure is discharged to waste, as is indicated by the solid line from step 4 labeled as "tailings" on the flow diagram.

When the copper ores employed as feed to this process contain chalcopyrite and other iron sulfide bearing minerals in addition to the "oxidized" and the sulfide copper minerals, the process of this invention may be described as follows:

The sulfide minerals containing iron that are employed in step 1 of the process, are available from the ore, and are recycled from the flotation step of the process, as is indicated on the flow diagram by the broken line labeled "FeS_2-$CuFeS_2$" between step 4 and step 1 of the process. The operating procedures for steps 1 to 4 of this process, otherwise are identical to those described above for ores that contain "oxidized" and sulfide copper minerals but contain no iron sulfide minerals.

Mixed copper ores which contain "oxidized" copper minerals, sulfide copper minerals and large quantities of iron sulfide minerals highly intermixed with the copper minerals, require all of the processing operations that are indicated on the flow diagram. The flow scheme of this invention, when employed to process these ores, may be described as follows:

The operating procedures previously described for steps 1, 2, 3 and 4 also are employed in this process. The flotation concentrate discharged from step 4, and indicated by the solid line on the flow diagram between steps 4 and 5 of the process, is reground to finer particles in an effort to subdivide physically the copper sulfide minerals from the iron sulfide minerals. The "liberated" particles of copper sulfide minerals then are separated from the iron sulfide minerals by differential flotation, and are recovered in the copper concentrate, as is indicated by the solid line from step 5 labeled "Cu Conc." on the flow diagram.

The sulfide minerals containing iron, that are employed in step 1, are recycled from step 5 of the process, as is indicated by the broken line from step 5 to step 1 and labeled "FeS_2-$CuFeS_2$" on the flow diagram. The remaining pyrite tailings from the differential flotation of step 5, which contains copper minerals that are not recovered in the copper concentrate, are discharged to the pyrite leach, as is indicated by the solid line between step 5 and step 6 on the flow diagram.

Recycle solution from step 7, or from any other convenient leach solution that contains both acid and soluble iron sulfate, is employed as leach solution, and the copper minerals are converted to soluble copper sulfate by oxidation leaching action of ferric sulfate on the copper minerals. The ferric sulfate is generated in situ by reactions between the soluble iron salts in the solution and the SO_2 and O_2 from two streams of gas which enters step 6 of the process, as is indicated on the flow diagram.

The invention will first be described in connection with the treatment of "mixed" copper ores containing a mixture

of sulfide copper minerals and oxidized copper minerals as well as a high percentage of iron sulfide minerals, and will be described in conjunction with the accompanying drawing which is a simplified flow sheet showing the principal steps involved and variations thereof in practicing the present invention.

"Mixed" copper ore containing both sulfide copper minerals and oxidized copper minerals are first ground to "liberate" the sulfide minerals from the ore to form a comminuted ore pulp. Dilute sulfuric acid then is added to the pulp to dissolve the "oxidized" fraction of the copper from the gangue minerals, as is conventionally practiced in carrying out the L.P.F. process.

After the sulfuric acid has dissolved the acid soluble fraction of the copper from the gangue minerals, a calcine material containing acid soluble iron sulfide and metallic iron, is added to precipitate the soluble copper from the solution and to produce a copper sulfide precipitate in the acid leach pulp.

Both the precipitated copper and the natural sulfide copper minerals from the ore are then separated from the pulp by conventional froth flotation procedures.

The chemical reactions involved in the precipitation of the soluble copper by the addition thereto of calcine containing acid soluble iron sulfide plus metallic iron, can be represented by the following equations:

(1) $CuSO_4+Fe^\circ=Cu^\circ+FeSO_4$

(2) $CuSO_4+FeS=FeSO_4+CuS$

The copper is precipitated primarily as copper sulfide rather than as metallic copper.

As can also be seen from the above Equation 1 the iron present in the precipitating agent employed according to this invention will react with copper sulfate to produce metallic copper and iron sulfate.

