

## [54] PROCESS FOR THE MANUFACTURE OF ELECTROLYTIC COPPER

[75] Inventors: **Bernard M. Fisher**, New Orleans; **Robert C. Hills**, Metairie; **Freddie J. Touro**, New Orleans, all of La.[73] Assignee: **Freeport Minerals Company**, New York, N.Y.[22] Filed: **Feb. 27, 1974**[21] Appl. No.: **446,314**[52] U.S. Cl. .... **204/108; 75/117; 423/140; 423/633; 423/602; 423/158; 423/37; 423/87; 423/522; 423/555; 423/35; 423/41**[51] Int. Cl. .... **C22d 1/16; C22b 15/00**[58] Field of Search ..... **75/117; 423/140, 158, 633, 423/602, 37, 87, 522, 555, 41; 204/108**

## [56] References Cited

## UNITED STATES PATENTS

3,637,371 1/1972 Maclaw et al. .... 75/117

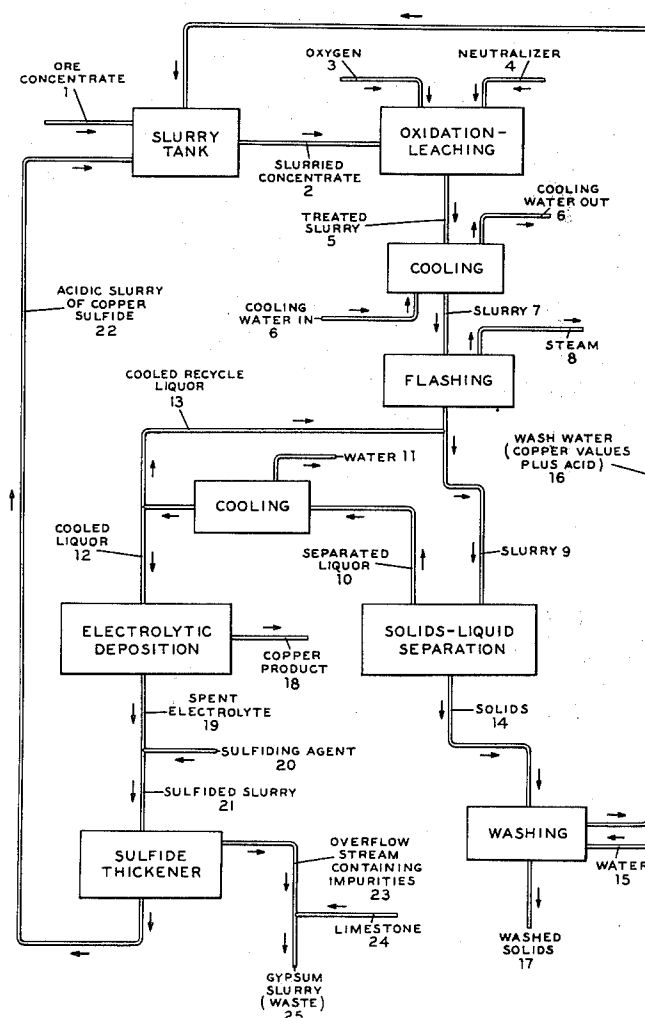
Primary Examiner—R. L. Andrews

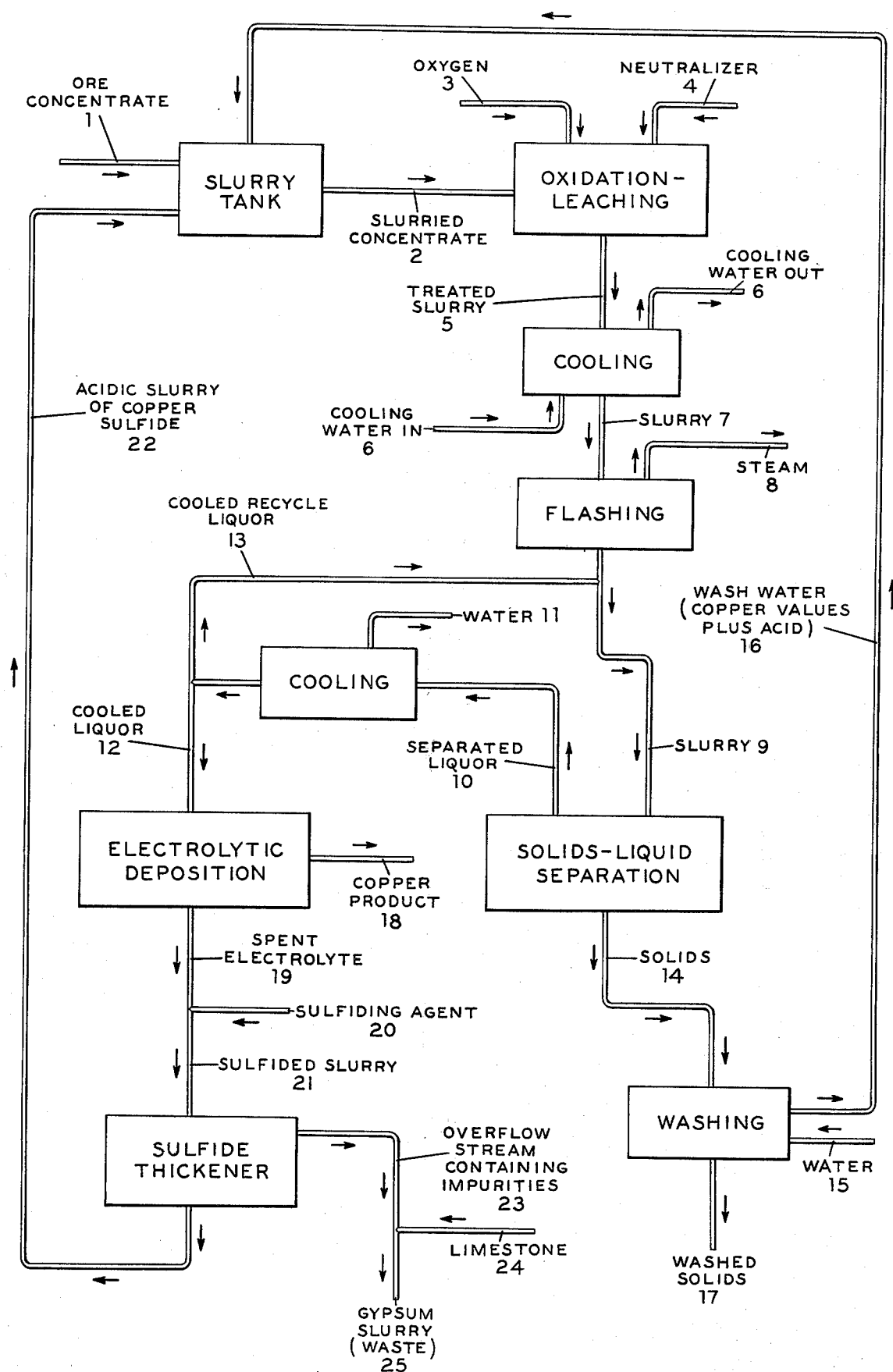
Attorney, Agent, or Firm—Lawrence W. Flynn

## [57] ABSTRACT

A process is described for making electrolytic copper of high quality from chalcopyrite flotation concentrates, and the like. The concentrates are first slurried and then subjected to a high temperature-high pressure oxidation-leaching operation in an autoclave system under controlled conditions. The resulting slurry from the oxidation-leaching operation is flashed to atmospheric pressure in order to remove heat and then subjected to a solids-liquid separation. The separated liquor from the solids-liquid separation system, containing the recovered copper values, is cooled and then fed to an electrolytic deposition operation where metallic copper cathodes of high purity are produced. The spent electrolyte is further subjected to a sulfide treatment to precipitate and recover, as copper sulfide, the residual amounts of copper not deposited in the electrolytic cells. The copper sulfide is then recycled in the form of a slurry to the initial stages of the process.

