

[54] **PROCESS FOR THE RECOVERY OF COPPER FROM ITS SULFIDE ORES**

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[51] Int. Cl. **C22d 1/16**

[58] Field of Search **204/107**

[56] **References Cited**

UNITED STATES PATENTS

| | | | |
|-----------|---------|---------|---------|
| 3,761,369 | 9/1973 | Tirrell | 204/107 |
| 3,767,543 | 10/1973 | Hazen | 204/107 |

Primary Examiner—R. L. Andrews

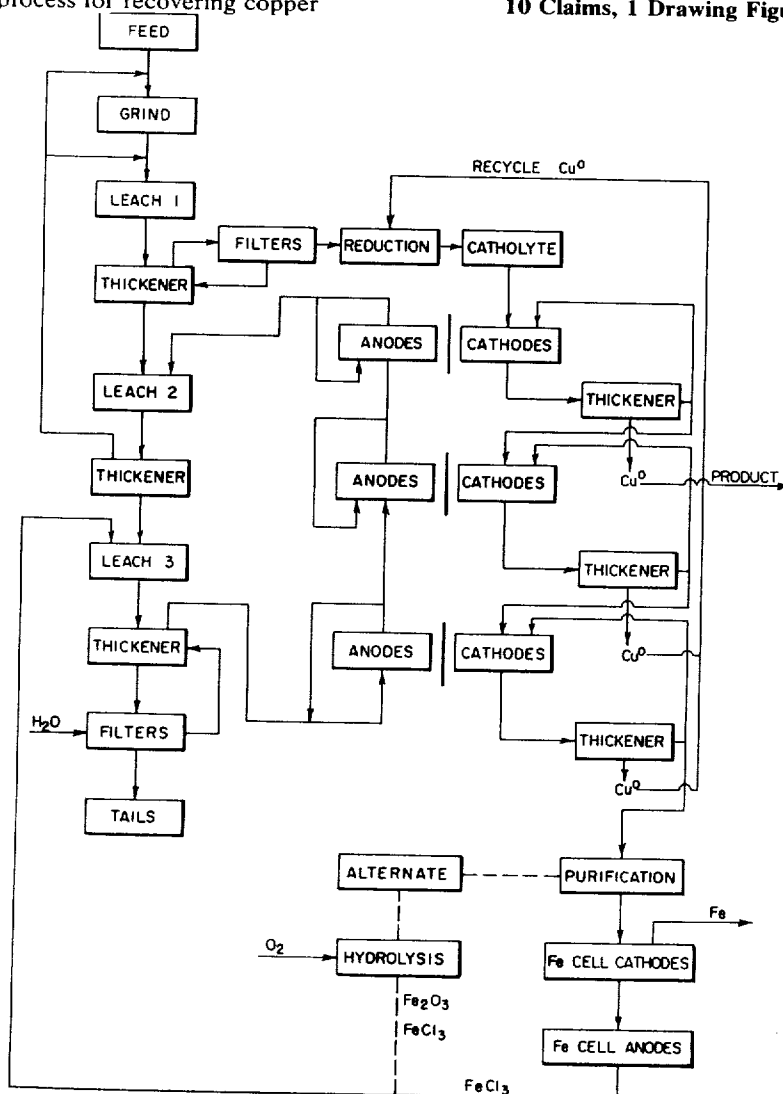
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from its sulfide ores or concentrates thereof which comprises treating the ore with cupric chloride and/or ferric chloride to form a copper chloride electrolyte and a residue, electrolytically recovering copper from the electrolyte and further treating the residue with ferric chloride to solubilize substantially all of the copper remaining therein for conversion to copper chloride electrolyte, with ferrous chloride from the electrolyte being regenerated to ferric chloride for leaching the residue, the improvement which comprises conducting the electrolysis without the conversion of any cuprous copper to cupric copper, using a separator between the anolyte and catholyte compartments of the electrolytic cell to prevent passage of ions of copper and iron between the catholyte and anolyte, continuously further treating the residue with regenerated ferric chloride of a concentration to insure there is no cuprous copper in the resulting solution and regenerating ferric chloride from ferrous chloride in the solution free of cuprous chloride by passing the solution through the anolyte compartment of the electrolytic cell as copper is continuously being recovered at the cathode of the cell.