The preferred precipitating reagents for use in the process of this invention are calcine reagents which have been generated from sulfide flotation concentrates that contain iron. These reagents, when reacted with the solution to precipitate the soluble copper, produce particles of precipitate which are similar in size to particles of the original flotation concentrate. Such precipitates are ideal in particle size for recovery from the pulp at high efficiency by the flotation procedures of the L.P.F. process.

The process of this invention also advantageously assures essentially complete removal of the copper from the leach solutions as a result of the chemical reactions which take place after the calcine reagents are added to the acid leach pulp. The chemical reactions which take place are as follows:

(3) $H_2SO_4+FeS=H_2S+FeSO_4$

(4) $CuSO_4+Cu^\circ+H_2S=H_2SO_4+Cu_2S$

When excess precipitating reagent is employed the above reactions proceed simultaneously with the reaction of Equations 1 and 2, and continue until all of the copper is removed from the solution.

The amount of precipitating agent employed should be sufficient to assure complete precipitation of the soluble copper from the leach solution. The use of the excess precipitating agent results in the generation of H_2S gas according to reaction (3) above. The H_2S gas thus produced in combination with the metallic precipitate, removes the last traces of copper from the leach solution according to reaction (4). The presence of a cuprous sulfide coating on the particles of precipitated metallic copper permits efficient recovery of the copper by conventional flotation procedures.

Lime or limestone may be added to the pulp in quantities large enough to neutralize the excess acid, and thus to prevent the objectionable generation of H_2S gas during the flotation procedure. Lime also can be added to the pulp in quantities large enough to produce an alkaline pulp, and thus to act as a depressant for pyrite during concentration of the copper by the flotation procedures of the L.P.F. process.

The calcine employed as a precipitating agent for soluble copper in the leach pulp is obtained by treating a sulfide concentrate or mineral mixture according to the process described in U.S. Pat. No. 3,053,651, issued Sept. 11, 1962 to P. J. McGauley. The acid soluble iron sulfide plus iron precipitating agent can be readily prepared by treating a sulfide concentrate or mineral mixture according to the process of the above patent with an excess of metallic iron at a temperature below the melting point of the sulfide mineral mixture for a period of time to produce a sulfide calcine in which a major fraction of the iron sulfide is soluble in dilute sulfuric acid. As described in the above patent, the metallic iron can be manufactured in situ within the sulfide mineral mixture and in practicing the present process it is advantageous to form the excess metallic iron in situ by roasting the sulfide mineral mixture first with air to produce iron oxide, then in the presence of reducing gases containing hydrogen which will remove the oxygen and will produce metallic iron in situ. The amount of excess metallic iron used to produce the acid soluble iron sulfide plus iron precipitating agent can be varied widely because both the iron sulfide and the metallic iron in this calcine are acid soluble and reactive with the soluble copper in the leach pulp, and essentially all of the iron will be capable of precipitating copper from the solution.

The calcine containing the acid soluble iron sulfide plus iron can be supplied to the process from any convenient source, but it is advantageous according to this invention to utilize sulfide minerals from the process as raw materials for production of the calcine. As shown in the drawing, and provided that they contain iron sulfide minerals, a fraction of the product from either of the flotation steps can be fed to the roasting step and treated according to the process of U.S. Pat. No. 3,053,651 to produce the calcine reagent containing the acid soluble FeS plus Fe. This calcine reagent can be recycled to the precipitating step of the L.P.F. process. In addition, if desired, iron sulfide minerals from the flotation tailings can be employed as feed to the roaster, and the calcine reagent from these tailings can be recycled to the precipitation step of the L.P.F. process.

The difficulties presented in separating copper sulfide minerals from the iron sulfide minerals by flotation from "mixed" copper ores which contain a high percentage of iron minerals generally produces a flotation concentrate or a copper concentrate of such a low grade that it is generally unacceptable to the smelter. These low grade copper concentrates may contain, for example, about 10% copper and 70% pyrite or other iron sulfide mineral.