22 Claims, 1 Drawing Figure





# PROCESS FOR THE MANUFACTURE OF ELECTROLYTIC COPPER

## BACKGROUND OF THE INVENTION

Increasingly, in recent years, consideration has been given to employing hydrometallurgical processes for the recovery of metal values from sulfide ores. One of the reasons for this is that hydrometallurgical processes, for the most part, do not involve the generation of sulfur dioxide and the consequent problems of air pollution characteristic of pyrometallurgical process. Another reason for considering hydrometallurgical processes is the extreme flexibility afforded with regard to the virtually infinite sets of unique conditions of temperature, pressure, retention time, specific solvents and additives and procedures that can be resorted to for whatever particular metallurgical separation one is confronted with.

Where the final step in a hydrometallurgical copper recovery process is to be based upon electrowinning, it would normally be desirable that the preliminary steps for producing the electrolyte include the best possible solids-liquid separation, reduction of dissolved iron and arsenic to minimal levels, and concentration of copper, as copper sulfate, to maximum levels in the feed to the electrowinning step. While a variety of methods are available for carrying out each of these steps, in most known processes these individual methods do not always complement each other, i.e., they lack in technological compatibility with regard to making up an efficient, economical, pollution-free process. It is an object of this invention to provide a process wherein each individual step is uniquely suited to the others and to the overall process for manufacturing a high quality metallic copper product efficiently and economically. A secondary object is to circumvent the production of sulfur dioxide and thereby negate the possibility of air pollution.

## BRIEF SUMMARY OF THE INVENTION

In accordance with and furtherance of this stated objective the present invention provides a process wherein a copper sulfide flotation concentrate, at least a portion of which is chalcopryite,  $\text{CuFeS}_2$ , is first mixed with water and recycle process liquors and slurries. Alternatively, the concentrate may be slurried with recycle process liquors and slurries only. The resulting slurry is then subjected to a high temperature-high pressure operation in an autoclave system, wherein the temperature is closely controlled and an oxygen partial pressure (from industrial oxygen or an oxygen-bearing gas) is maintained. The autoclave system may be a single vessel or a series of vessels. The oxidation in the high temperature-high pressure operation results in the formation of sulfuric acid and the solubilization of the metal constituents of the concentrate in the form of sulfates. In addition to copper, iron and arsenic also are dissolved by the acid, but the latter two are removed from solution, after solubilization of virtually all of the copper, by the neutralization of the greater portion of the sulfuric acid with a neutralizing agent such as limestone. The neutralization of the sulfuric acid results in the precipitation of virtually all of the dissolved iron and arsenic.

Exiting the high temperature-high pressure operation, the slurry is flashed to atmospheric pressure and fed to a solids-liquid separation system. The separated

liquor from the solids-liquid separation system is then cooled and fed to an electrolytic deposition operation where end-product copper cathodes are produced. The solids from the solids-liquid separation operation are normally washed with water and the return wash water, containing residual copper values, is recycled back to the initial stages of the process. The washed solids, composed of the ore gangue and the materials precipitated in the autoclave— $\text{Fe}_2\text{O}_3$  (hematite), iron and calcium arsenates, and  $\text{CaSO}_4$  (anhydrite)—are sent on for further processing or to waste. The spent electrolyte from the electrolytic deposition operation is then treated with a sulfiding agent, such as hydrogen sulfide, to precipitate, as copper sulfide, the copper values not deposited with the copper cathodes. The copper sulfide slurry is then thickened to a solids content of between about 3 and 15 percent and recycled back to the initial stages of the process.

It is significant of the process of this invention that the various steps required are uniquely compatible with each other and with the overall process. For example, the high-temperature precipitation of iron and calcium as hematite and anhydrite, respectively, makes the subsequent solids-liquid separation much easier than if the precipitated materials were ferric hydroxide and gypsum as would be obtained in a low-temperature process. Additionally, the steps wherein water vapor is removed from the liquor in the process of venting non-condensable gases, or controlling the temperature, or flashing, etc., are compatible with the overall object of the leaching step, that is, providing a liquor with a maximum concentration of copper as copper sulfite and a very low concentration of dissolved iron.