[57] **ABSTRACT**

An improvement in the process for recovering copper

10 Claims, 1 Drawing Figure



PROCESS FOR THE RECOVERY OF COPPER FROM ITS SULFIDE ORES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to hydrometallurgical processes for recovering copper from its sulfide ores in which the sulfide sulfur is recovered as elemental sulfur so that the sulfur dioxide pollution problem characteristic of pyrometallurgical processes is eliminated. Particularly, the invention is related to those processes wherein the copper in copper sulfide is solubilized by treating the ore with cupric chloride and/or ferric chloride with the copper being recovered from the resulting copper chloride solution by electrolysis. The present process results in the recovery of high yields of commercial grade copper with economic consumption of power in the electrolysis step due to an improvement by which no cuprous copper is converted to cupric copper during electrolysis and the anode of the cell is utilized for the conversion of ferrous chloride from spent ferric chloride leach solution to ferric chloride for further leaching while substantially all of the copper is being continuously plated from the electrolyte.

2. Prior Art

As is well known, the main source for copper today is copper sulfide ores, principally, chalcopyrite. Conventional pyrometallurgical processes by which the copper was formerly recovered from its sulfide ores are objectionable today because of the polluting effect of the sulfur dioxide produced by these processes. Accordingly, there is a great deal of activity in the copper industry to develop pollution-free processes for the recovery of copper from its sulfide ores.

A large number of hydrometallurgical processes are being developed in which the copper in its sulfide ores is solubilized by treatment of the ore with ferric chloride and/or cupric chloride with the formation of elemental sulfur followed by recovery of the copper from the resulting solution or electrolyte by electrolysis. The sulfur dioxide pollution problem is eliminated in these processes in which the sulfide sulfur is converted to elemental sulfur.

The steps for solubilizing copper in chalcopyrite usually include the procedure of first reacting the raw ore with cupric chloride followed by further reaction of the resulting solution with a reducing agent such as metallic copper to provide an electrolyte which is essentially all cuprous chloride. The residue from the cupric chloride reaction step is then treated with ferric chloride to solubilize essentially all of the remaining copper. In order for these processes to be commercially feasible, they must be highly efficient in the consumption of electrical energy, regeneration of reagents, removal of impurities, recovery of other metals contained in the ore, and they must not generate undesirable amounts of sulfate ions with the consequent prohibitive consumption of electrical energy or reagents.

It is well known that for the economic recovery of copper by electrolysis the copper in the electrolyte must be in the cuprous form. It is also well known that the presence of ferric or cupric ions at the cathode where copper is being plated from cuprous chloride interferes with the plating of the copper. An expedient to keep these ions away from the cathode is the use of a separator to prevent the circulation of electrolyte from cathode to anode as the plating is in progress. Another

expedient is to avoid the presence of ferric ions in the anolyte by leaving enough cuprous copper in the electrolyte for oxidation to cupric copper to prevent any oxidation of ferrous ion to ferric ion as the first oxidation has precedence over the latter. This procedure eliminates ferric ions in the electrolyte which might travel to the cathode, but it also requires circulation of the electrolyte from cathode to anode or some other procedure to prevent cupric ions from coming in the vicinity of the cathode. An objection to the latter procedure is, of course, that large amounts of copper are being recirculated in a continuous process when only a portion of the copper entering the cell is being recovered.

In these procedures in which electrolysis is performed on an electrolyte resulting from initially leaching the copper sulfide ores with ferric chloride and/or cupric chloride, the ferrous chloride entering the cell in the electrolyte passes on through the cell unaffected and is conventionally oxidized to ferric chloride in the spent electrolyte and the resulting ferric chloride recirculated to leach chalcopyrite residue from the initial cupric chloride leaching step. Ordinarily, only one effective leaching can be performed with the recirculated ferric chloride without regeneration as it is substantially reduced to ferrous chloride in the leaching of the chalcopyrite residue. An efficient means utilizing the electrolytic cell for regenerating the ferric chloride after leaching the chalcopyrite residue for further leaching of residue is desirable. In accordance with this invention a process is provided by which the anode of the electrolytic cell is used to regenerate spent ferric chloride from chalcopyrite residue leaching while copper is being continuously recovered at the cathode in the absence of ferric and cupric ions.