In order to obtain a high grade copper concentrate acceptable to the smelter according to this invention, the low grade copper concentrate or pyritic copper concentrate is reground and subjected to a second flotation step. This regrind and reflotation is controlled to produce a high grade copper concentrate of commercial quality and a pyrite tailings or concentrate low in copper content. The pyrite concentrate is then leached with ferric sulfate to insure substantial removal of the remaining copper from the pyrite concentrate to form a solution of copper sulfate and a pyrite leach tailings that is low in copper content and can be discarded without significant loss of copper.

The copper sulfate solution is then separated from the tailings and the copper is precipitated from the solution by adding thereto a calcine containing acid soluble iron sulfide plus iron produced as described above and in U.S. Pat. No. 3,053,651. The products from the precipitation process are copper sulfide precipitates and a ferrous sulfate solution. The copper sulfide precipitates can be combined with the high grade copper concentrate from the second froth flotation step as a finished product of the process.

The pyrite tailings from the leaching process will be low in copper content and can be discarded. These tailings, if desired, also can be employed as a source of iron sulfide minerals for the generation of precipitating agents by the process of U.S. Pat. No. 3,053,651.

It is advantageous, however, to utilize a portion of the pyrite concentrate feed to the oxidation leaching step as the sulfide mineral mixture from which the calcine containing the soluble iron sulfide plus iron is obtained.

The reaction occurring in the precipitation of the copper from the copper sulfate solution by the calcine addition would be essentially the same as those described above when used in connection with the L.P.F. process.

The oxidation leaching of copper from the pyrite concentrate with ferric sulfate may be represented by the following reaction equations:

(6) $Cu_2S+Fe_2(SO_4)_3=CuSO_4+CuS+2FeSO_4$

and

(7) $CuS+Fe_2(SO_4)_3=CuSO_4+S°$

If oxidized copper minerals are present in the pyrite tailings they will be dissolved by a leaching reaction wihich can be represented by the following reaction equation:

(8) $CuO+H_2SO_4=CuSO_4+H_2O$

The process of this invention further involves regeneration of the ferric sulfate from ferrous sulfate in the leach solution by reactions of the following type:

(9) $2FeSO_4+SO_2+O_2=Fe_2(SO_4)_3$

and

(10) $4FeSO_4+2H_2SO_4+O_2=2Fe_2(SO_4)_3=2H_2O$

The above equations illustrate the fact that the oxidation leaching reactions consume ferric sulfate and produce ferrous sulfate, while the regeneration reactions involve the oxidation of ferrous sulfate to ferric sulfate. The soluble ferrous sulfate is regenerated cyclically and, therefore, serves as a catalyst or a carrier of oxygen from the gas phase (air, for example) to the active surface of the minerals in the pulp.

Although the ferrous sulfate could be oxidized back to ferric sulfate by conventional procedures, such as by removing the solution from the solids and passing a stream of oxygen or air through the solution, and then recycling the solution to the leaching step, this invention includes an improved process which involves the use of a stream of SO_2 and O_2 in air as the oxidizing agent for the regeneration reactions, as represented in Equations 9 and 10. The regeneration reactions, moreover, are carried out simultaneously with the oxidation leaching reactions and in the same reaction vessels. Because the soluble iron is both oxidized and reduced by different phases of the same system, the leach solutions employed may be very dilute with respect to both iron and acid. The oxygen content of the gas phase, however, should be maintained at a reasonable high concentration if the desired reactions are to be carried out at reasonable reaction rates.

In carrying out this phase of this invention, the pyrite concentrate containing copper minerals is first mixed with ferrous sulfate and a stream of air containing both oxygen and sulfur dioxide gas is bubbled through the solution to produce ferric sulfate in the leach solution "in situ." After the copper has been leached from the pyrite, the copper sulfate solution is separated from the leach tailings, and the copper is precipitated with the prepared calcine containing acid soluble iron sulfide plus iron. The resulting ferrous sulfate solution is recycled to the leaching step, as required, and is converted to ferric sulfate "in situ" to leach copper from additional pyrite concentrate.