These and other aspects of the invention will be understood more thoroughly in the light of the following description, as illustrated in the accompanying drawing.

## BRIEF DESCRIPTION OF THE DRAWING

The drawing is a flow sheet illustrating the preferred embodiment of the invention.

## DETAILED DESCRIPTION

The preferred embodiment of the invention involves the treatment of a chalcopryite flotation concentrate and is best illustrated with reference to the drawing. Referring to the drawing, then, a chalcopryite flotation concentrate 1, containing between about 20 and 30% copper, is fed into a slurry tank and mixed with recycle wash water 16 containing residual amounts of copper sulfate and sulfuric acid, and with a recycle acidic slurry of copper sulfide 22. The resultant slurry 2 is fed continuously to a high temperature-high pressure oxidation-leaching operation which, in a preferred embodiment, is carried out in a multi-compartment, horizontal autoclave system equipped with agitators.

Within the autoclave system the slurry temperature is maintained between  $350^\circ$  and  $450^\circ\text{F}$ , and preferably between  $425^\circ$  and  $450^\circ\text{F}$ . The total pressure is maintained at between about 300 and 1000 psig, and preferably between about 400 and 600 psig, by the introduction of a high quality oxygen-containing gas 3 so as to provide an oxygen partial pressure of between about 50 and 500 psi, and preferably between about 100 and 200 psi. The oxygen-containing gas used should have an oxygen content of at least about 95% and preferably in the order of 99%.

The oxidizing chemical reactions in the autoclave system result in the formation of sulfuric acid and the

dissolution of the copper and iron as sulfates. Because the oxidizing reactions are exothermic, heat must be removed to maintain the temperature within the desired range. Water may be removed from the system during the oxidation-leaching operation, resulting in a desirable increase in the concentration of the sulfates in the slurry liquor. The autoclave system may be a single pressurized vessel or may include several pressurized vessels.

A suitable process and apparatus for the removal of heat and water during the oxidation-leaching operation is described in copending application for U.S. Pat. Ser. No. 446,412, filed Feb. 27, 1974 by Freddie J. Touro, one of the present inventors.

Removal of water also serves to increase the concentration of the acidity of the slurry, which is desirable, since increased acidity results in increased copper extraction rates when the oxidation-leaching operation is carried out under the preferred temperature conditions of 425°–450°F. Control of the acidity during the oxidation-leaching of chalcopyrite forms the subject matter of another copending application for U.S. Pat. Ser. No. 446,315, filed Feb. 27, 1974 by Freddie J. Touro, one of the present inventors.

To insure maximum removal of iron from the leach liquor, a neutralizing agent such as limestone slurry 4 is added in the autoclave system so as to reduce the acidity to less than about 40 grams per liter  $H_2SO_4$ , preferably between about 10 and 20 grams per liter  $H_2SO_4$ , and permit the hydrolysis of  $Fe_2(SO_4)_3$  and precipitation of iron as  $Fe_2O_3$ . Neutralization of the acidity at a temperature between 425°–450°F in the autoclave is a particularly preferred embodiment of the process because in this temperature range the iron is precipitated as hematite ( $Fe_2O_3$ ) and the calcium as anhydrite ( $CaSO_4$ ), both of which are crystalline in nature and their precipitation in this form results in the satisfactory separation of the solids from the liquid later in the process. In contrast, the precipitates obtained at low temperatures (iron as ferric hydroxide, and calcium as gypsum) are much more difficult to separate from the liquid phase.

While limestone, i.e., calcium carbonate, has been described as the neutralizing agent used in the preferred embodiment, other neutralizing agents may be utilized. For example, the hydroxides, oxides and carbonates of calcium, strontium and barium, all of which form insoluble sulfate, may be used as the neutralizing agent.