U.S. Pat. No. 333,815 discloses an electrolytic process for the recovery of copper from ferric chloride leach solutions of copper sulfide ores in which ferric chloride is regenerated at the anode. However, this process is performed with cuprous ions in the presence of the anode and would obviously be inefficient to regenerate ferric chloride because of the precedence of the oxidation of cuprous to cupric ions over the oxidation of ferrous to ferric ions. Also, no procedure is provided for preventing cupric and ferric ions from contacting the cathode or preventing the conversion of cuprous to cupric ions during the cell operation.

U.S. Pat. No. 3,767,543 discloses the regeneration of ferric chloride from ferrous chloride at the anode as copper is being electrolytically recovered at the cathode from a ferric chloride leach solution of chalcopyrite. However, since cuprous ions are present in the anolyte an inefficient regeneration of ferric chloride will result. Further, no provision is made to prevent the conversion of cuprous to cupric ions.

U.S. Pat. Nos. 3,764,490 and 3,776,826 both disclose the conversion of cuprous to cupric copper at the anode and the processes of these patents are not concerned with the regeneration of ferric chloride from ferrous chloride at all as ferric chloride is not used in leaching the copper sulfide ores.

U.S. Pat. No. 3,785,944 discloses a process in which copper in chalcopyrite is initially solubilized by treatment with cupric chloride and/or ferric chloride with ferric chloride being used to treat residue from the initial treatment of the chalcopyrite ore concentrate. An electrolyte is produced in a second reduction stage with

metallic copper in which essentially all of the copper is reduced to cuprous chloride and the iron reduced to ferrous chloride. The only regeneration of ferric chloride is by oxidation of the ferrous chloride in the spent electrolyte, the resulting ferric chloride being used to oxidize chalcopyrite residue from the initial cupric chloride treatment of the chalcopyrite concentrate. The patent teaches against the formation of ferric chloride at the anode and to prevent this only a portion of copper is recovered from the cuprous chloride electrolyte with enough being left in solution for the express purpose of preventing the oxidation of ferrous to ferric chloride at the anode. Electrolyte is circulated from cathode to anode to prevent the cupric chloride being formed at the anode from contacting the cathode where copper is being plated from cuprous chloride electrolyte. The process does not provide for regeneration of ferric chloride in the cell and is expressly directed to the conversion of cuprous ions to cupric ions during electrolysis.

Accordingly, the principal object of this invention is to provide an improvement in the step for electrolytically recovering copper from cuprous chloride electrolyte produced by treatment of chalcopyrite ores with metal chlorides by which efficient utilization of the cell is obtained by using the anode to regenerate ferric chloride from spent ferric chloride leach solution while copper is being simultaneously plated at the cathode of the cell cuprous chloride electrolyte without the conversion of cuprous ions to cupric ions.

BRIEF SUMMARY OF THE INVENTION

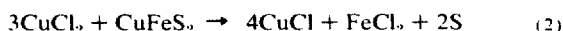
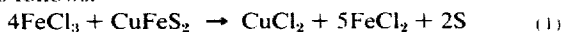
In accordance with the invention, finely ground chalcopyrite ore concentrate is treated with cupric chloride in a first leaching step followed by separation of the solution and chalcopyrite residue. The copper in the solution is further reduced with metallic copper or other reducing agent to provide an electrolyte in which the copper is essentially all in the cuprous form. The electrolyte is subjected to electrolysis in an electrolytic cell in which the anode and cathode compartments are separated by a separator which prevents passage of ions of iron and copper from the cathode to anode. The spent electrolyte goes to purification for recovery of the metals other than copper followed by electrolytic recovery of iron, with simultaneous regeneration of ferric chloride at the anode. An alternative procedure at this point is the removal of excess iron by hydrolysis with oxidation of ferrous chloride to ferric chloride for recirculation. The regenerated ferric chloride in both instances is circulated to leaching and the spent ferric chloride leach solution is circulated through the anode of the cell as copper is being plated at the cathode for regeneration of ferric chloride for use in further leaching. The result is that all of the copper can be recovered from the electrolyte without the conversion of cuprous to cupric ions with simultaneous use of the cathode for plating copper and the anode to regenerate ferric chloride for multiple leachings with overall effective utilization of electrical energy.