The present invention, when employed to recover oxidized copper from an ore that contains both sulfide and "oxidized" copper minerals, but is low in iron sulfide minerals, it will be necessary to practice only the first few steps of the invention. As can be seen from the drawing, this will involve the conventional grinding operation to produce a pulp, the leaching of the pulp with dilute sulfuric acid to dissolve the acid soluble oxidized copper and to precipitate the soluble copper by addition of the calcine reagent to the acid leach pulp. The precipitated copper together with the sulfide minerals from the ore can be recovered by conventional flotation procedures to produce the high grade copper concentrate designated in step 3 in the drawing.

Pyrite concentrates containing small amounts of copper minerals, as discussed above, can be advantageously treated according to the process of this invention. For example, a low grade copper concentrate can be prepared by the conventional L.P.F. process, and the low grade copper concentrate can be concentrated to an acceptable commercial grade by the subsequent process of regrinding, reflotation and the oxidation leaching procedure described above and set forth in the drawing.

The oxidation leach of copper from pyrite concentrates containing small amounts of copper minerals also can be performed independently, utilizing the leaching procedure in which the ferrous sulfate is converted to ferric sulfate in situ in the leaching vessel by bubbling oxygen and sulfur dioxide therethrough. The soluble copper can be recovered by utilizing the calcine containing acid soluble iron sulfide plus iron as the precipitating agent for copper from the copper sulfate solution, and either or both of these processes can be employed irrespective of the source of the copper containing pyrite concentrate.

The process of this invention, as disclosed herein, can be varied widely to suit most conditions and to produce products and by-products of the type most desired in the particular location at which the process is being practiced. For example, the copper concentrate produced by conventional flotation generally contains iron, and this concentrate can be employed advantageously as the source of the calcine containing the acid soluble iron sulfide plus iron used in the precipitation step of the process. The precipitation procedure of this invention then will remove additional iron from this concentrate and will precipitate copper from the solution in exchange for this iron. The resulting product will contain copper from both the original minerals and from the solution, and the copper content and value of the concentrate will be significantly higher and the weight and the cost of the transportation to the smelter will be significantly lower than the corresponding values and costs of original concentrate.

The chemical leaching and precipitation steps of this invention also can be employed to simplify the mechanical concentration procedures of the conventional grinding and flotation process. The invention permits the omission of one or more stages of regrinding and recleaning of copper concentrates and enables the recovery of additional copper by extraction from the pyrite tailings by the chemical leaching process of this invention. This results in improved total recovery of copper from the ore, and copper concentrate of improved grade and value, and results in lower costs for each unit of copper that is recovered by the combined process.

The invention further includes the use of mine water as a leach solution and/or as a wash solution in the leaching and precipitation steps of the process of this invention, and is thus one example of the adaptability of the process of this invention to local conditions.

Mine waters generally contain iron, copper and sulfuric acid at low concentration, and when employed in connection with the process of this invention, contribute additional units of copper to the product of the process. These additional units of copper recovered by employing mine water in the process of this invention are recovered at little or no increase in the operating cost of the process and plant.

The process of this invention, by utilizing low cost sulfide minerals containing iron which generally are avail-

able from the ore, is low in both original cost and in operating cost. Because the process removes the copper to very low levels of concentration in the solution, and produces copper sulfide precipitates than can be extracted from the pulp at high efficiency by the flotation process, it is highly efficient in recovering the acid soluble fraction of the copper content of "mixed" copper ores.