Following the addition of the neutralizing agent, the slurry is provided additional retention time in the autoclave system at the preferred temperature of between 425° and 425°F, and at the stated oxygen partial pressure with constant mechanical agitation. During this time, additional iron is precipitated and further oxidation and dissolution of copper may occur. A vapor-space bleed-stream may be vented to atmosphere from the autoclave to purge the gradual buildup of contaminant nitrogen (introduced with the oxygen-containing gas). Some oxygen is lost with this bleedstream as well as some water vapor. The loss of the latter again serves to increase the copper concentration in the leach liquor and to remove some heat.

In the preferred embodiment the treated slurry stream 5 leaving the autoclave is made up of a liquid phase composed of a solution of acidic copper sulfate and solids composed of gangue, anhydrite ( $CaSO_4$ ), and hematite ( $Fe_2O_3$ ). Before this liquid phase is sepa-

rated from these solids, the slurry is subjected to a flashing operation. The flashing operation may optionally be preceded by an indirect cooling operation. In the preferred embodiment, the flashing operation is preceded by an indirect cooling operation, as indicated in the drawing. Exiting the autoclave, then, the slurry is first cooled with water 6 in an indirect heat exchanger to approximately 275°–400°F while maintaining the same pressure as used in the autoclave. The heat exchanger may be a waste heat boiler, for example, generating 15 psig steam. This reduction in temperature is provided so that when the cooled slurry 7 is finally flashed to atmospheric pressure, the volume of flashed steam produced 8 is significantly less than that which would be produced if flashing occurred at the original temperature of between 425° and 450°F. As a result, the velocity of the slurry-steam mixture through the let-down valve is decreased and the erosion of the valve reduced in severity.

In the process of being flashed to atmospheric pressure, additional water vapor is lost and the copper concentration of the liquor further increased. After flashing, the temperature of the slurry is approximately 230°F (somewhat elevated for atmospheric pressure due to the content of dissolved salts). Further cooling of the liquor, down to approximately 150°F, may be carried out before the separation of the liquid and solids by blending recycle liquor 13, cooled to about 120°F in a subsequent cooling operation (described below), with the 230°F slurry. The resultant slurry 9, cooled to about 150°F, is then fed to a solids-liquid separation system with separated liquor 10 going to a cooling operation and solids 14 going to a washing system. In a preferred embodiment a barometric condenser is used to cool stream 10 to about 120°F. A portion of the cooled separated liquor 13 is recycled to cool the slurry, as it leaves the flashing operation, as described above. In the barometric condenser additional water 11 is removed under vacuum at about 120°F to further increase the copper concentration of the leach liquor. Removal of water at this point has the beneficial effect of increasing the wash water-to-tailings ratio that may be used in the washing system.

In the washing system the solids are washed with water 15 to recover the retained copper sulfate solution. The return wash water 16, containing copper values and dilute sulfuric acid, is recycled back to the slurry preparation facilities. The washed solids tailings 17 may be sent to a tailings pond or to further treatment for the recovery of gold or silver, etc. It is to be noted that any type of solids-liquid separation techniques, such as filtration, centrifuging, etc., may be employed in these operations; however, a thickener or a combination of thickeners is preferred. In the preferred embodiment, the portion of the 120°F liquor from the barometric condenser that is not recycled 12 is fed to the electrolytic cells. At this point, the concentration of copper in the separated copper sulfate solution has been increased to about 75 grams per liter.

In the electrolytic deposition process copper cathodes 18 of as high as 99.9 percent purity can be produced as final product. Heat is liberated during this operation and should be removed in order to keep the temperature in the electrolytic cells at about 150°F or less. Sulfuric acid is also produced to the stoichiometric extent of the copper deposited so that the spent electrolyte 19 normally contains between about 5 and 15 grams per liter of copper and between about 100 and

170 grams per liter of sulfuric acid.