BRIEF DESCRIPTION OF THE DRAWING

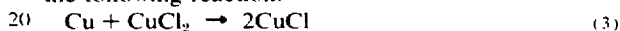
The single drawing is a flow diagram of the process of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to the flow diagram, feed of chalcopyrite ore concentrate ground to an average particle size preferably 90% — 200 mesh is subjected to a cupric chloride leach in leach 1. The leaching solution may or may not contain ferric chloride. The reactions between chalcopyrite and ferric chloride and cupric chloride are as follows:



The solids are separated as chalcopyrite residue and the solution subjected to a reduction stage with recycled copper from the electrolysis in which cupric chloride is reduced to cuprous chloride in accordance with the following reaction.



The solution containing ferrous chloride and substantially all of the copper as cuprous chloride is introduced into the cathode compartment of an electrolytic cell for recovery of copper. The ferrous chloride is not affected by the electrolysis and passes on through the cell in the spent electrolyte.

The electrolytic cell is provided with a separator between the anode and cathode separating it into anolyte and catholyte compartments. The separator used prevents ions of copper and iron from travelling from the cathode to the anode. The separator also prevents the direct flow of catholyte to anolyte or vice versa. An example of a suitable membrane is a microporous polypropylene film sold under the trademark "CELGARD" by the Celanese Plastics Company, Newark, N.J.

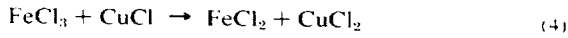
The electrolyte is about 2.5 molar in ferrous chloride at a pH of 0.5. A cell temperature of about 80°C is used. An anode current density of about 80–120 amps per sq. ft. and a cathode current density of about 50–100 amps per sq. ft. are used. Some of the copper recovered at the cathode is recycled to the reduction stage for reducing cupric to cuprous chloride. These are preferred but not limiting process limitations.

Sulfate ion is removed from the electrolyte after electrolysis by precipitation with barium or calcium in the purification step. The elemental sulfur formed in leach 1 is separated with the solids and is eventually removed in the tails from which it is recovered by a conventional procedure.

As will be seen from the flow diagram, the chalcopyrite residue from leach 1 is subjected to two leaching steps, that is, leach 2 and leach 3. This is done to insure that substantially all of the copper is removed from the chalcopyrite concentrate. Solution from leach 2 containing some copper is continuously recirculated to leach 1. Leach 3 is performed with ferric chloride resulting from oxidation of ferrous chloride in the spent electrolyte. The spent ferric chloride leach solution from leach 3 is not recirculated to leach 1 but is passed through the anode compartment of the cell for conversion of the ferrous chloride therein to ferric chloride. This solution entering the anode compartment is substantially depleted of ferric chloride which will have been converted to ferrous chloride in the oxidation of the chalcopyrite residue from leach 2. The cuprous copper present is oxidized to cupric chloride before the

solution enters the anode. The chalcopyrite residue received in leach 3 from leach 2 is heavily depleted in copper. The process is operated so that leach 3 will always be conducted with a substantial excess of ferric chloride so that all of the copper in the chalcopyrite will be completely solubilized and no copper will be lost in the tails. The reaction is preferably conducted at a temperature between 105°-110°C.

The leach solution entering leach 3 from leach 2 with residue will contain some cuprous ions in addition to ferrous and cupric ions. However, as leach 3 is done with a substantial excess of ferric ion the following reaction occurs:



The result is that the solution leaving leach 3 for the anode contains substantially all of the iron as ferrous iron with some little ferric iron, and all of the copper as cupric chloride with no cuprous chloride being present. This is essential for the economical conversion of ferrous chloride to ferric chloride at the anode as the oxidation of cuprous to cupric chloride takes precedence over the oxidation of ferrous to ferric chloride and if any cuprous copper is present it will be oxidized to cupric chloride before any ferrous chloride will be oxidized to ferric chloride and this will substantially diminish the efficiency of the cell in converting ferrous chloride to ferric chloride.

As a precautionary measure, not more than about 85% of the ferrous chloride is oxidized to ferric chloride at the anode because it is advisable to always maintain some ferrous chloride in the solution so that if the cell operation is upset at any time there will always be some ferrous ion at the anode for conversion of ferric ion to keep the cell from discharging oxygen or chlorine.