The precipitation process of this invention, because of its low cost and high efficiency in removing copper from dilute solutions, also is applicable to the commercial recovery of copper from the oxidized copper ores by the Acid Leaching Process as previously described. In this application of the process, however, the acid leach solutions and wash solutions first are removed from the ore. These solutions then are reacted with appropriate quantities of the acid soluble iron sulfide plus iron generated from sulfide minerals. The resulting copper sulfide precipitates are separated from the solution and are marketed as high grade feed materials to conventional copper smelters.

The following example illustrates one method of treating both a copper ore that contains a mixture of oxidized copper minerals, sulfide copper minerals, and a high weight ratio of iron sulfide minerals, and mine water that contains a small quantity of copper.

The approximate composition of the dry ore is as follows:

Component	Lbs./ton ore	Weight percent
Acid soluble, Cu	2.0	0.10
Sulfide, Cu	18.0	0.90
Total, Cu	20.0	1.00
Sulfide minerals	200.0	10.0
Gangue minerals	1,800.0	90.0
Total Ore	2,000.0	100.0

The copper of the above composition is crushed and ground to release the sulfide minerals from the gangue rock. Water is employed during the grinding, and a recycle leach solution that is generated in a later step of the process, and contains about 2.7 pounds of soluble copper and about 10.0 pounds of H_2SO_4 for each ton of the dry ore, is added to the ground pulp. The acid reacts at ambient temperatures with both the oxidized copper minerals and the alkaline minerals in the gangue rock. On the basis of one ton of ore, the significant components of the leach slurry are as follows:

Component	Lbs./ton ore	Weight percent
Water	5,000	
Soluble, Cu	4.7	
Sulfuric acid	8.5	
Other soluble salts	11.8	
Total solution	5,025	71.5
Total dry solids	2,005	28.5
Total slurry	7,030	100.0

About 10 pounds of a calcine precipitating agent that is produced in a later step of the process, and which contains about 8.5 pounds of acid soluble iron sulfide and metallic iron, is fed to the above slurry. The acid soluble iron in the particles of the precipitating agent reacts with the soluble copper and acid in the solution to produce particles of precipitate which are easily recoverable by flotation. The ore pulp is then separated by flotation into a primary sulfide concentrate that contains both the copper precipitates and the sulfide minerals from the ore, and a siliceous tailings product that contains the gangue rock. On the basis of one ton of ore to the process, the products from the leach-precipitation-float (L.P.F.) process described above are as follows:

Products	Lbs./ton ore	Percent of solids	Lbs. Cu	Percent Cu
Flotation conc.	220	10.9	22.0	10.0
Flotation tailings	1,800	89.2	0.7	0.04
Total dry solids	2,020	100.0	22.7	
Total solution	5,015			
Total slurry	7,035			

The above solution, although shown in the table as an individual product, actually is distributed about 10% with the flotation concentrate and about 90% with the flotation tailings. The slurry of flotation tailings, containing about 3.5% of the copper in the ore, is discarded as waste from the process. The sulfide flotation concentrate is dewatered, neutralized with lime, and reground to subdivide the particles of sulfide minerals into particles containing the copper, and particles containing the pyrite and other diluent components of the sulfide concentrate.

The reground sulfide concentrate is treated by a second flotation procedure that is designed to separate the sulfide minerals into a high grade copper concentrate suitable as smelter feed, and a pyrite tailings product that contains minimum copper. On the basis of one ton of copper ore to the process, the products from the regrinding and secondary flotation procedure are as follows:

Products	Lbs./ton ore	Lbs. Cu	Percent Cu
Cu concentrate	53	19	35.8
Pyrite tailings	167	3	1.8
Total dry solids	220	22	

The above copper concentrate is the finished product from the process of this invention. The copper content of this product includes about 94% of the copper content of the ore and essentially 100% of the copper content of the mine water employed in the process described below.

The above pyrite tailings product is dewatered and is divided into two separate fractions. The first fraction, which contains about 15 pounds of the pyrite tailings per ton of the original ore, is oxidation roasted and reduction roasted by the process of U.S. Pat. No. 3,053,651 to produce both a calcine reagent that will precipitate copper from acid solutions, and a roaster gas that contains SO_2. The calcine from this procedure is recycled to the precipitation procedure of the L.P.F. process, which was described previously.