The spent solution 19 is then treated with a sulfiding agent 20 to precipitate the copper as copper sulfide. Any one of a number of sulfiding agents which cause the precipitation of the copper from spent electrolyte 19 as copper sulfide, such as hydrogen sulfide ( $H_2S$ ), ammonium sulfide ( $NH_4)_2S$ ), sodium sulfide ( $Na_2S$ ), ammonium hydrosulfide ( $NH_4HS$ ), sodium hydrosulfide ( $NaHS$ ), potassium sulfide ( $K_2S$ ) and potassium hydrosulfide ( $KHS$ ), may be used. Preferably hydrogen sulfide ( $H_2S$ ) is used. Preferably an amount in excess of that stoichiometrically required is employed in order to assure that precipitation of virtually all of the copper present in the spent electrolyte. The sulfided slurry 21 is processed in a thickener and the thickened acidic copper sulfide ( $CuS$ ) slurry 22, having a solids content of between about 3 percent and 15 percent and preferably higher than 5 percent, is recycled to the feed slurry tank. About 70–90% of spent electrolyte stream 19 can be bled from the process via stream 23 by this method with minimal loss of copper. This bleed serves to eliminate from the process certain soluble impurities such as calcium, magnesium, nickel and cobalt. The acidic supernatant liquor stream 23 from the thickener may be treated with a limestone slurry 24, as shown in the drawing, and the resultant gypsum slurry 25 pumped to waste, i.e., to holding ponds or land-fill areas, or it may be used in any other process which requires the use of a dilute sulfuric acid solution.

#### Example

The following example illustrates the manner in which the process of this invention may be operated.

Chalcopyrite concentrate 1 may be fed to the system of the drawing and mixed with recycle streams 16 and 22 as previously indicated. The composition of stream 1 is given below, in Table 1, together with the typical compositions of other pertinent streams of the process.

Oxidation-leaching of the slurried concentrate 2 is carried out at 425°F and 100 psi of oxygen partial pressure in an autoclave system. Total pressure is 445 psig. Limestone 4 is used to partially neutralize the acidity during oxidation-leaching so that the exiting slurry 5 going to the indirect cooler has an acidity of about 20 grams per liter  $H_2SO_4$ . The temperature of slurry 5 is decreased in the indirect cooler to about 320°F. Partially cooled slurry 7 is then flashed to atmospheric pressure and to a temperature of about 230°F, and blended with cooled recycle liquor stream 13 for further cooling to 150°F before entering the solids-liquid separation system.

The solids-liquid separation is carried out in one thickener, and the bottoms 14 from this thickener are washed with water in a countercurrent fashion using three thickeners. Tailings 17 from the last washing

thickener may be sent to waste. The overflow 10 from the solids-liquid separation thickener is further cooled to 120°F using a barometric condenser and then divided into stream 13, which is used for blending with the flashed slurry, as described above, and stream 12, which is fed to the electrolytic deposition operation.

Copper cathodes 18 of high purity are produced in the electrolytic cells. The temperature in this operation normally tends to rise and so an external cooler (not shown) is provided to maintain it at about 150°F. In the electrolytic deposition operation the copper content of the electrolyte is reduced from about 60–80 grams per liter (in stream 12) to about 5 grams per liter (in stream 19). Depletion of the copper, during electrolysis, to below about 5 grams per liter is not deemed economically attractive in view of the convenience of scavenging the copper values not deposited during electrolysis which is provided by the subsequent sulfiding operation of our process.

Spent electrolyte 19 is treated with hydrogen sulfide 20 in an amount sufficient to precipitate as copper sulfide virtually all of the copper present in solution at this point. Sulfided slurry 21 is thickened and recycled as stream 22 to the slurry feed tank. The overflow stream 23 from the sulfide thickener contains most of the impurities not rejected in the oxidation-leaching as precipitated solids and is conveniently treated with limestone 24 and pumped to waste 25. It is significant of the process of this invention that these impurities are rejected from the system in the manner just described and without losing any significant amount of copper values. By contrast, a process in which the spent electrolyte 19 is sent to waste would lose significant amounts of copper values as dissolved copper in the waste spent electrolyte.