The solution leaving the anode for leach 2 preferably contains not more than about 85% ferric chloride, 15% ferrous chloride and the remainder cupric chloride. This means that the solution is high in ferric chloride for effective leaching in leach 2 of the chalcopyrite residue from the reduction step. Reactions 1 and 2 above occur in leach 2. The solution from leach 2, which is recirculated to leach 1, contains ferrous chloride plus some cupric and cuprous ions.

In leach 1 the solution containing ferrous, cuprous and some cupric ions is contacted with fresh feed so that reaction 2 above occurs. Thus most of the cupric ions are reduced to cuprous ions. However, chalcopyrite is insufficiently active to reduce all of the cupric ion present to cuprous ion so that the solution overflowing the first stage thickener contains ferrous plus cuprous ions plus some cupric ions. Since it is required that the cupric ions in the solution from leach 1 be at a minimum during electrolysis, the solution is contacted with recycled copper powder to reduce the remaining cupric ions to cuprous ions in accordance with equation 3 above. The result is that the solution which becomes the electrolyte contains iron and copper almost exclusively as ferrous and cuprous ions.

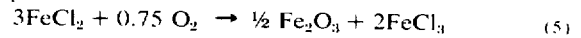
At the cathode, copper powder is plated in three stages. The copper from stage 1 is product copper and may be sold as such or further refined for sale. Copper further depleted from the electrolyte in electrolytic stages 2 and 3 may be recycled to the reduction stage for the reduction of cupric ion. The electrolyte de-

pleted in copper is sent to the purification stage where sulfate ion is removed as explained above.

In the purification stage, the last residue of copper and undesired impurities such as zinc, lead, arsenic, antimony, bismuth, etc., are removed from spent electrolyte which then proceeds either to iron plating or hydrolysis as shown in the flow diagram.

If the solution is sent to iron plating, iron is plated at the cathode for sale. The iron plating cells are equipped with the same separators as the copper plating cells thereby preventing the mixing of catholyte and anolyte and preventing migration of ferric ions from the anolyte to the catholyte. The depleted (anion) catholyte goes to the anode of the iron cell where ferrous iron is oxidized to ferric iron which is circulated to leach 3.

If the solution is sent to hydrolysis as an alternate procedure, the purified ferrous solution is treated with oxygen to regenerate ferric chloride and precipitate hydrated iron oxide in accordance with the following equation:



The ferric chloride formed is then circulated to leach 3.

Based on the chemical reactions of the process set forth above and the use of the separator between anolyte and catholyte it is apparent that there is no possibility for the conversion of cuprous to cupric ions in the electrolytic cell. No cuprous ions from the catholyte reach the anolyte to be converted to cupric ions as the separator prevents the travel of cuprous ions from catholyte to anolyte. In order to demonstrate that no cuprous ions are introduced into the anolyte from leach 3, and to demonstrate the efficient conversion of ferrous ions from leach 3 to ferric ions with economical use of electrical power during cell operation, the following procedure was carried out using the flow sheet of the invention with the results given below being obtained. All percentages are given as weight percentages.

LEACH 3

Partially reacted chalcopyrite residue from leach 2 gave the following analysis:

| Element | Weight % |
|-----------------|----------|
| Fe | 14.1 |
| Cu | 7.1 |
| Zn | 0.028 |
| Pb | 0.0018 |
| S ²⁻ | 34.2 |

Two hundred grams of the above residue entered Leach 3 where the solution from the cathode operation also entered after purification and regeneration. One liter of this purified solution which contained mainly ferric chloride in excess (118.2 g/l Fe³⁺) encountered the reacted residue for a thorough leach. The leaching operation of Leach 3 was aimed at a complete depletion of the copper in chalcopyrite to produce tails ready to be discarded. The leaching was performed at 106°C and at pH 0.5.

It was found that the system allowed no possibility of formation of cuprous ions, the solution leaving Leach 3 having the following analysis:

| | | | | |
|------------------|------------------|-----------------|------------------|----------------|
| Fe ³⁺ | Fe ²⁺ | Cu ⁺ | Cu ⁺⁺ | S ⁻ |
| 42.5 g/l | 69.5 g/l | 0 | 13.7 g/l | 1.44 g/l |

Clear solution from Leach 3 with the above composition was fed to the cell anode during cell operation for anodic oxidation whereby the ferrous ions were converted to additional ferric ions at the anode.