The second, and major fraction of the pyrite tailings, which contains about 152 pounds, or about 91% of the above pyrite tailings, is repulped to about 50% solids with a heated (about 140–150° F.) leach liquor recycled from a later step of the process, and which contains ferrous sulfate and sulfuric acid. It is advisable to use heat for this leaching step and the heat of reaction can advantageously be used. Both air and the SO_2 gas from the pyrite roaster are dispersed into this pulp in a series of agitated leach vessels. The ferrous sulfate and SO_2 are converted to ferric sulfate and the ferric sulfate extracts copper from the pyrite as copper sulfate.

The slurry discharged from the above pyrite leaching system is washed in thickeners with both mine water containing about 0.2 pound of soluble copper per ton of original ore, and with water. The washed pyrite residue, containing about 2.5% of the copper from the ore, is discarded to waste as a second tailings product from the process of this invention.

The combined leach solution and wash water from the above secondary leaching operation is divided into two

fractions. The first fraction, containing about 2.7 pounds of soluble Cu and about 10.0 pounds of H_2SO_4, is recycled to the primary leaching section of the L.P.F. process described previously, and the acid content of this solution is employed to extract the oxidized copper from the ore.

The second fraction of the above secondary leach solution is employed first to cool the gases from the pyrite roaster, and then is recycled to repulp and to leach copper from the pyrite tailings in the secondary leaching system of the process, as described previously.

The above example represents the best mode of carrying out the invention known at the present time with respect to the particular ore being treated. Different ores can be treated in a similar manner as detailed above, depending upon the ratios of the available components, as will be apparent to those skilled in the art. Generally, the entire process can be carried out at ambient temperature, but as stated in column 10, line 58, the use of heat for leaching the second and major fraction of the pyrite tailings is important. Other variations of the process can of course be used as will be apparent to those skilled in the art.

I claim:

1. The process of recovering copper from comminuted copper ore containing a mixture of oxidized copper minerals and copper sulfide minerals which comprises:
   (a) leaching the comminuted copper ore containing a mixture of oxidized copper minerals and copper sulfide minerals with sulfuric acid to extract the acid soluble copper as copper sulfate,
   (b) precipitating the soluble copper in the leach solution by adding a calcine that contains a mixture of acid soluble iron sulfide and metallic iron, said calcine being obtained from a sulfide mineral mixture by heating the sulfide minerals mixture below the melting point of the mixture in the presence of metallic iron which is present in an amount in excess of the excess sulfur associated with the iron in the sulfide mineral mixture until the iron sulfide contained therein is rendered soluble in dilute sulfuric acid, and
   (c) separating both the copper precipitates and the copper sulfide minerals from the ore by froth flotation procedures to produce a copper concentrate of commercial quality and flotation tailings that are essentially free of recoverable copper.

2. The process of recovering copper from comminuted copper ore containing a mixture of copper sulfide minerals, oxidized copper minerals and iron sulfide minerals which comprises:
   (a) leaching the comminuted copper ore with sulfuric acid to extract the acid soluble copper therefrom as copper sulfate,
   (b) roasting a sulfide mineral mixture containing iron at a temperature below the melting point of the mixture in the presence of a metallic iron, wihch is present in an amount in excess of the excess sulfur associated with the iron in the sulfide mineral mixture, until the major portion of the iron sulfide contained therein is rendered soluble in dilute mineral acid to produce a calcine in which a major fraction of the iron content is soluble in dilute sulfuric acid,
   (c) adding the calcine produced according to the step (b) to the acid leach solution produced according to step (a) to precipitate the soluble copper in the ore, and
   (d) separating both the copper precipitates and the copper sulfide minerals from the ore by froth flotation procedures to produce a copper concentrate of commercial quality and flotation tailings that are essentially free of recoverable copper.