It is also significant of the process of this invention that the copper values not deposited in the electrolytic deposition operation are conveniently recovered by the recycling of a relatively concentrated copper sulfide slurry 22 to the initial stages of the process without the recycling of impurities or large quantities of undesirable water to the initial stages of the process. By contrast, a process which chose to recycle the spent electrolyte 19 from the electrolyte deposition operation in order to recover the copper values not deposited during electrolysis would do so at the expense of recycling the impurities associated with the spent electrolyte and, of course, of not being able to remove water from the system at this point. The inability to remove water from the system at this point would have the effect, in such case, of decreasing the wash water-to-tailings ratio which may be used in the washing operation of the process and this, in turn, would increase the number of thickeners necessary to effectively carry out the washing.

TABLE 1

| Stream*                 | 1    | 12    | 17   | 19  | 22    | 23    |
|-------------------------|------|-------|------|-----|-------|-------|
| Composition**           | %    | gpl   | %    | gpl | %     | gpl   |
| Copper (Cu)             | 26.1 | 75.1  | 0.70 | 5   |       | 0.001 |
| Iron (Fe)               | 28.6 | 1.0   | 27.0 |     | 0.05  | 1.0   |
| Total Sulfur            | 33.9 |       | 13.6 |     |       |       |
| Free Acid ( $H_2SO_4$ ) |      | 20.0  |      | 130 |       | 140.0 |
| Calcium                 | 0.18 | 0.57  | 13.5 |     | 0.06  | 0.57  |
| Magnesium               |      | 0.33  |      |     | 0.013 | 0.32  |
| Aluminum                |      | 0.55  |      |     | 0.01  | 0.55  |
| Lead                    |      | 0.01  | 0.12 |     |       | 0.005 |
| Antimony                |      | 0.007 | 0.05 |     |       | 0.007 |
| Bismuth                 |      | 0.009 | 0.04 |     |       | 0.009 |

TABLE 1-continued

| STREAM COMPOSITIONS OF A TYPICAL RUN OF<br>PROCESS FOR THE MANUFACTURE OF ELECTROLYTIC COPPER |   |       |    |     |       |       |
|-----------------------------------------------------------------------------------------------|---|-------|----|-----|-------|-------|
| Stream*                                                                                       | 1 | 12    | 17 | 19  | 22    | 23    |
| Composition**                                                                                 | % | gpl   | %  | gpl | %     | gpl   |
| Nickel                                                                                        |   | 0.06  |    |     | 0.008 | 0.06  |
| Cobalt                                                                                        |   | 0.05  |    |     | 0.002 | 0.05  |
| Zinc                                                                                          |   | 0.25  |    |     | 0.003 | 0.24  |
| Manganese                                                                                     |   | 0.015 |    |     |       | 0.015 |

\*All stream numbers refer to the drawing.

\*\*Compositions of streams No. 1, 17 and 22 are given on a dry basis.

The terms and expressions which have been used here are used as terms of description and not of limitation, and there is no intention, in the use of such terms and expressions, of excluding equivalents of the features shown and described, or portions thereof, it being recognized that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. Process for recovering copper from a copper-bearing sulfide ore containing iron comprising the steps of: passing an aqueous slurry of said ore through an oxidation-leaching operation in an autoclave system while maintaining the temperature within said autoclave system at between 350°F and 450°F and providing an oxygen partial pressure within said autoclave system of between about 50 and 500 pounds per square inch to form sulfuric acid and to solubilize the metal constituents in said slurry as sulfate solutions,

reducing the acidity of said solutions in said autoclave system by the addition of a neutralizing agent during said oxidation-leaching operation to precipitate substantially all of the solubilized iron in said solutions as insoluble ferric oxide,

withdrawing from said autoclave system the treated slurry comprising a liquid phase of acidic copper sulfate and solids comprising ore gangue and the precipitated ferric oxide,

flashing the treated slurry to atmospheric pressure, separating said liquid phase from said solids, washing said separated solids with an aqueous wash medium to recover retained copper sulfate solution and recycling said recovered copper sulfate solution to said autoclave system,

cooling said separated liquid phase, electrolytically treating said separated liquid phase to produce electrolytic copper and a spent electrolyte comprising sulfuric acid and a residual amount of copper,

treating said spent electrolyte with a sulfiding agent to precipitate substantially all of said residual amount of copper from said electrolyte as copper sulfide,

thickening said treated spent electrolyte to separate said precipitated copper sulfide from said treated spent electrolyte as a thickened copper sulfide slurry, and

recycling said thickened copper sulfide slurry to said autoclave system.

2. The process as defined in claim 1 wherein water vapor produced during said oxidation-leaching operation within said autoclave system is removed from said autoclave system whereby the concentration of said sulfate solutions is increased.

3. The process as defined in claim 1 wherein the acidity of said solutions in said autoclave system is reduced

to less than 40 grams per liter of sulfuric acid by the addition of said neutralizing agent.

4. The process as defined in claim 1 further comprising the step of cooling the treated slurry withdrawn from said autoclave system to between about 275°F and 400°F while maintaining the same total pressure used in said oxidation-leaching operation prior to said flashing operation.

5. The process as defined in claim 1 further comprising the step of cooling the treated slurry to approximately 150°F prior to said separating step.

6. The process as defined in claim 5 wherein the concentration of copper in said separated liquid phase following said cooling and water removal step is about 75 grams per liter of copper.

7. The process as defined in claim 1 wherein water is removed from said separated liquid phase during said cooling step.

8. The process as defined in claim 1 wherein a portion of said cooled separated liquid phase is blended with said treated slurry prior to separating said liquid phase from said solids.

9. The process as defined in claim 1 wherein the temperature of said separated liquid phase is reduced to about 120°F by said cooling step.

10. The process as defined in claim 1 wherein said cooling of said separated liquid phase is carried out using a barometric condenser.

11. The process as defined in claim 1 wherein said spent electrolyte has a concentration of between about 5 and 15 grams per liter of copper and between about 100 and 170 grams per liter of sulfuric acid.

12. The process as defined in claim 1 wherein said sulfiding agent is hydrogen sulfide.

13. The process as defined in claim 1 wherein said sulfiding agent is selected from the group consisting of hydrogen sulfide, ammonium sulfide, sodium sulfide, ammonium hydrosulfide, sodium hydrosulfide, potassium sulfide, and potassium hydrosulfide.

14. The process as defined in claim 1 wherein said treated spent electrolyte is thickened to a solids content of between about 3 and 15 percent.

15. The process as defined in claim 1 wherein the copper content of said liquid phase is reduced from between about 60 and 80 grams per liter to about 5 grams per liter in said electrolytic treatment.

16. The process as defined in claim 1 wherein the acidity of said solutions in said autoclave system is reduced to between about 10 and 20 grams per liter of sulfuric acid by the addition of said neutralizing agent.

17. The process as defined in claim 1 wherein the oxidation-leaching operation is carried out at a temperature between 425°F and 450°F.

18. The process as defined in claim 1 wherein the oxidation-leaching operation is carried out using an oxygen partial pressure of between about 100 and 200

9

pounds per square inch.

19. The process as defined in claim 1 wherein said neutralizing agent is selected from the group consisting of the hydroxides, oxides and carbonates of calcium, strontium and barium.

20. The process as defined in claim 1 wherein said neutralizing agent is calcium carbonate, wherein the calcium in said calcium carbonate forms insoluble calcium sulfate and wherein said calcium sulfate is withdrawn from said autoclave as part of the solids in said treated slurry.

21. The process as defined in claim 20 wherein said copper bearing sulfide ore also contains arsenic,

10

wherein a first part of said calcium in said calcium carbonate forms insoluble calcium sulfate, wherein said arsenic, solubilized to a metal sulfate in said oxidation-leaching operation, is precipitated with at least a part of said calcium as insoluble iron and calcium arsenates upon the addition of said calcium carbonate, and wherein said iron and calcium arsenates are withdrawn from said autoclave as part of the solids in said treated slurry.

22. The process as defined in claim 1 wherein the electrolytic copper produced is about 99.9 percent pure.

\* \* \* \* \*

15

20

25

30

35

40

45

50

55

60

65