The tails from Leach 3 ready for disposal were analyzed to contain the following:

| | | |
|-------|-------|----------------|
| Fe | Cu | S ^o |
| 7.18% | 0.34% | 52.4% |

The overall recovery of copper after Leach 3 is shown by the following metallurgical balance:

| Copper in Feed | Copper Solubilized | Copper in Tails | % Copper Leaching Recovery |
|----------------|--------------------|-----------------|----------------------------|
| 104 g | 103.52 g | 0.48 g | 99.54 |

Cell Anode Conversion

The cell anode received from the thickener overflow of Leach 3 a clear solution with composition as indicated above. The cell anode was operated at 120 amperes per square foot of graphite anode area. At total power input of 27 ampere-hours was used for the anodic oxidation of ferrous ion to ferric ion at 75°C.

It was found that 54.9 grams of iron in ferric form was produced through anodic oxidation of ferrous iron. The rate of power consumption was 0.49 ampere-hours per gram of Fe⁺⁺⁺ processed. This FIGURE compared with 0.48 ampere-hours per gram Fe⁺⁺⁺ (Fe⁺⁺ to Fe⁺⁺⁺) theoretical. The current efficiency for the process was 98 percent.

After completing the desired anodic reaction the solution with the following composition was advanced to leach 2:

| | | | | |
|-------------------|------------------|-----------------|------------------|----------------|
| Fe ⁺⁺⁺ | Fe ⁺⁺ | Cu ⁺ | Cu ⁺⁺ | S ⁻ |
| 97.4 g/l | 15.2 g/l | 0 | 13.7 g/l | 0 |

As stated previously, it is preferred not to oxidize all of the ferrous ion to ferric ion in the cell operation.

LEACH 2

Leach 2 received the anode processed solution having the above composition from the cell anode. Partially reacted chalcopyrite containing 26.4% Fe; 18.8% Cu and 6.88% S^o from Leach 1 entered Leach 2. The leaching operation was conducted at 80°-90°C and at pH 0.5. This leach consumed the available ferric ion in the anode processed solution leaving a heavily copper depleted chalcopyrite to be proceeded to Leach 3 with a composition as follows:

| | | |
|-------|------|----------------|
| Fe | Cu | S ^o |
| 14.1% | 7.1% | 34.7% |

The leach liquor from Leach 2 was advanced to Leach 1 as an overflow from thickener 2.

LEACH 1

The fresh feed of chalcopyrite with head assay of:

| | | | | |
|-----|-----|--------|--------|-------|
| Fe | Cu | Zn | Pb | S |
| 26% | 26% | 0.126% | 0.063% | 28.2% |

was contacted with leach liquor from Leach 2, through thickener 2 which contained essentially ferrous, cuprous and some cupric ions with the following analysis:

| | | | |
|-------------------|------------------|-----------------|------------------|
| Fe ⁺⁺⁺ | Fe ⁺⁺ | Cu ⁺ | Cu ⁺⁺ |
| 0 | 120 g/l | 11.5 g/l | 28.2 g/l |

The leach was conducted at 80°C and at pH 0.5. This leach produced the partially reacted chalcopyrite which entered Leach 2 with the composition indicated earlier (see Leach 2 for the partially reacted chalcopyrite analysis). As shown in the flow sheet, the leach liquor was filtered and advanced to the cathode operation whereby the solution contacted recycled copper powder from the cathode during the reduction process to reduce cupric to cuprous copper. As a result the solution entered the cathode as catholyte bearing mainly ferrous and cuprous ions.

From the above data it is seen that the process of the flow sheet operates with no cuprous ions being converted to cupric ions in the cell operation and with the use of the anode of the cell to convert ferrous chloride in spent ferric chloride leach solution to ferric chloride, with economical consumption of electrical power as copper is being plated at the cathode.

The process is not restricted to any particular number of electrolysis of leach stages, as more or less than the three stages of each used for illustrating the invention can be utilized. The spent ferric chloride from any leaching stage can be sent to the anolyte for regeneration so long as all of the copper in it is in the cuprous stage. Each of the leaching stages may contain any number of leaching steps.

From the above description of the invention, it will be noted that the advantage provided is that the cell anode can be used for regeneration of ferric chloride while copper is being simultaneously plated at the cathode. The advantage of this is that the ferric chloride regenerated in the spent electrolyte can be used for a number of oxidation steps with regeneration to insure complete removal of copper from the chalcopyrite concentrate, the additional oxidation steps being possible because of regeneration of the ferric chloride between steps in the anode of the cell. It is obvious that this is much more economical than using oxygen in separate oxidation steps for continued oxidation of the spent ferric chloride leach solution from Leach 3 to regenerate ferric chloride.

Although the invention has been disclosed with the use of cupric chloride alone in Leach 1, it includes the use of ferric chloride. Other reductants than metallic copper can be used to reduce the cupric chloride to cuprous chloride in the reduction stage. Any excess sulfate ions generated in the electrolysis process can be removed from the spent electrolyte by precipitation with barium or calcium. The process can be conducted with multiple stages of cells and may be conducted batch or continuous.

While the invention has been illustrated by its application to chalcopyrite, a common copper sulfide mineral, it is equally applicable to other copper sulfide minerals, such as, covellite and chalcocite.

What is claimed is:

- 1. A process for the recovery of copper from copper sulfide ores and their concentrates comprising:
 - a. leaching the ore or concentrate feed with a material comprising cupric chloride in a first leaching stage with separation of the solids from the resulting solution and sending the solids to a second leaching stage;
 - b. reducing substantially all of the copper chloride content of the solution from said first leaching stage to cuprous chloride;
 - c. recovering copper from the solution of step (b) by subjecting the solution to electrolysis in the cathode compartment of an electrolytic cell having an anode and a cathode and a separator therebetween to keep ions of copper and iron from travelling from the cathode to the anode, with the ferrous chloride ions in the cathode unaffected by the electrolysis;
 - d. leaching the solids from said first leaching stage with materials comprising ferric chloride and cupric chloride with separation of the solids and spent leach solution and sending the latter to said first leaching stage and the solids to a third leaching stage;
 - e. oxidizing the ferrous chloride in the spent catholyte from said electrolysis to ferric chloride and sending the ferric chloride to said third leaching stage to leach the solids from said second leaching stage followed by separation of the resulting solids and spent leach solution, and
 - f. introducing the spent leach solution of step (e) containing ferrous, ferric and cupric chlorides into the anode compartment of said cell to oxidize said ferrous chloride to ferric chloride with the cupric chloride being unaffected by the electrolysis, and transferring said electrolytically oxidized solution to said second leaching stage; whereby the electrolytic cell is operated without the conversion of any cuprous ions to cupric ions.
- 2. The process of claim 1 in which the solution from

said second leach is returned to leach (1).

- 3. The process of claim 1 performed as a continuous process.
- 4. The process of claim 1 performed in multiple steps and stages.
- 5. The process of claim 1 in which in step (b) the reduction is performed with metallic copper.
- 6. The process of claim 1 in which the leaching materials in step (a) include ferric chloride.
- 7. The process of claim 1 in which in step (f) up to about 85% of the ferrous chloride is oxidized to ferric chloride.
- 8. In the process for recovering copper from copper sulfide ores or their concentrates in which the ore or concentrate is leached with cupric chloride and/or ferric chloride, the resulting solution and residue separated, substantially all of the copper chloride in the solution reduced to cuprous chloride, the resulting cuprous chloride solution electrolyzed to recover copper, and the ferrous chloride in the spent electrolyte oxidized to ferric chloride which is recycled for leaching at least part of the chalcopyrite residue, the improvement which comprises: conducting said electrolysis in an electrolytic cell having an anode and a cathode divided by a separator to keep ions of copper and iron from travelling from the cathode to the anode, to recover substantially all of the copper in solution at the cathode without the formation of cupric copper in the cell.
- 9. The improved process of claim 8 including solubilizing at least a part of the copper in said residue with said recycled ferric chloride to produce cupric chloride and ferrous chloride in solution, introducing said latter solution into the anode compartment of said electrolytic cell to oxidize the ferrous chloride therein to ferric chloride as metallic copper is being simultaneously recovered at the cathode and using the ferric chloride regenerated by the electrolytic oxidation of ferrous chloride in the anode to leach additional chalcopyrite residue.
- 10. The improved process of claim 9 in which up to about 85% of the ferrous chloride in solution is converted to ferric chloride in the anode compartment.

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