3. The process of claim 2 in which the flotation tailings containing iron sulfide minerals are concentrated to produce an iron sulfide concentrate and this concentrate is recycled as the sulfide feed to the roasting step (b) of the process.

4. The process of claim 2 in which a fraction of the flotation concentrate containing iron sulfide minerals is recycled as a feed to the roasting step (b) of the process.

5. The process of recovering copper from comminuted copper ore that contain oxidized copper minerals, sulfide copper minerals, and iron sulfide minerals intermixed with the copper minerals, which comprises:
   (a) leaching the comminuted copper ore with dilute sulfuric acid to extract the acid soluble copper therefrom as copper sulfate,
   (b) precipitating the soluble copper in the acid leach solution by adding to the ore a calcine containing a mixture of acid soluble iron sulfide and metallic iron, said calcine being obtained from a sulfide mineral mixture by heating the sulfide mineral mixture to a temperature below the melting point of the mixture in the presence of metallic iron which is present in an amount in excess of the excess sulfur associated with the iron and the sulfide minerals mixture until the iron sulfide contained therein is rendered soluble in dilute sulfuric acid, and
   (c) separating both the precipitated copper and the copper sulfide from the ore by froth flotation procedures to produce gangue tailings that are low in copper content and a sulfide concentrate that contains both the precipitated copper and the copper sulfide minerals from the ore.

6. The process of recovering the copper from copper ores high in pyrite minerals which comprises:
   (a) subjecting the ore to froth flotation procedures to extract therefrom a high grade copper concentrate of commercial quality and a pyrite concentrate low in copper content, but still containing recoverable copper,
   (b) leaching the pyrite concentrate with acid ferric sulfate to form leach tailings that are essentially free of recoverable copper, and a solution of cupric sulfate,
   (c) separating the solution from the leach tailings, and
   (d) precipitating the copper by adding to the solution a calcine containing a mixture of acid soluble iron sulfide and metallic iron, said calcine being obtained by heating a sulfide mineral mixture to a temperature below the melting point of the mixture in the presence of metallic iron which is present in an amount in excess of the excess sulfur associated with the iron and the sulfide mineral mixture until the iron sulfide contained therein is rendered soluble in the dilute mineral acid.

7. The process of claim 6, in which a fraction of the pyrite concentrate feed to the ferric sulfate leaching step is roasted in the presence of excess iron to form a calcine containing acid soluble iron sulfide and excess metallic iron, and this calcine is employed to precipitate the copper from the copper sulfate leach solution.

8. The process of recovering copper from pyrite concentrates having a low copper content which comprises:
   (a) leaching the pyrite concentrate with a solution of acid ferric sulfate to produce a solution containing cupric sulfate and pyrite tailings essentially free of recoverable copper,
   (b) separating the solution from the solids,
   (c) precipitating the copper from the solution by adding thereto a calcine containing acid soluble iron sulfide and metallic iron to form a copper precipitate and a solution containing ferrous sulfate,
   (d) separating the copper precipitate from the ferrous sulfate solution.

9. The process of claim 8 in which the ferrous sulfate solution is recycled to the leaching step, mixed with the pyrite concentrate, and the ferric sulfate leaching solution produced in situ by oxidizing the ferrous sulfate to

ferric sulfate by the addition of gases containing both oxygen and sulfur dioxide.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,544,306 Dated December 1, 1970

Inventor(s) Patrick J. McGauley

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

Column 2, line 16, --of are-- should read "or are"

Column 7, line 20, --$CuS+Fe_2(SO_4)_3=CuSO_4+S°$-- should read "$CuS+Fe_2(SO_4)_3=CuSO_4+2FeSO_4+S°$".

Column 10, line 7, --89.2-- should read "89.1".

Column 14, line 2, --2,568,963 9/1951 23-125 X--should read "3,053,651 75 116"

SIGNED AND
SEALED
MAR 9 1971

(SEAL)
Attest:

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Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents