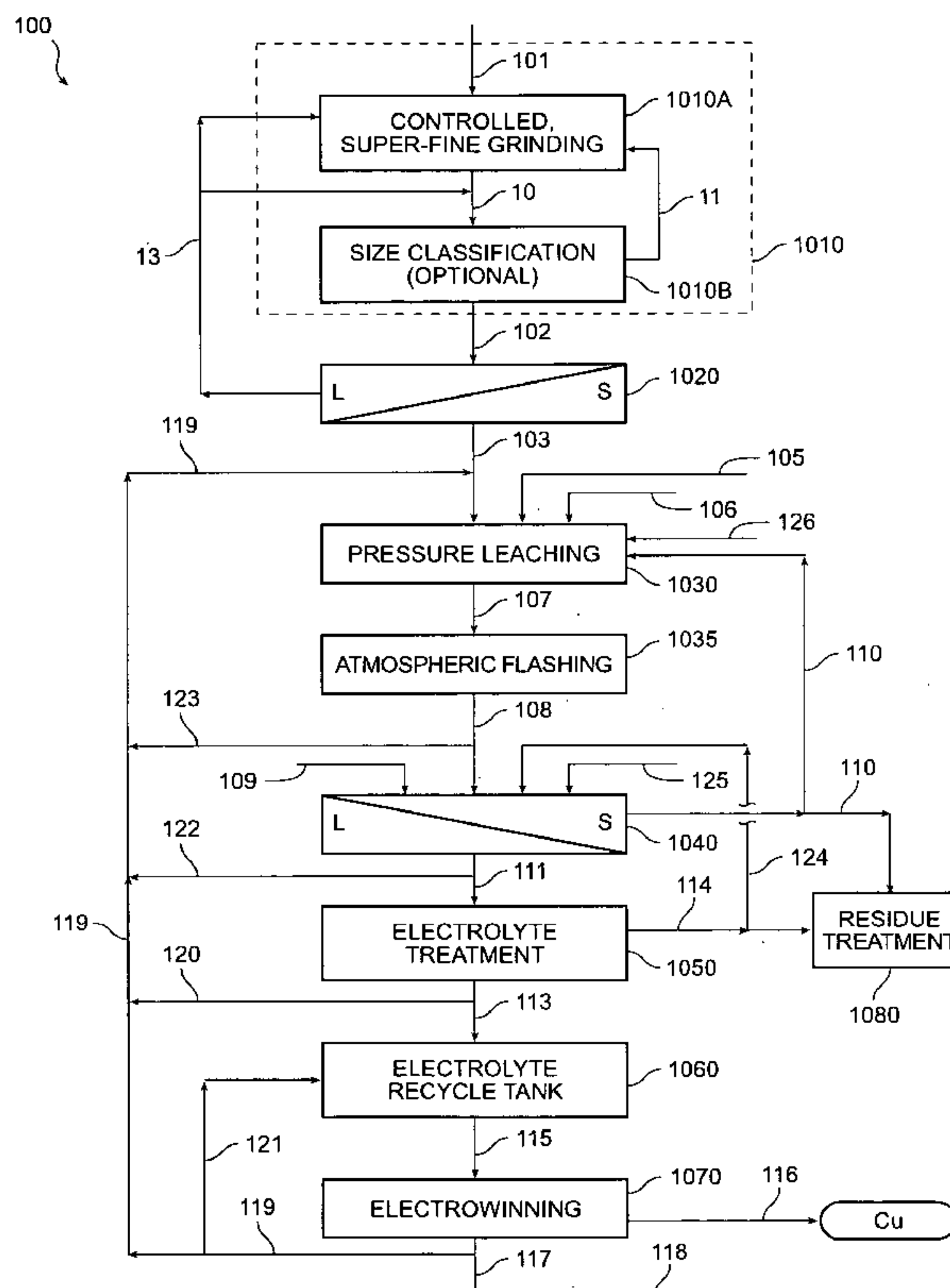


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(19) **United States**(12) **Patent Application Publication**  
Marsden et al.(10) **Pub. No.: US 2005/0126923 A1**(43) **Pub. Date: Jun. 16, 2005**(54) **PROCESS FOR RECOVERY OF COPPER  
FROM COPPER-BEARING MATERIAL  
USING MEDIUM TEMPERATURE  
PRESSURE LEACHING, DIRECT  
ELECTROWINNING AND  
SOLVENT/SOLUTION EXTRACTION****Related U.S. Application Data**(63) Continuation-in-part of application No. 10/756,574,  
filed on Jan. 12, 2004, which is a continuation of  
application No. 09/915,105, filed on Jul. 25, 2001,  
now Pat. No. 6,676,909.Continuation-in-part of application No. 10/737,420,  
filed on Dec. 15, 2003, which is a continuation of  
application No. 10/238,399, filed on Sep. 9, 2002,  
now Pat. No. 6,663,689, which is a continuation of  
application No. 09/912,921, filed on Jul. 25, 2001,  
now Pat. No. 6,451,089.(60) Provisional application No. 60/517,192, filed on Nov.  
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(US)****Publication Classification**(51) **Int. Cl.<sup>7</sup> ..... C25C 1/12**(52) **U.S. Cl. .... 205/580; 205/586**(57) **ABSTRACT**

The present invention relates generally to a process for recovering copper from a metal-bearing ore, concentrate, or other copper-bearing material using pressure leaching and direct electrowinning. More particularly, the present invention relates to a substantially acid-autogenous process for recovering copper from chalcopyrite-containing ore using pressure leaching and direct electrowinning in combination with a leaching, solvent/solution extraction and electrowinning operation.

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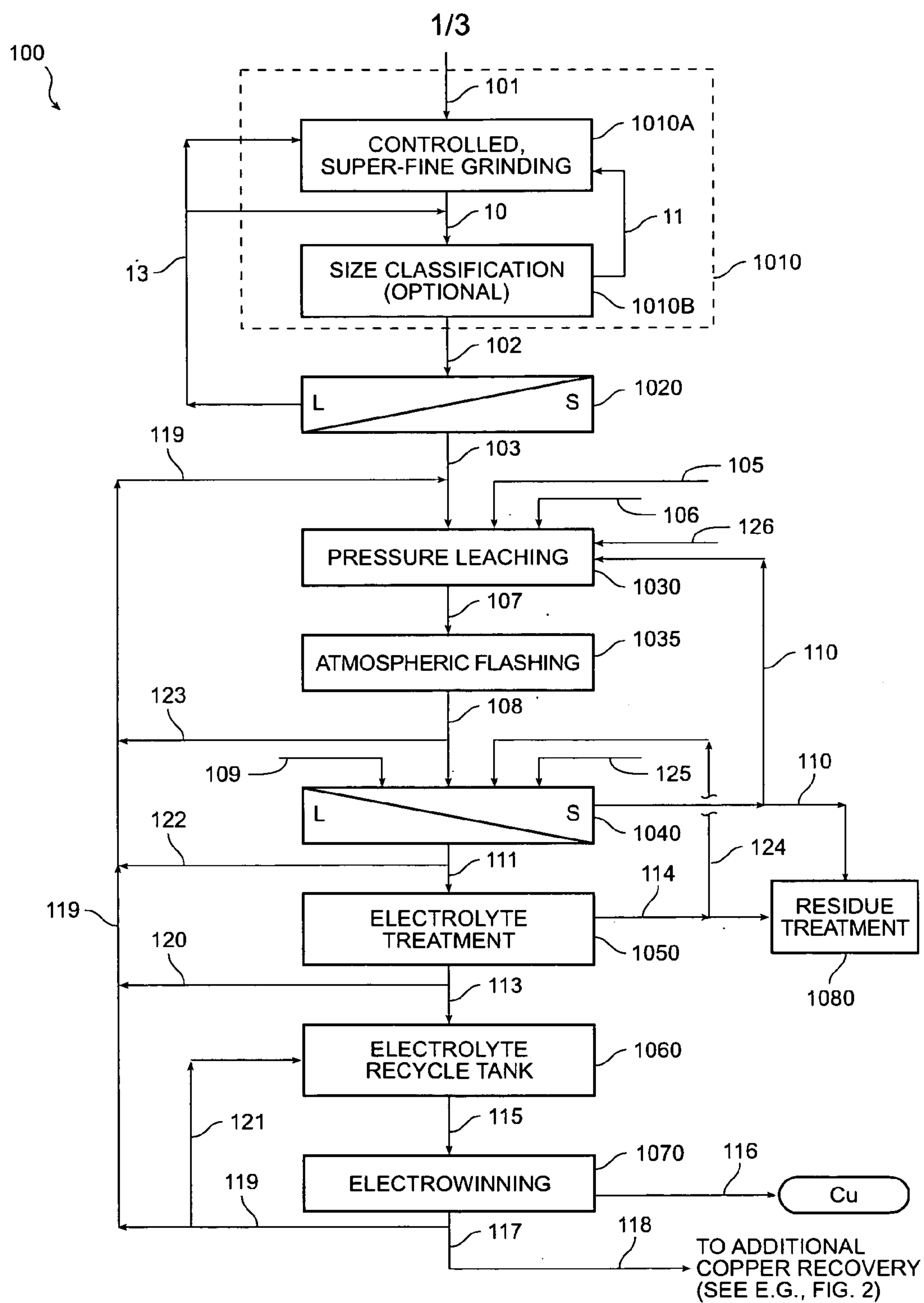


FIG. 1

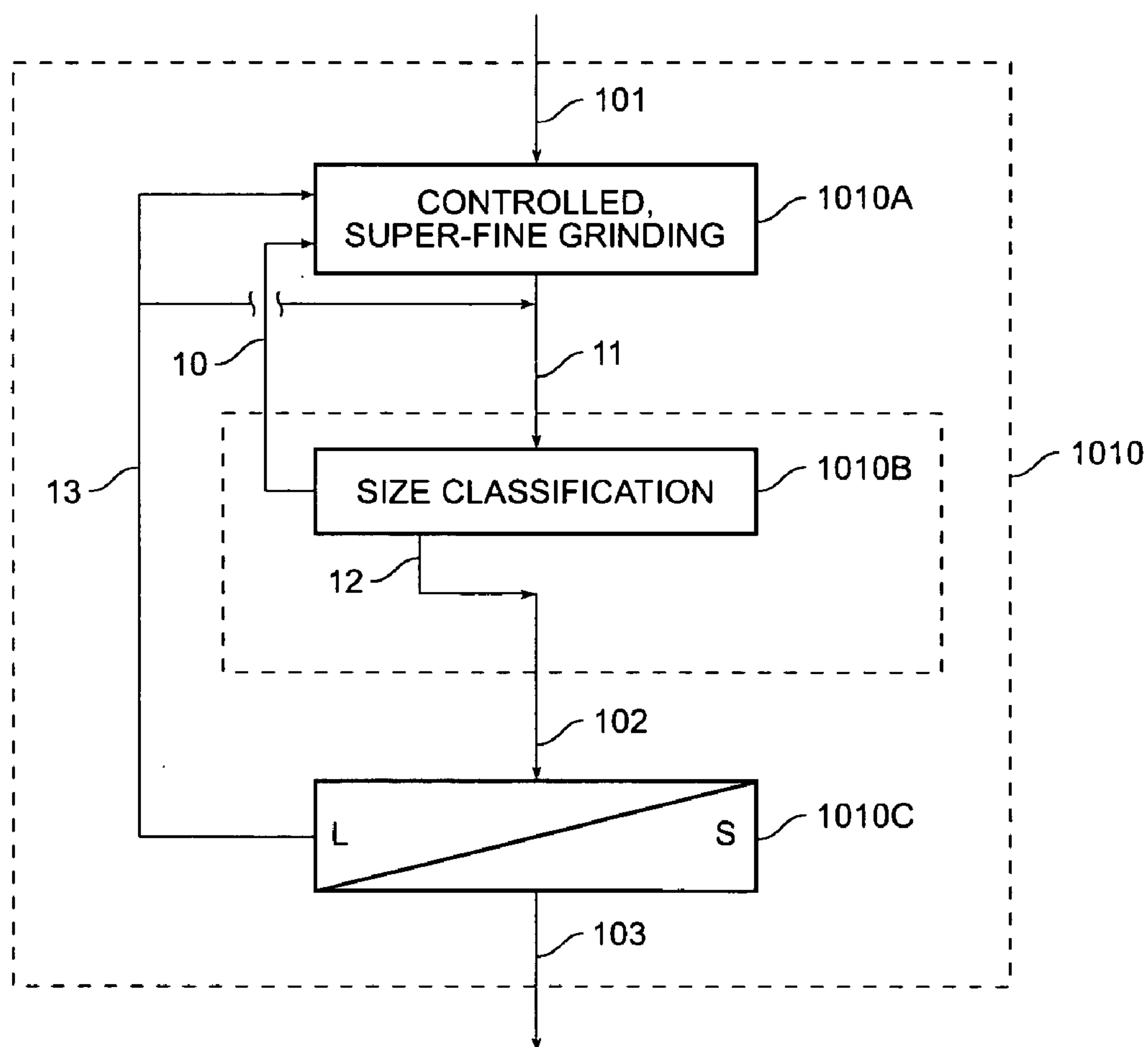


FIG. 1A

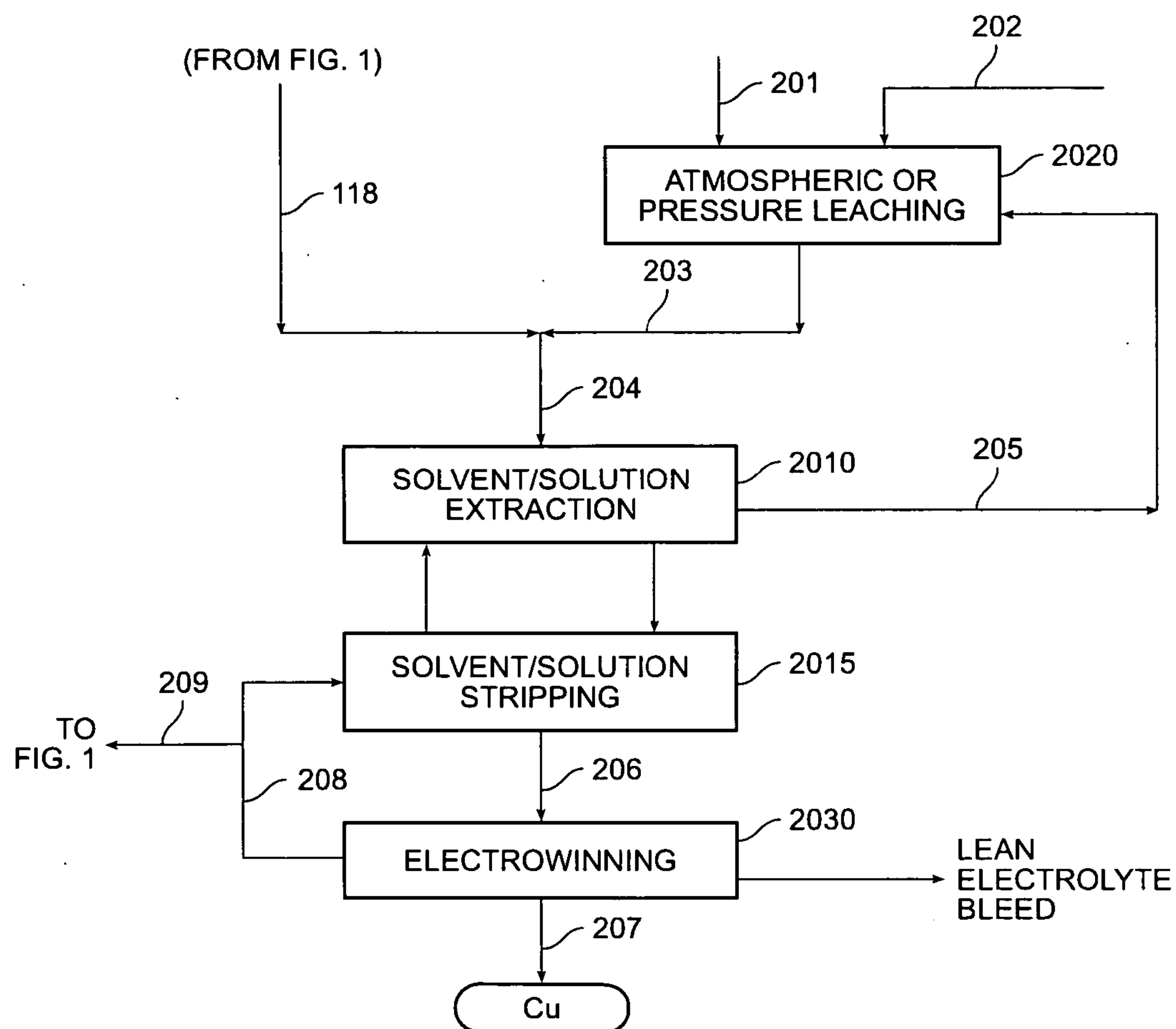


FIG. 2

FIG. 3

Residue Copper vs. Total Acid Addition  
160 deg. C, 90 min, P(98) = 15 micron

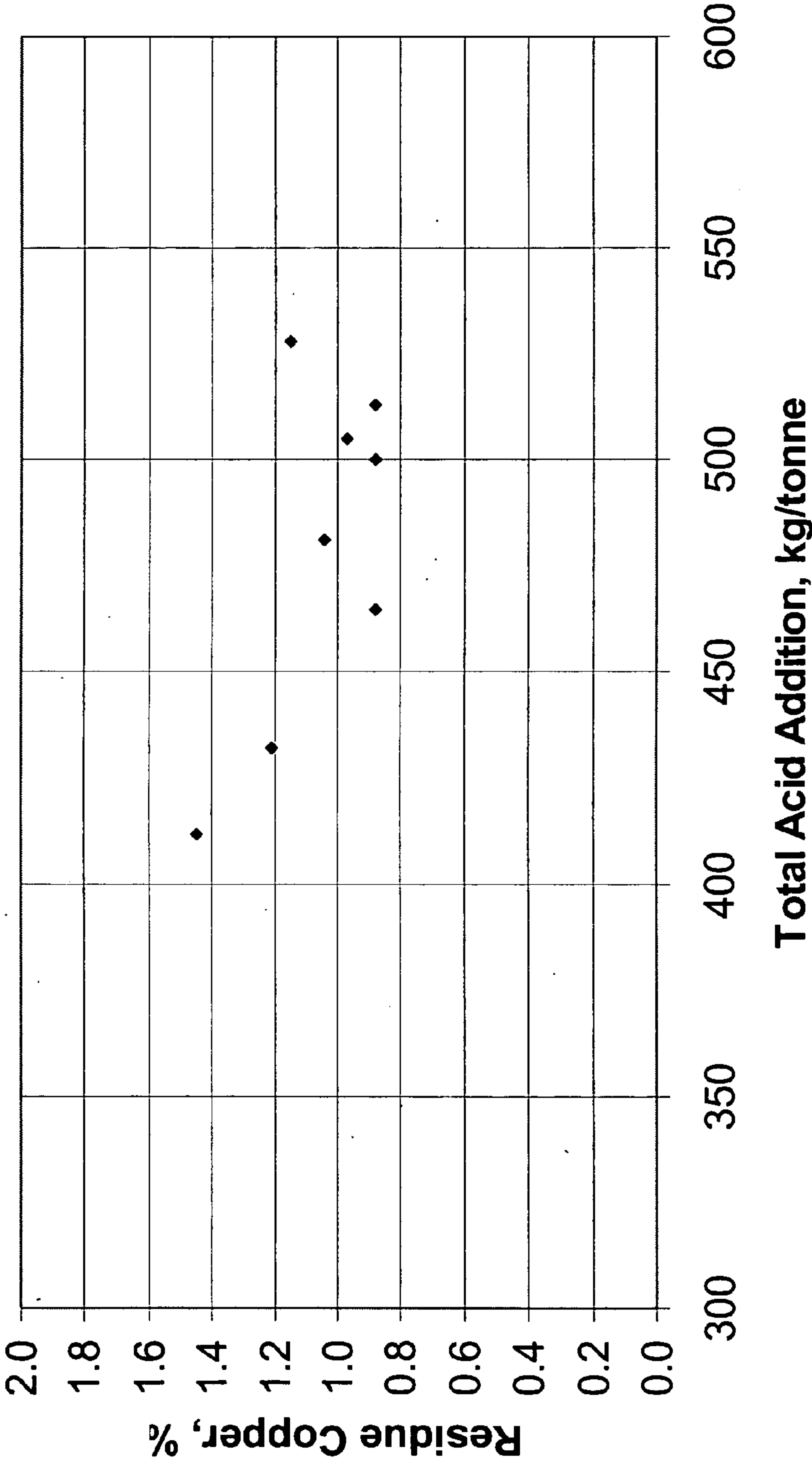
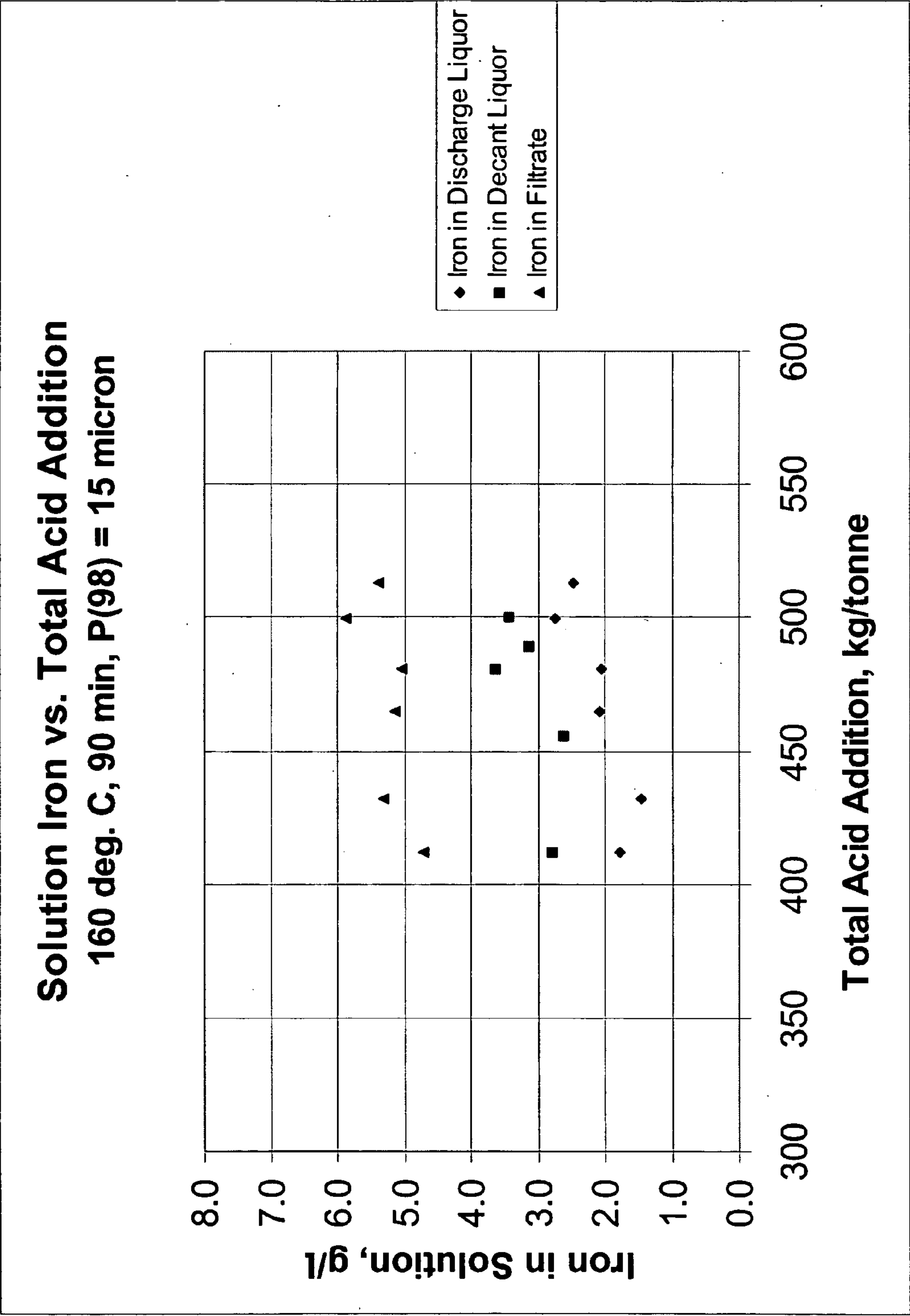


FIG. 4





**PROCESS FOR RECOVERY OF COPPER FROM  
COPPER-BEARING MATERIAL USING MEDIUM  
TEMPERATURE PRESSURE LEACHING, DIRECT  
ELECTROWINNING AND SOLVENT/SOLUTION  
EXTRACTION**

**CROSS REFERENCE TO RELATED  
APPLICATIONS**

[0001] This application is a continuation-in-part of U.S. patent application Ser. No. 10/756,574, filed on Jan. 12, 2004, which is a continuation of U.S. patent application Ser. No. 09/915,105, which was filed on Jul. 25, 2001 and issued as U.S. Pat. No. 6,676,909 on Jan. 13, 2004, the disclosures of which are incorporated by reference herein. This application is also a continuation-in-part of U.S. patent application Ser. No. 10/737,420, filed on Dec. 15, 2003, which is a continuation of U.S. patent application Ser. No. 10/238,399, which was filed on Sep. 9, 2002 and issued as U.S. Pat. No. 6,663,689 on Dec. 16, 2003, which is a continuation of U.S. patent application Ser. No. 09/912,921, which was filed on Jul. 25, 2001 and issued as U.S. Pat. No. 6,451,089 on Sep. 17, 2002, the disclosures of which are incorporated by reference herein. This application also claims priority to U.S. Provisional Application Ser. No. 60/517,192, filed on Nov. 3, 2003, the disclosure of which is incorporated by reference herein.

**FIELD OF INVENTION**

[0002] The present invention relates generally to a process for recovering copper from a metal-bearing material using medium temperature pressure leaching and direct electrowinning. More particularly, the present invention relates to a process using controlled, super-fine grinding, pressure leaching, and direct electrowinning in combination with solvent/solution extraction to recover metal from the metal-bearing material.

**BACKGROUND OF THE INVENTION**

[0003] Hydrometallurgical treatment of copper-containing materials, such as copper ores, copper-bearing concentrates, and other copper-bearing materials, has been well established for many years.

[0004] An effective and efficient method to recover copper from metal-bearing materials, such as, for example, chalcopyrite, chalcocite, bornite, covellite, digenite, and enargite, that enables high copper recovery to be achieved at a reduced cost over conventional processing techniques would be advantageous.

[0005] An effective and efficient method to recover copper from metal-bearing materials, especially copper sulfides, that minimizes the use of fresh acid also would be advantageous. For example, a process for recovering copper from metal-bearing materials comprising a pressure leaching operation, in which little or no fresh, concentrated make-up acid has to be added to the pressure leaching operation due to the utilization of acid-bearing streams from operations elsewhere in the process would be advantageous.

**SUMMARY OF THE INVENTION**

[0006] While the way in which the present invention addresses the deficiencies and disadvantages of the prior art is described in greater detail hereinbelow, in general, accord-

ing to various aspects of the present invention, a process for recovering copper and other metal values from a metal-bearing material includes various physical conditioning, reaction, and recovery processes. For example, in accordance with the various embodiments of the present invention, controlled, super-fine grinding of the metal-bearing material prior to reactive processing, such as by medium temperature (as will be defined hereinbelow) pressure leaching, results in enhanced metal value recovery and various other advantages over prior art metal recovery processes. Moreover, proper conditioning enables direct electrowinning of copper from a pressure leaching product stream without the use of an intermediate solvent/solution extraction step. Further, at least a portion of the impurities and excess acid in the process stream are removed through the use of a lean electrolyte bleed stream from electrowinning that may be further processed in a solvent/solution extraction and electrowinning operation.

[0007] In accordance with an exemplary embodiment of the present invention, a process for recovering copper from a metal-bearing material includes the steps of (i) providing a feed stream containing copper-bearing material; (ii) subjecting the copper-bearing feed stream to controlled, super-fine grinding; (iii) pressure leaching the copper-bearing feed stream to yield a copper-containing solution; (iv) recovering cathode copper from the copper-containing solution; (v) treating at least a portion of a lean electrolyte stream from the copper recovery step in a solvent/solution extraction and electrowinning operation; and (vi) recycling at least a portion of the lean electrolyte stream to the pressure leaching step to provide some or all of the acid requirement of the pressure leaching operation.

[0008] In accordance with another aspect of an exemplary embodiment of the invention, a bleed stream of lean electrolyte from the electrowinning stage advantageously removes at least a portion of the excess acid from the metal recovery process and also impurities contained therein, thus preventing such impurities from accumulating to deleterious levels in the process and negatively impacting production efficiencies and product (e.g., copper cathode) quality. In accordance with one embodiment of the invention, excess acid removed in the lean electrolyte bleed stream may be utilized in other copper extraction processes, or the acid may be consumed by using suitable materials, such as, for example, low grade copper ore, mining waste products, and/or other rock products containing acid neutralizing minerals, such as limestone, dolomite, feldspar, and the like.

[0009] In accordance with one aspect of an exemplary embodiment of the invention, acid generated in the pressure leaching and electrowinning steps is recycled to the pressure leaching step and provides acid needed for effective leaching of copper. In this way, the use of recycled acid-containing solution, rather than concentrated sulfuric acid, is economically advantageous.

[0010] These and other advantages of a process according to various aspects of the present invention will be apparent to those skilled in the art upon reading and understanding the following detailed description with reference to the accompanying figures.

**BRIEF DESCRIPTION OF THE DRAWING**

[0011] The subject matter of the present invention is particularly pointed out and distinctly claimed in the con-



cluding portion of the specification. A more complete understanding of the present invention, however, may best be obtained by referring to the detailed description and claims when considered in connection with the drawing figures, wherein like numerals denote like elements and wherein:

[0012] **FIG. 1** illustrates a flow diagram of a copper recovery process in accordance with one exemplary embodiment of the present invention;

[0013] **FIG. 1A** illustrates a flow diagram of an aspect of an exemplary embodiment of the present invention;

[0014] **FIG. 2** illustrates a flow diagram of various aspects of a copper recovery process in accordance with an exemplary embodiment of the present invention;

[0015] **FIG. 3** is a graph plotting copper concentration in the pressure leaching residue as a function of acid addition in accordance with various aspects of an exemplary embodiment of the invention; and

[0016] **FIG. 4** is a graph plotting ferric iron concentration in the pressure leaching discharge as a function of acid addition plus acid equivalent addition in accordance with various aspects of an exemplary embodiment of the invention.

#### DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0017] Various embodiments of the present invention exhibit significant advancements over prior art processes, particularly with regard to copper recovery and process efficiency. In accordance with an exemplary embodiment of the present invention, a process for recovering copper from a metal-bearing material includes the steps of (i) providing a feed stream containing copper-bearing material; (ii) subjecting at least a portion of the copper-bearing feed stream to controlled, super-fine grinding; (iii) pressure leaching the copper-bearing feed stream to yield a copper-containing solution; (iv) recovering cathode copper from the copper-containing solution by electrowinning, (v) treating at least a portion of a lean electrolyte stream from the copper recovery step by solvent/solution extraction followed by an electrowinning operation; and (vi) recycling at least a portion of the lean electrolyte stream to the pressure leaching step.

[0018] Existing copper recovery processes that utilize conventional atmospheric or pressure leaching, solvent/solution extraction and electrowinning process steps may, in many instances, be easily retrofitted to exploit the many commercial benefits the present invention provides. Medium temperature pressure leaching processes for chalcopyrite are generally thought of as those processes operating at temperatures from about 120° C. to about 190° C. It has been demonstrated that rapid copper sulfide oxidation kinetics can be achieved by reducing particle size, providing sufficient acid addition to the pressure leaching stage, providing sufficient oxygen overpressure, elevating the temperature of the pressure leaching operation and adding a dispersant to the pressure leaching operation.

[0019] Referring first to **FIG. 1**, in accordance with various aspects of the present invention, a metal-bearing material **101** is provided for processing. Metal-bearing material **101** may be an ore, a concentrate, a precipitate, or any other material from which copper and/or other metal values may

be recovered. Metal values such as, for example, copper, gold, silver, platinum group metals, nickel, cobalt, molybdenum, rhenium, uranium, rare earth metals, and the like, may be recovered from metal-bearing materials in accordance with various embodiments of the present invention. The various aspects and embodiments of the present invention, however, prove especially advantageous in connection with the recovery of copper from copper-bearing sulfide ores, such as, for example, ores and/or concentrates and/or precipitates containing chalcopyrite ( $\text{CuFeS}_2$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ), covellite ( $\text{CuS}$ ), enargite ( $\text{Cu}_3\text{AsS}_4$ ), digenite ( $\text{Cu}_9\text{S}_5$ ) and mixtures thereof. Thus, metal-bearing material **101** preferably is a copper ore, concentrate or precipitate, and, more preferably, is a copper-bearing sulfide ore, concentrate or precipitate. For ease of discussion, the description of various exemplary embodiments of the present invention hereinbelow generally focuses on the recovery of desired metal values from chalcopyrite-containing ore or concentrate.

[0020] Metal-bearing material **101** may be prepared for metal recovery processing in any manner that enables the conditions of metal-bearing material **101** to be suitable for the chosen processing method, as such conditions may affect the overall effectiveness and efficiency of processing operations. For example, feed stream conditions such as particle size, composition, and component concentrations can affect the overall effectiveness and efficiency of downstream processing operations, such as, for example, atmospheric leaching or pressure leaching. Desired composition and component concentration parameters can be achieved through a variety of chemical and/or physical processing stages, the choice of which will depend upon the operating parameters of the chosen processing scheme, equipment cost and material specifications.

[0021] In accordance with an exemplary embodiment of the present invention, copper is the metal to be recovered from a metal-bearing material, such as a copper sulfide concentrate. One aspect of this exemplary embodiment involves use of a copper sulfide concentrate produced by froth flotation. In preparation for froth flotation, the metal-bearing material feed stream is ground to a particle size suitable to liberate mineral-bearing particles from gangue materials.

[0022] It is generally known that hydrometallurgical processes, particularly pressure leaching processes, are sensitive to particle size. Thus, it is common practice in the area of extractive hydrometallurgy to finely divide, grind, and/or mill mineral species to reduce particle sizes prior to processing by pressure leaching. It generally has been appreciated that reducing the particle size of a mineral species, such as, for example, a copper sulfide, enables pressure leaching under less extreme conditions of pressure and temperature to achieve the same metal extraction as achieved under conditions of higher temperature and pressure. A variety of acceptable techniques and devices for reducing the particle size of the metal-bearing material are currently available, such as ball mills, tower mills, superfine grinding mills, attrition mills, stirred mills, horizontal mills and the like, and additional techniques may later be developed that may achieve the desired result of increasing the surface area of the material to be processed. With regard to one aspect of an exemplary embodiment of the invention, such a result is desired because the reaction rate during



leaching generally increases as the surface area of the metal-bearing material increases, such that increasing the fineness of the metal-bearing material before subjecting the material stream to pressure leaching generally will allow for more moderate temperature and pressure conditions to be employed within the pressure leaching vessel, and may reduce the residence time of the oxidation reaction during pressure leaching. The particle size distribution can also affect other leaching conditions, such as, for example, acid concentration and oxygen overpressure.

[0023] In accordance with one embodiment of the present invention, and with reference to **FIG. 1** and **FIG. 1A**, metal-bearing material **101** is prepared for metal recovery processing by controlled, super-fine grinding **1010**. Preferably, it is advantageous not only to reduce the size of the metal-bearing material particles in the process stream, but also to ensure that the weight proportion of the coarsest particles is minimized. Significant advantages in processing efficiency and copper recovery are achievable by enabling substantially all particles to react substantially completely.

[0024] As used herein, the term “controlled, super-fine grinding” refers to any process by which the particle size of the material being processed is reduced such that substantially all of the particles are small enough to react substantially completely during pressure leaching within the temperature ranges disclosed herein. For example, in accordance with one aspect of the present invention, a particle size distribution of approximately 98 percent passing about 25 microns is preferable, and more preferably, the metal-bearing material stream has a particle size distribution of approximately 98 percent passing from about 10 to about 23 microns, and optimally from about 13 to about 15 microns. These preferred particle size distributions were determined by comparison of pressure leaching results with particle size analysis of the feed through the use of a Malvern optical particle size analyzer. Other methods and apparatus, however, may be utilized.

[0025] In accordance with one aspect of an exemplary embodiment of the invention, satisfactory controlled, super-fine grinding of chalcopyrite concentrate with an as-received particle size of approximately 98 percent passing about 172 microns may be achieved using a fine grinding apparatus, such as, for example, a stirred horizontal shaft mill with baffles or a vertically stirred mill without baffles. Such exemplary apparatus include the Isamill developed jointly by Mount Isa Mines (MIM), Australia, and Netzsch Feinmahltechnik, Germany and the SMD or Detritor mill, manufactured by Metso Minerals, Finland. Preferably, if a horizontal mill is utilized, the grinding medium would be 1.2/2.4 mm or 2.4/4.8 mm Colorado sand, available from Oglebay Norton Industrial Sands Inc., Colorado Springs, Colo. However, any grinding medium that enables the desired particle size distribution to be achieved may be used, the type and size of which may be dependent upon the application chosen, the product size desired, grinding apparatus manufacturer's specifications, and the like. Exemplary media include, for example, sand, silica, metal beads, ceramic beads, and ceramic balls.

[0026] Preferably, grinding in accordance with the present invention proceeds in a staged or closed-circuit manner. That is, preferably the coarsest particles of metal-bearing material **101** are suitably ground to the desired level, while particles

already at or below the desired level are not subjected to additional grinding. As such, cost savings can be obtained in connection with grinding operations, while at the same time limiting the size and weight proportion of the coarsest particles. However, open-circuit grinding may also produce an acceptable product. With reference to **FIG. 1A**, while control of controlled, super-fine grinding step **1010** may be accomplished in any now known or hereafter devised manner, preferably cyclone technology, such as, for example, use of cyclones, or mini-cyclones, is utilized to facilitate size classification step **1010B** by separating relatively coarse materials from relatively fine materials. As noted hereinabove, preferably material **101** is super-finely ground in controlled, super-fine grinding step **1010A**, and then the coarse material **10** is suitably separated from the fine material **12**, such that coarse material **10** may be further ground, as shown in **FIG. 1A** in stream **11**. Similarly, in accordance with one aspect of an exemplary embodiment of the invention wherein the chosen grinding method and apparatus utilize a liquid processing agent (such as, for example, process water) to facilitate grinding in super-fine grinding stage **1010**, an optional solid-liquid separation stage **1010C** may be utilized to remove excess processing liquid **13** from the process stream **102** prior to pressure leaching, and preferably recycle excess process liquid **13** to super-fine grinding stage **1010A** for reuse. Depending upon the configuration of the grinding apparatus, solid-liquid separation stage **1010C** may or may not be required. If, however, process liquid is added to copper-containing material **101** prior to or during super-fine grinding **1010**, it may be desirable to remove at least a portion of the added process liquid from copper-containing material stream **102** prior to pressure leaching operation **1030** to optimize slurry density.

[0027] In another aspect of an exemplary embodiment of the present invention, the comminuted metal-bearing material is combined with a liquid prior to entering reactive processing stage **1030** (described hereinbelow). Preferably, the liquid comprises water, but any suitable liquid may be employed, such as, for example, raffinate, pregnant leach solution, or lean electrolyte. For example, a portion of the lean electrolyte from the direct electrowinning process (for example, stream **119**) may be combined with comminuted metal-bearing material to form metal-bearing material stream **103** for delivery to reactive processing stage **1030**. In this way, acid is recycled to the process stream such that it helps to satisfy the acid demand of reactive processing stage **1030**.

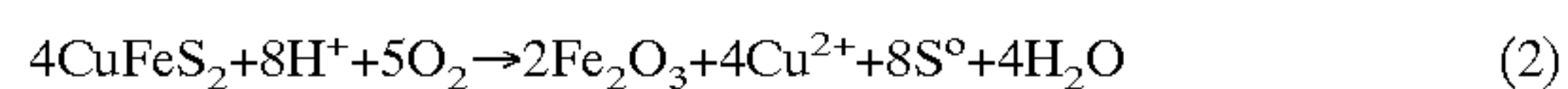
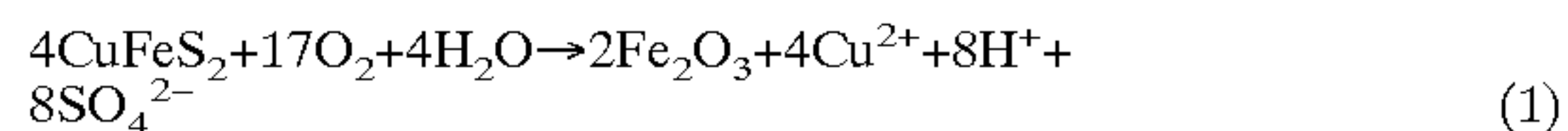
[0028] The combination of a liquid with the metal-bearing material can be accomplished using any one or more of a variety of techniques and apparatus, such as, for example, in-line blending or using a mixing tank or other suitable vessel. In accordance with an exemplary aspect of an embodiment of the invention, the concentration of solid metal-bearing material in the material stream (i.e., the slurry density) is on the order of less than about fifty (50) percent by weight of the stream, and preferably about forty (40) percent by weight of the stream. Other slurry densities that are suitable for transport and subsequent processing may, however, be used.

[0029] Referring again to **FIG. 1**, after metal-bearing material stream **103** has been suitably prepared for processing by controlled, super-fine grinding, liquid addition, and, optionally, other physical and/or chemical conditioning pro-



cesses, it is subjected to a reactive processing step **1030**, for example, metal extraction via pressure leaching. However, reactive processing step **1030** may be any suitable process or reaction that puts the copper in metal-bearing material stream **103** in a condition such that it may be subjected to later copper recovery processing. In accordance with one embodiment of the present invention, reactive processing step **1030** comprises pressure leaching. Preferably, reactive processing step **1030** is a medium temperature pressure leaching process operating at a temperature in the range of about 140° C. to about 180° C. and more preferably in the range of about 150° C. to about 170° C. Generally, the present inventors have found that temperatures above about 160° C., and more preferably in the range of about 160° C. to about 170° C. are useful in connection with the various aspects of the present invention.

[**0030**] In accordance with one aspect of the present invention, the optimum temperature range selected for operation will tend to maximize the extraction of copper and other metals, optimize production of elemental sulfur (S°), minimize fresh acid consumption, and thereby minimize make-up acid requirements. Acid and sulfur are made from oxidation of sulfide according to the following reactions:



[**0031**] Preferably, in accordance with the present invention, the conditions (temperature, acid concentration) for the pressure leaching step are suitably selected to achieve an advantageous balance between reactions (1) and (2), but tending to reduce or eliminate fresh make-up acid consumption and thus the costs associated with acid make-up, but without sacrificing copper extraction to any significant extent.

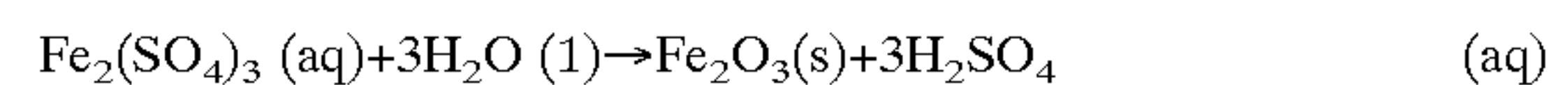
[**0032**] The amount of acid introduced into the pressure leaching vessel varies depending upon the reaction parameters, particularly, reaction temperature, iron dissolution, copper extraction, and sulfide oxidation. Make-up acid may be introduced into the pressure leaching vessel in the form of fresh acid or recycled acid from the same recovery process or another process. In certain cases, make-up acid is introduced on the order of from about 300 to about 650 kilograms per tonne of concentrate, or less; however, lower make-up acid is required at higher temperatures.

[**0033**] The present inventors have discovered that operating parameters of the metal recovery process of the present invention may be optimized to achieve any number of economic, processibility, or production objectives. Generally speaking, for example, at a fixed acid recycle rate, as the temperature in the pressure leaching stage is increased, more oxygen is consumed, more acid is produced, and less elemental sulfur is produced. Iron dissolution can be controlled at higher temperatures by reducing recycled acid from stream **119**. Moreover, keeping all other parameters constant, as the temperature in the pressure leaching stage is increased, copper recovery may be maximized. Thus, at increased temperatures and a fixed acid recycle rate, more acid may be produced during pressure leaching (i.e., excess acid that must be consumed) and more oxygen may be consumed, but higher copper recovery may be possible. At lower temperatures (e.g., 140-150° C.), the pressure leaching operation may require more recycled acid and copper

recovery may be reduced, but less oxygen is demanded and the cost of consuming excess acid is reduced. Within a temperature range of from about 150° C. to about 170° C., however, an acid autogenous process may be possible that is, the pressure leaching operation may produce approximately the acid that it requires. As such, it may be possible to reduce or eliminate the costs of make-up acid and acid attenuation while achieving acceptable copper recovery and moderate oxygen consumption.

[**0034**] It should be noted that any of the above scenarios may be desirable under certain circumstances. That is, extrinsic factors—such as power and raw material costs or the market price of copper and/or other recoverable metal values—may dictate whether it would be most economically desirable to operate the pressure leaching operation at lower temperatures (e.g., if cost of acid attenuation is higher than acid purchase, if oxygen is expensive, if power costs are high, and/or if copper price is low), or higher temperatures (e.g., if cost of acid attenuation is lower than acid purchase, if acid can be used beneficially elsewhere, if oxygen is inexpensive, if power costs are low, and/or if copper price is high).

[**0035**] At medium temperature conditions, ferric ion in solution will hydrolyze in the pressure leaching vessel to form hematite and sulfuric acid by the following reaction:



[**0036**] As the iron concentration in the pressure leaching vessel increases, the iron concentration in the rich electrolyte stream (i.e., the pressure leaching discharge liquor) also increases. Moreover, as shown in **FIGS. 3 and 4**, as the lean electrolyte acid addition and/or PLS acid addition plus iron equivalent (e.g., additional recycled lean electrolyte acid from cooling water and recycled pressure leaching discharge solution introduced to the pressure leaching vessel) addition increases, the amount of iron in the pressure leaching discharge liquor increases. Increasing iron in the pressure leaching discharge generally results in an undesirable drop in the current efficiency in subsequent electrowinning operations. Decreased current efficiency in electrowinning results in increased operating costs per unit of copper recovered through electrowinning.

[**0037**] The total acid addition (free acid in solution plus iron-equivalent acid content of solution) to the pressure leaching step is preferably controlled to optimize the copper extraction (as indicated by the copper in the residue) and iron in the rich electrolyte for direct electrowinning. In general, the residue copper content decreases with increasing total acid addition to the pressure leaching step, as shown in **FIG. 3**. For example, a 50 kg/tonne increase in total acid addition generally decreases the residue copper content by approximately 0.15-0.20%, down to a minimum level of about 0.8-0.9% copper at about 450 to about 500 kg/tonne total acid addition. The value of a 0.20% change in residue copper content has a value of approximately \$0.002/lb. of copper produced at 2003 prices.

[**0038**] The amount of iron in solution increases with increasing total acid addition, as shown in **FIG. 4**. For example, a 50 kg/tonne increase in total acid addition generally increases the level of iron in solution by about 0.5 g/L.

[**0039**] In accordance with an exemplary embodiment of the invention, a process for recovering copper from copper-



bearing material is operated such that the highest total acid addition to the pressure leaching vessel is utilized above which there is little or no additional benefit to the residue copper content. In accordance with one embodiment of the invention, the total acid addition to the pressure leaching vessel is in the range of from about 400 to about 500 kg/tonne.

[0040] Turning again to **FIG. 1**, reactive processing step **1030** may occur in any pressure leaching vessel suitably designed to contain the pressure leaching mixture at the desired temperature and pressure conditions for the requisite pressure leaching residence time. In accordance with one aspect of an exemplary embodiment of the invention, the pressure leaching vessel used in processing step **1030** is an agitated, multi-compartment horizontal pressure leaching vessel. However, it should be appreciated that any pressure leaching vessel that suitably permits metal-bearing material stream **103** to be prepared for copper recovery may be utilized within the scope of the present invention.

[0041] During reactive processing step **1030**, copper and/or other metal values may be solubilized or otherwise liberated in preparation for later recovery processes. Any substance that assists in solubilizing—and thus liberating—the metal value, and thus releasing the metal value from a metal-bearing material, may be used. For example, where copper is the metal being recovered, an acid, such as sulfuric acid, may be contacted with the copper-bearing material such that the copper may be liberated for later recovery steps. However, it should be appreciated that any suitable method of liberating metal values in preparation for later metal recovery steps may be utilized within the scope of this invention.

[0042] Any agent capable of assisting in the solubilization of the copper, such as, for example, sulfuric acid, may be provided during the reactive processing step **1030**, such as, for example, medium temperature pressure leaching, in a number of ways. For example, such acid may be provided in a cooling stream provided by the recycle of lean electrolyte **119** from electrowinning stage **1070**. However, it should be appreciated that any method of providing for the solubilization of copper is within the scope of the present invention. The amount of acid added during pressure leaching preferably is balanced according to the acid needed to optimize copper extraction and, if desired, to achieve a substantially acid autogenous process. As used herein, the term “acid autogenous” is used to describe a process that, during normal continuous operation, requires little or no fresh concentrated make up acid to be added to pressure leaching step due to a sufficient supply of recycled acid from elsewhere in the process and generates little acid that must be attenuated.

[0043] The medium temperature pressure leaching process occurs in a manner suitably designed to promote substantially complete solubilization of the copper. Various parameters influence the medium temperature pressure leaching process. For example, during pressure leaching, it may be desirable to introduce materials to enhance the pressure leaching process. In accordance with one aspect of the present invention, during pressure leaching in a pressure leaching vessel, sufficient oxygen **105** is injected into the vessel to maintain an oxygen partial pressure from about 50 to about 250 psig, preferably from about 75 to about 220

psig, and most preferably from about 150 to about 200 psig. Furthermore, due to the nature of medium temperature pressure leaching, the total operating pressure (including oxygen partial pressure) in the pressure leaching vessel is generally superatmospheric, preferably from about 100 to about 750 psig, more preferably from about 250 to about 400 psig, and most preferably from about 270 to about 350 psig.

[0044] The residence time for the medium temperature pressure leaching process can vary, depending on factors such as, for example, the characteristics of the copper-bearing material and the operating pressure and temperature of the pressure leaching vessel. In one aspect of an exemplary embodiment of the invention, the residence time for the medium temperature pressure leaching of chalcopyrite ranges from about 30 to about 180 minutes, more preferably from about 60 to about 150 minutes, and most preferably on the order of about 80 to about 120 minutes.

[0045] Control of the pressure leaching process, including control of the temperature in the pressure leaching vessel, may be accomplished by any conventional or hereafter devised method. For example, with respect to temperature control, preferably the pressure leaching vessel includes a feedback temperature control feature. For example, in accordance with one aspect of the invention, the temperature of the pressure leaching vessel is maintained at a temperature in the range of about 140° C. to about 180° C. and more preferably in the range of about 150° C. to about 175° C. Generally, the present inventors have found that temperatures above about 160° C., and more preferably in the range of about 160° C. to about 170° C. are useful in connection with the various aspects of the present invention. As discussed in detail above, however, due to the optimization capabilities of the present invention, the desired temperature ranges may vary within the range of about 140° C. to about 180° C. to accommodate any number of extrinsic factors. Due to the exothermic nature of pressure leaching of metal sulfides, the heat generated by medium temperature pressure leaching is generally more than that needed to heat the feed stream to the desired operating temperature. Thus, in order to maintain preferable pressure leaching temperature, a cooling liquid **106** may be introduced into the pressure leaching vessel during pressure leaching. In accordance with one aspect of an embodiment of the present invention, cooling liquid **106** is preferably contacted with the feed stream in the pressure leaching vessel during pressure leaching. Cooling liquid **106** may comprise make-up water, but can be any suitable cooling fluid from within the process or from an outside source, such as recycled liquid from the product slurry, lean electrolyte, or a mixture of cooling fluids. Cooling liquid **106** may be introduced into the pressure leaching vessel through the same inlet as feed slurry, or alternatively in any manner that effectuates cooling of the feed slurry. The amount of cooling liquid **106** added to the feed slurry during pressure leaching may vary, depending on the copper and acid concentration of the liquid, the amount of sulfide minerals in the feed slurry and the pulp density of the feed slurry, as well as other parameters of the pressure leaching process. In an exemplary aspect of this embodiment of the invention, a sufficient amount of cooling liquid is added to the pressure leaching vessel to yield a solids content in product stream **108** on the order of less than about 50% solids by weight, more preferably ranging from about 3 to about 35% solids by weight, and most preferably ranging from about 6 to about 15%



solids by weight. In accordance with one embodiment of the invention, the cooling liquid is added as lean electrolyte, which effectively controls the acid, iron and copper concentrations in the discharge slurry.

[0046] In accordance with an exemplary aspect of the present invention, medium temperature pressure leaching of stream **103** is performed in the presence of a dispersing agent **126**. Suitable dispersing agents useful in accordance with this aspect of the present invention include, for example, organic compounds such as lignin derivatives, such as, for example, calcium and sodium lignosulfonates, tannin compounds, such as, for example, quebracho, ortho-phenylene diamine (OPD), alkyl sulfonates, such as, for example, sodium alkylbenzene sulfonates, and combinations of the above. Dispersing agent **126** may be any compound that resists degradation in the temperature range of medium temperature pressure leaching (i.e., from about 140° C. to about 180° C.) long enough to disperse the elemental sulfur produced during the medium temperature pressure leaching process and that achieves the desired result of preventing elemental sulfur from passivating copper values, which may reduce copper extraction. Dispersing agent **126** may be introduced to the pressure leaching vessel in an amount and/or at a concentration sufficient to achieve the desired result. In one aspect of an exemplary embodiment of the invention, favorable results are achievable during pressure leaching of chalcopyrite using calcium lignosulfonate in an amount of about 2 to about 20 kilograms per tonne, and more preferably in an amount of about 4 to about 12 kilograms per tonne; and more preferably in an amount of about 6 to about 10 kilograms per tonne of chalcopyrite concentrate.

[0047] In accordance with an aspect of an exemplary embodiment of the present invention, a seeding agent may be introduced into reactive processing step **1030**. A suitable seeding agent preferably comprises any material capable of forming a nucleation site for the crystallization and/or growth of solid species. Accordingly, the seeding agent may be any particle which acts as a site for particle accumulation and/or precipitation, and may originate from recycled materials from other stages of the metal recovery process or may be provided by the addition of substances that are foreign to the metal recovery process. In some cases, the seeding agent comprises any material that promotes crystallization, precipitation, and/or growth of unwanted materials—for example in the preferred case of copper recovery, hematite, gangue, and the like—that may otherwise tend to partially or completely encapsulate the desired metal values, rendering the desired metal values (e.g., copper and gold) generally unavailable or less accessible to a lixiviant solution.

[0048] One source of suitable seeding agents useful in accordance with an aspect of this exemplary embodiment are those materials which can be found in the pressure leaching vessel discharge, which materials may be recycled for seeding purposes. Use of the recycled pressure leaching vessel discharge may be desirable for economic reasons, and using a seeding agent that is similar or identical to unwanted particles in the pressure leaching process slurry may tend to encourage the accumulation of unwanted material. For example, in metal recovery processes where an unwanted material, such as hematite, is either present in the metal-bearing material or is produced as a by-product, introduction of recycled hematite-containing residue from previous pressure leaching processes likely will tend to provide newly

formed or liberated hematite a preferential nucleation site. In the absence of this nucleation site, unreactive particles may occlude the desired metal values to solubilization by precipitating on the surface of the metal values, rendering the metal values unrecoverable. Therefore, introducing a seeding agent to prevent such occlusion may assist in providing better metal recovery. In accordance with the exemplary embodiment illustrated in **FIG. 1**, a portion of the solid residue stream **110** from solid-liquid separation step **1040** provides a suitable seeding material to reactive processing step **1030**.

[0049] Subsequent to metal-bearing material stream **103** undergoing reactive processing step **1030**, the copper and/or other metal values that have been made available by the reactive process undergo one or more of various metal recovery processes. Referring again to **FIG. 1**, metal recovery process **1070** (discussed hereinbelow) is a process for recovering copper and/or other metal values, and may include any number of preparatory or conditioning steps. For example, a copper-bearing solution may be prepared and conditioned for metal recovery through one or more chemical and/or physical processing steps. The product stream from reactive processing step **1030** may be conditioned to adjust the composition, component concentrations, solids content, volume, temperature, pressure, and/or other physical and/or chemical parameters to desired values and thus to form a suitable copper-bearing solution. Generally, a properly conditioned copper-bearing solution will contain a relatively high concentration of soluble copper in, for example, an acid sulfate solution, and preferably will contain few impurities. In accordance with one aspect of an exemplary embodiment of the invention, however, impurities in the conditioned copper-bearing solution ultimately may be decreased through the use of a separate solvent/solution extraction stage and discussed in connection with the embodiment illustrated in **FIG. 2**. Moreover, the conditions of the copper-bearing solution preferably are kept substantially constant to enhance the quality and uniformity of the copper product ultimately recovered.

[0050] In one aspect of an exemplary embodiment of the present invention, conditioning of a metal-bearing solution for copper recovery in an electrowinning circuit begins by adjusting certain physical parameters of the product slurry from the reactive processing step. In an exemplary aspect of this embodiment of the invention, wherein the reactive processing step is medium temperature pressure leaching, it is desirable to reduce the temperature and pressure of the product slurry to approximately ambient conditions. An exemplary method of so adjusting the temperature and pressure characteristics of the metal-bearing product slurry from a medium temperature pressure leaching stage is atmospheric flashing (such as atmospheric flashing stage **1035** shown in **FIG. 1**). Further, flashed gases, solids, solutions, and steam may optionally be suitably treated, for example, by use of a venturi scrubber wherein water may be recovered and hazardous materials may be prevented from entering the environment.

[0051] In accordance with further aspects of this preferred embodiment, after the product slurry has been subjected to atmospheric flashing using, for example, a flash tank, to achieve approximately ambient conditions of pressure and temperature, the product slurry may be further conditioned in preparation for later metal-value recovery steps. For



example, one or more solid-liquid phase separation stages (such as solid-liquid separation stage **1040** illustrated in **FIG. 1**) may be used to separate solubilized metal solution from solid particles. This may be accomplished in any conventional manner, including use of filtration systems, counter-current decantation (CCD) circuits, thickeners, and the like. As illustrated in **FIG. 1**, in accordance with one embodiment of the invention, conditioning of the product slurry for metal recovery comprises a solid-liquid separation step **1040** and an optional electrolyte treatment step **1050**, which further conditions product liquid **111** such as, for example, through filtration, to remove fine solid particles and colloidal matter, such as, for example, silica and/or silica-bearing material. A variety of factors, such as the process material balance, environmental regulations, residue composition, economic considerations, and the like, may affect the decision whether to employ a CCD circuit, one thickener or multiple thickeners, one filter or multiple filters, and/or any other suitable device or combination of devices in a solid-liquid separation apparatus. However, it should be appreciated that any technique of conditioning the product slurry for later metal value recovery is within the scope of the present invention.

[0052] As further discussed hereinbelow, the separated solids may further be subjected to later processing steps, including precious metal or other metal value recovery, such as, for example, recovery of gold, silver, platinum group metals, molybdenum, zinc, nickel, cobalt, uranium, rhenium, rare earth metals, and the like, by cyanidation or other techniques. Later processing steps may also include treatment processes to remove or recover other mineral constituents from the separated solids. Alternatively, the separated solids may be subject to impoundment or disposal, or, as noted hereinabove, a portion of the separated solids may be introduced into the reactive processing stage as a seeding agent.

[0053] Thus, in accordance with an exemplary aspect of the embodiment illustrated in **FIG. 1**, product slurry **107** from reactive processing step **1030** is subjected to atmospheric flashing **1035** in one or more atmospheric flash tanks or any other suitable atmospheric system to release pressure and to evaporatively cool the product slurry **107** through the release of steam to form a flashed product slurry **108**. The flashed product slurry preferably has a temperature ranging from about 90° C. to about 101° C., a copper concentration of from about 40 to about 120 grams/liter, and an acid concentration of from about 16 to about 50 grams/liter. In accordance with an aspect of an exemplary embodiment of the invention, a portion of flashed product slurry **108** (stream **123** in **FIG. 1**), is recycled to pressure leaching stage **1030**.

[0054] Flashed product slurry **108** also may contain a particulate solid residue containing, for example, the iron oxide by-product of pressure leaching, elemental sulfur and other by-products, precious metals and other components that are undesirable for a feed stream to an electrowinning circuit. Thus, in accordance with the same principles discussed above, it may be desirable to subject the flashed product slurry to a solid-liquid separation process, such that the liquid portion of the slurry—the desired copper-containing solution—is separated from the solid portion of the slurry—the undesired residue.

[0055] Referring still to **FIG. 1**, in the illustrated embodiment of the invention, flashed product slurry **108** is directed

to a solid-liquid separation stage **1040**, such as a CCD circuit. In an alternative embodiment of the invention, solid-liquid separation stage **1040** may comprise, for example, a thickener or one or more filters. In one aspect of an exemplary embodiment of the invention, a CCD circuit uses conventional countercurrent washing of the residue stream with wash water **109** to recover leached copper to the copper-containing solution product and to minimize the amount of soluble copper advancing to either precious metal recovery processes or residue disposal. Preferably, large wash ratios and/or several CCD stages are utilized to enhance the effectiveness of solid-liquid separation stage **1040**—that is, relatively large amounts of wash water **109** are added to the residue in the CCD circuit and/or several CCD stages are used. Preferably, the solution portion of the residue slurry stream is diluted by wash water **109** in the CCD circuit to a copper concentration of from about 5 to about 200 parts per million (ppm) in the solution portion of residue stream **110**. In accordance with another aspect of an exemplary embodiment of the invention, addition of a chemical reagent to liquid/solid separation stage **1040** may be desirable to remove deleterious constituents from the process stream. For example, a polyethylene oxide may be added to effectuate removal of silica by precipitation, or other flocculants and/or coagulants might be utilized to remove other undesirable species from the process stream. One such suitable chemical reagent is POLYOX™ WSR-301, available from Dow Chemical.

[0056] Depending on its composition, residue stream **110** from liquid/solid separation stage **1040** may be neutralized, impounded, disposed of, or subjected to further processing, such as, for example, precious metal recovery, treatment to recover other metal values, treatment to attenuate or remediate metals of concern, or other treatment to recover or remove other mineral constituents from the stream. For example, if residue stream **110** contains economically significant amounts of gold, silver, and/or other precious metals, it may be desirable to recover this gold fraction through a cyanidation process or other suitable recovery process. If gold or other precious metals are to be recovered from residue stream **110** by cyanidation techniques, the content of contaminants in the stream, such as elemental sulfur, amorphous iron precipitates, unreacted copper minerals and dissolved copper, is preferably minimized. Such materials may promote high reagent consumption in the cyanidation process and thus increase the expense of the precious metal recovery operation. As mentioned above, it is therefore preferable to use a large amount of wash water or other diluent or several stages during the solid-liquid separation process to maintain low copper and acid levels in the solids-containing residue stream in an attempt to optimize the conditions for subsequent precious metal recovery. Optionally, as illustrated in **FIG. 1** as an aspect of one exemplary embodiment of the invention, one or more additional electrolyte treatment stages **1050** may be utilized to further condition and/or refine process stream **111** from solid-liquid separation stage **1040**, such as, for example, through filtration, thickening, counter-current decantation, or the like. Moreover, a portion of process stream **111** (stream **122** in **FIG. 1**) may be recycled to pressure leaching stage **1030**, either directly or through combination with lean electrolyte recycle stream **119** (as shown) and/or other suitable process streams entering the pressure leaching operation. In accordance with an exemplary embodiment,



residue stream **114** from electrolyte treatment stage **1050** is subjected to further treatment **1080**, wherein, depending on the conditions of residue stream **114**, all or a portion of the stream may be neutralized, impounded, disposed of, or subjected to further processing as described above. Copper-containing solution stream **113** from electrolyte treatment stage **1050** is then preferably subjected to copper recovery; however, a portion of copper-containing solution stream **113** (stream **120** in **FIG. 1**) may be recycled to pressure leaching stage **1030**.

[0057] Careful control of the conditions of a copper-containing solution entering an electrowinning circuit—especially maintenance of a substantially constant copper composition—an enhance the quality of the electrowon copper by, among other things, enabling even plating of copper on the cathode and avoidance of surface porosity in the cathode copper, which degrades the copper product and thus may diminish its economic value. Such process control can be accomplished using any of a variety of techniques and equipment configurations, so long as the chosen system and/or method maintains a sufficiently constant feed stream to the electrowinning circuit.

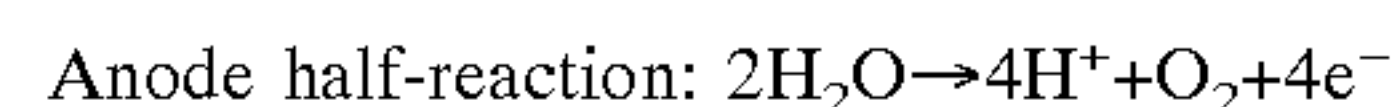
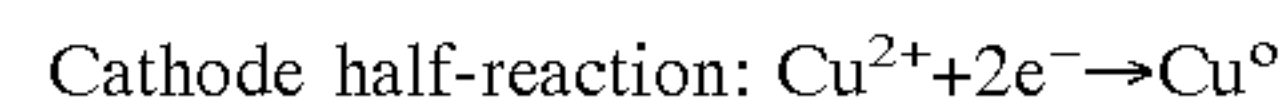
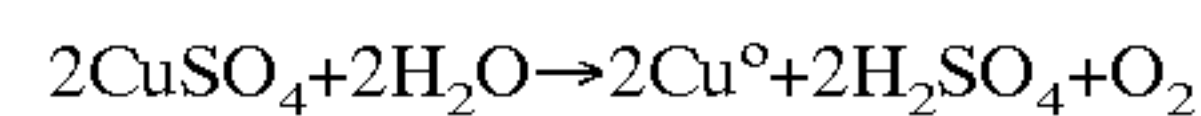
[0058] Referring again to **FIG. 1**, in accordance with one aspect of an embodiment of the invention, copper-containing solution stream **113** from electrolyte treatment stage **1050** is sent to an electrolyte recycle tank **1060**. Electrolyte recycle tank **1060** suitably facilitates process control for electrowinning circuit **1070**, as will be discussed in greater detail below. Copper-containing solution stream **113**, which generally contains from about 40 to about 120 grams/liter of copper and from about 15 to about 25 grams/liter acid, is preferably blended with a lean electrolyte stream **121** in electrolyte recycle tank **1060** at a ratio suitable to yield a product stream **115**, the conditions of which may be chosen to optimize the resultant product of electrowinning circuit **1070**.

[0059] Referring again to **FIG. 1**, preferably, the copper composition of product stream **115** is maintained substantially constant. While product stream **115** may contain a copper concentration up to the copper solubility level under the prevailing conditions, preferably product stream **115** has a copper concentration of about 15 to about 80 grams/liter, and more preferably of about 20 to about 60 grams/liter, and often above 30 grams/liter. Similarly, while product stream **115** may contain an acid in a concentration sufficient to provide conductivity for effective electrowinning, preferably product stream **115** has an acid concentration of about 140 to about 180 grams/liter, and more preferably of about 150 to about 165 grams/liter. In one aspect of an exemplary embodiment of the invention, control valves are positioned on each of the pipelines feeding lean electrolyte stream **121** and copper-containing solution stream **113** to electrolyte recycle tank **1060** to facilitate blending control within the tank.

[0060] With continued reference to **FIG. 1**, copper from the product stream **115** is suitably electrowon to yield a pure, cathode copper product (stream **116**). In accordance with the various aspects of the invention, a process is provided wherein, upon proper conditioning of a copper-containing solution, a high quality, uniformly-plated cathode copper product **116** may be realized without subjecting the copper-containing solution to a solvent/solution extraction process prior to entering the electrowinning circuit.

[0061] As those skilled in the art are aware, a variety of methods and apparatus are available for the electrowinning of copper and other metal values, any of which may be suitable for use in accordance with the present invention, provided the requisite process parameters for the chosen method or apparatus are satisfied. For the sake of convenience and a broad understanding of the present invention, an electrowinning circuit useful in connection with various embodiments of the invention may comprise an electrowinning circuit, constructed and configured to operate in a conventional manner. The electrowinning circuit may include electrowinning cells constructed as elongated rectangular tanks containing suspended parallel flat cathodes of copper alternating with flat anodes of lead alloy, arranged perpendicular to the long axis of the tank. A copper-bearing leach solution may be provided to the tank, for example at one end, to flow perpendicular (referring to the overall flow pattern) to the plane of the parallel anodes and cathodes, and copper can be deposited at the cathode and water electrolyzed to form oxygen and protons at the anode with the application of current. Other electrolyte distribution and flow profiles may be used.

[0062] The primary electrochemical reactions for electrowinning of copper from acid solution is believed to be as follows:



[0063] Turning again to **FIG. 1**, in a preferred embodiment of the invention, product stream **115** is directed from electrolyte recycle tank **1060** to an electrowinning circuit **1070**, which contains one or more conventional electrowinning cells. It should be understood, however, that any method and/or apparatus currently known or hereinafter devised suitable for the electrowinning of copper from acid solution, in accordance with the above-referenced reactions or otherwise, is within the scope of the present invention.

[0064] In accordance with a preferred aspect of the invention, electrowinning circuit **1070** yields a cathode copper product **116**, optionally, an offgas stream (not shown), and a relatively large volume of copper-containing acid solution, herein designated as lean electrolyte stream **117**. As discussed above, in the illustrated embodiment of the invention, a portion of lean electrolyte stream **117** (lean electrolyte recycle stream **119** in **FIG. 1**) is preferably recycled to pressure leaching stage **1030** and/or to electrolyte recycle tank **1060**. Optionally, a portion of copper-containing solution stream **113** (stream **120** in **FIG. 1**) from electrolyte treatment stage **1050** is combined with lean electrolyte recycle stream **119** and is recycled to pressure leaching stage **1030**. Moreover, in accordance with one aspect of an exemplary embodiment of the invention, a portion of lean electrolyte stream **117** (lean electrolyte bleed stream **118** in **FIG. 1**) is removed from process **100** for the removal of impurities and acid and/or residual copper recovery operations, such as, for example, those illustrated in **FIG. 2**. Lean electrolyte stream **117** has a lower copper concentration than product stream **115**, but typically has a copper concentration of less than about 40 grams/liter.

[0065] Preferably, lean electrolyte recycle stream **119** comprises at least about 50 percent by weight of lean electrolyte stream **117**, more preferably from about 60 to



about 95 percent by weight of lean electrolyte stream **117**, and more preferably from about 80 to about 90 percent by weight of lean electrolyte stream **117**. Preferably, lean electrolyte bleed stream **118** comprises less than about 50 percent by weight of lean electrolyte stream **118**, more preferably from about 5 to about 40 percent by weight of lean electrolyte stream **117**, and more preferably from about 10 to about 20 percent by weight of lean electrolyte stream **117**.

[0066] Preferably, the copper composition of product stream **115** is maintained substantially constant at a value from about 20 to about 65 grams/liter, more preferably at a value from about 30 to about 50 grams/liter. Copper values from the metal-bearing product stream **115** are removed during electrowinning step **1070** to yield a pure, cathode copper product. It should be appreciated that in accordance with the various aspects of the invention, a process wherein, upon proper conditioning of the metal-bearing solution, a high quality, uniformly-plated cathode copper product may be realized without subjecting the metal-bearing solution to solvent/solution extraction prior to entering the electrowinning circuit is within the scope of the present invention. As previously noted, careful control of the conditions of the metal-bearing solution entering an electrowinning circuit—especially maintenance of a substantially constant copper composition in the stream—can enhance the quality of the electrowon copper by, among other things, enabling even plating of copper on the cathode and avoidance of surface porosity in the cathode copper, which degrades the copper product and thus may diminish its economic value. In accordance with this aspect of the invention, such process control can be accomplished using any of a variety of techniques and equipment configurations, so long as the chosen system and/or method maintains a sufficiently constant feed stream to the electrowinning circuit. As those skilled in the art are aware, a variety of methods and apparatus are available for the electrowinning of copper and other metal values, any of which may be suitable for use in accordance with the present invention, provided the requisite process parameters for the chosen method or apparatus are satisfied.

[0067] In accordance with an exemplary embodiment of the invention illustrated in **FIG. 2**, lean electrolyte bleed stream **118** from electrowinning unit **1070** (**FIG. 1**) is sent to a solvent/solution extraction stage **2010**. In accordance with one embodiment of the invention, solvent/solution extraction stage **2010** is configured to treat materials from atmospheric and/or pressure leach operations **2020** as well as lean electrolyte bleed stream **118**. Leach operation **2020** may utilize any conventional or hereinafter developed atmospheric or pressure leaching method, including, for example, heap leaching, stockpile leaching (also sometimes referred to in the art as “dump leaching”), vat leaching, tank leaching, agitated tank leaching, in situ leaching, pressure leaching, or other process. In accordance with one aspect of a preferred embodiment of the invention, leach operation **2020** is a conventional acid-consuming heap leach operation, wherein a low grade ore **201** is contacted with an acid-containing stream **202** and, optionally, other process streams, such as raffinate stream **205** from solvent/solution extraction unit **2010**. In leach operation **2020**, the acid percolates downward through the ore heap, solubilizing the copper in the copper-containing ore in the form of copper sulfate, to form a copper-rich pregnant leach solution (PLS)

stream **203**. In accordance with one aspect of a preferred embodiment of the invention, PLS **203** from a heap leach operation **2020** is combined with lean electrolyte bleed stream **118** prior to entering solvent/solution extraction stage **2010** as process stream **204**.

[0068] In accordance with a further aspect of this embodiment of the present invention, as previously briefly mentioned, lean electrolyte bleed stream **118** advantageously may remove impurities from the process, for example the electrowinning process. Such impurities include, without limitation, iron, aluminum, silica, selenium, magnesium, manganese, sodium, potassium and others. In the absence of removal, such impurities may accumulate to deleterious levels, and, as such negatively impact production efficiencies and product (e.g., copper cathode) quality. The presence of such impurities in lean electrolyte bleed stream **118** generally does not negatively impact the aforementioned handling of lean electrolyte bleed stream **118**.

[0069] In accordance with one aspect of a preferred embodiment of the invention illustrated in **FIG. 2**, solvent/solution extraction stage **2010** and solution stripping stage **2015** purify copper-bearing process stream **204** in two unit operations—an extraction operation, which may have multiple stages, followed by a stripping operation. In the extraction stage, process stream **204** is contacted with an organic phase consisting of a diluent in which a copper selective reagent (i.e., the extractant) is admixed. When the solutions are contacted, the organic extractant chemically removes the copper from stream **204**, forming a copper-depleted aqueous raffinate stream. The raffinate and organic streams are subsequently separated in a settler. After separation of the organic and aqueous phases in the settler, a portion of the aqueous phase (stream **205**) is typically returned to one or more leaching operations to be reloaded with copper from the ore in the atmospheric leach to form the PLS, or may be recycled to other process areas or appropriately disposed of. The organic stream passes on to the second unit operation of the solvent/solution extraction process, the stripping operation. In the stripping operation, the organic stream is contacted with a strongly acidic electrolyte. This acidic solution “strips” the copper from the extractant, leaving the organic phase substantially depleted of copper. At least a portion of the loaded strip solution aqueous phase (stream **206**) is advanced to an electrowinning plant **2030** as a copper “rich” solution. Aqueous stream **206** is processed in electrowinning plant **2030** to yield cathode copper **207** and a copper-containing lean electrolyte stream **208**, which, in one aspect of a preferred embodiment of the invention, may be recycled in part to solvent/solution extraction unit **2010** and/or to pressure leaching stage **1030** (stream **209** to **FIG. 1**) and/or to other process areas.

[0070] In accordance with one alternative aspect of the invention, aqueous stream **206** may not be subjected to electrowinning immediately after leaving the solvent/solution extraction unit, but may instead be blended with other copper-containing process streams, and the resultant stream then sent to an electrowinning circuit. For example, all or a portion of aqueous stream **206** may be blended with a copper-containing solution stream (not shown) and a lean electrolyte stream (not shown) in electrolyte recycle tank **1060** (from **FIG. 1**) to form a resultant product stream suitable for electrowinning in an electrowinning circuit. In such cases the stripping solutions used in solvent/solution



extraction **2010** likely will be comprised of spent electrolyte from electrowinning circuit **1070** (from **FIG. 1**).

[**0071**] The Example set forth hereinbelow is illustrative of various aspects of a preferred embodiment of the present invention. The process conditions and parameters reflected therein are intended to exemplify various aspects of the invention, and are not intended to limit the scope of the claimed invention.

#### EXAMPLE 1

[**0072**] Copper was recovered from chalcopyrite-containing concentrate using continuous medium temperature pressure leaching and direct electrowinning in accordance with an exemplary embodiment of the invention Table 1, below, sets forth the process conditions and operating parameters utilized.

<u>FEED</u>	
Concentrate Type	Chalcopyrite
Concentrate Analyses, %	
Cu	31.6
Fe	30.5
S	34.2
Grind Size, P <sub>90</sub> , $\mu$ m	15
<u>PRESSURE LEACHING</u>	
Temperature, ° C.	160
Time, min	90
Acid Addition Rate, kg acid/tonne feed	450
CLS Addition Rate, kg CLS/tonne feed	10
Oxygen Overpressure, psi	200
Total Pressure, psi	290
Feed Solids to Compartment 1, %	10.3
Weight Loss, %	20
Discharge Solids, %	7.4
Discharge Solution, g/L	
Cu	102
Fe	4.6
H <sub>2</sub> SO <sub>4</sub>	11.6
Discharge Solids, %	
Cu	1.5
Fe	35.9
Cu Extraction, %	96.6
Sulfide Oxidized to Elemental Sulfur, %	69
Sulfide Oxidation to Sulfate, %	27
<u>ELECTROWINNING</u>	
Current Density, A/m <sup>2</sup>	308
Cell Temperature, ° C.	50
Specific Flow, L/min-m <sup>2</sup>	3.0
FC-1110 (Mist Control), gal/10 <sup>6</sup> lb Cu	10
PD-4201 (Leveling Agent), g/tonne Cu	334
Lean Electrolyte, g/L	
Cu	34
Fe	3.3
H <sub>2</sub> SO <sub>4</sub>	135
Current Efficiency, %	88
Copper Removed by Electrowinning, %	84

[**0073**] An effective and efficient method to recover copper from metal-bearing materials, especially copper from copper sulfides, such as chalcopyrite, that enables high copper recovery at a reduced cost over conventional processing techniques has been presented herein. In accordance with the present invention, it has been shown that copper recovery in excess of about 96 to about 98 percent is achievable while realizing various important economic benefits of medium temperature pressure leaching and circumventing processing

problems historically associated with medium temperature pressure leaching. Moreover, the present invention provides a substantially acid-autogenous process for recovering copper from chalcopyrite-containing ore using pressure leaching and direct electrowinning in combination with an atmospheric leaching, solvent/solution extraction, and electrowinning steps.

[**0074**] The present invention has been described above with reference to a number of exemplary embodiments and examples. It should be appreciated that the particular embodiments shown and described herein are illustrative of the invention and its best mode and are not intended to limit in any way the scope of the invention as set forth in the claims. Those skilled in the art having read this disclosure will recognize that changes and modifications may be made to the exemplary embodiments without departing from the scope of the present invention. Further, although certain preferred aspects of the invention are described herein in terms of exemplary embodiments, such aspects of the invention may be achieved through any number of suitable means now known or hereafter devised. Accordingly, these and other changes or modifications are intended to be included within the scope of the present invention, as expressed in the following claims.

What is claimed is:

1. A method of recovering copper from a metal-bearing material, comprising the steps of:

- providing a feed stream comprising a metal-bearing material;
- subjecting at least a portion of said feed stream to controlled, super-fine grinding;
- leaching at least a portion of said inlet stream in an oxidizing environment at an elevated temperature and pressure to yield a product slurry comprising a metal-bearing solution and a residue;
- conditioning said product slurry without the use of solvent/solution extraction techniques to yield a metal-bearing solution suitable for electrowinning;
- electrowinning copper from said metal-bearing solution to yield cathode copper and a metal-bearing lean electrolyte stream;
- recycling a portion of said lean electrolyte stream to said leaching stage; and
- processing a portion of said lean electrolyte stream using solvent/solution extraction techniques.

2. The method of claim 1, wherein said step of providing a feed stream comprising a metal-bearing material comprises providing a feed stream comprising a copper-bearing sulfide ore, concentrate, or precipitate.

3. The method of claim 1, wherein said step of providing a feed stream comprising a metal-bearing material comprises providing a feed stream comprising at least one of chalcopyrite, chalcocite, bornite, covellite, digenite, and enargite, or mixtures or combinations thereof.

4. The method of claim 3, wherein said step of providing a feed stream comprising a metal-bearing material comprises providing a feed stream comprising chalcopyrite.

5. The method of claim 1, wherein said step of providing a feed stream comprising a metal-bearing material com-



prises providing a feed stream comprising a metal-bearing material and a solution stream comprising copper and acid.

6. The method of claim 1, wherein said step of subjecting at least a portion of said feed stream to controlled, super-fine grinding comprises reducing the particle size of said feed stream such that substantially all of the particles in said feed stream react substantially completely during pressure leaching.

7. The method of claim 6, wherein said step of subjecting at least a portion of said feed stream to controlled, super-fine grinding comprises reducing the particle size of said feed stream to a P98 of less than about 25 microns.

8. The method of claim 6, wherein said step of subjecting at least a portion of said feed stream to controlled, super-fine grinding comprises reducing the particle size of said feed stream to a P98 of from about 10 to about 23 microns.

9. The method of claim 6, wherein said step of subjecting at least a portion of said feed stream to controlled, super-fine grinding comprises reducing the particle size of said feed stream to a P98 of from about 13 to about 15 microns.

10. The method of claim 1, wherein said leaching step comprises leaching at least a portion of said feed stream in a pressure leaching vessel.

11. The method of claim 1, wherein said leaching step comprises leaching at least a portion of said feed stream in a pressure leaching vessel at a temperature of from about 140° C. to about 180° C. and at a total operating pressure of from about 50 psi to about 750 psi.

12. The method of claim 11, wherein said leaching step further comprises injecting oxygen into the pressure leaching vessel to maintain an oxygen partial pressure in the pressure leaching vessel of from about 50 psi to about 250 psi.

13. The method of claim 1, wherein said step of pressure leaching said feed stream comprises pressure leaching said feed stream in the presence of a surfactant selected from the group consisting of lignin derivatives, orthophenylene diamine, alkyl sulfonates, and mixtures thereof.

14. The method of claim 1, wherein said step of pressure leaching said feed stream comprises pressure leaching said feed stream in the presence of calcium lignosulfonate.

15. The method of claim 1, wherein said conditioning step comprises subjecting at least a portion of said product slurry to solid-liquid separation, wherein at least a portion of said metal-bearing solution is separated from said residue.

16. The method of claim 15, wherein said conditioning step further comprises blending at least a portion of said metal-bearing solution with at least a portion of one or more metal-bearing streams to achieve a desired copper concentration in said metal-bearing solution.

17. The method of claim 15, wherein said conditioning step further comprises blending at least a portion of said metal-bearing solution with at least a portion of one or more metal-bearing streams to achieve a copper concentration of from about 15 grams/liter to about 80 grams/liter in said metal-bearing solution.

18. The method of claim 15, wherein a portion of said metal-bearing solution is recycled to step (c).

19. The method of claim 1, wherein said conditioning step comprises subjecting at least a portion of said product slurry to filtration, wherein at least a portion of said metal-bearing solution is separated from said residue.

20. The method of claim 1, wherein said conditioning step comprises separating at least a portion of said residue from

said metal-bearing solution in said product slurry, and further comprises using at least a portion of said residue as a seeding agent in step (c).

21. The method of claim 1, further comprising the step of (h) using a portion of said lean electrolyte stream in a leaching operation.

22. The method of claim 21, wherein said step of using a portion of said lean electrolyte stream in a leaching operation comprises using a portion of said lean electrolyte stream in at least one of a heap leaching operation, a stockpile leaching operation, a vat leaching operation, a tank leaching operation, a pressure leaching operation, or an in-situ leaching operation.

23. A method of recovering copper from a metal-bearing material, comprising the steps of:

(a) providing a feed stream comprising a metal-bearing material;

(b) subjecting at least a portion of said feed stream to controlled, super-fine grinding,

(c) leaching at least a portion of said inlet stream in an oxidizing environment at an elevated temperature and pressure to yield a product slurry comprising a metal-bearing solution and a residue;

(d) recycling at least a portion of said product slurry to said leaching step;

(e) conditioning said product slurry without the use of solvent/solution extraction techniques to yield a metal-bearing solution suitable for electrowinning;

(f) electrowinning copper from said metal-bearing solution to yield cathode copper and a metal-bearing lean electrolyte stream; and

(g) processing a portion of said lean electrolyte stream using solvent/solution extraction techniques.

24. The method of claim 23, wherein said step of providing a feed stream comprising a metal-bearing material comprises providing a feed stream comprising a copper-bearing sulfide ore, concentrate, or precipitate.

25. The method of claim 23, wherein said step of providing a feed stream comprising a metal-bearing material comprises providing a feed stream comprising at least one of chalcopyrite, chalcocite, bornite, covellite, digenite, and enargite, or mixtures or combinations thereof.

26. The method of claim 23, wherein said step of providing a feed stream comprising a metal-bearing material comprises providing a feed stream comprising a metal-bearing material and a solution stream comprising copper and acid.

27. The method of claim 23, wherein said step of subjecting at least a portion of said feed stream to controlled, super-fine grinding comprises reducing the particle size of said feed stream such that substantially all of the particles in said feed stream react substantially completely during pressure leaching.

28. The method of claim 27, wherein said step of subjecting at least a portion of said feed stream to controlled, super-fine grinding comprises reducing the particle size of said feed stream to a P98 of less than about 25 microns.

29. The method of claim 27, wherein said step of subjecting at least a portion of said feed stream to controlled,



super-fine grinding comprises reducing the particle size of said feed stream to a P98 of from about 10 to about 23 microns.

**30.** The method of claim 27, wherein said step of subjecting at least a portion of said feed stream to controlled, super-fine grinding comprises reducing the particle size of said feed stream to a P98 of from about 13 to about 15 microns.

**31.** The method of claim 23, wherein said leaching step comprises leaching at least a portion of said feed stream in a pressure leaching vessel at a temperature of from about 140° C. to about 180° C. and at a total operating pressure of from about 50 psi to about 750 psi.

**32.** The method of claim 23, wherein said leaching step further comprises injecting oxygen into the pressure leaching vessel to maintain an oxygen partial pressure in the pressure leaching vessel of from about 50 psi to about 250 psi.

**33.** The method of claim 23, wherein said conditioning step comprises subjecting at least a portion of said product slurry to solid-liquid separation, wherein at least a portion of said metal-bearing solution is separated from said residue.

**34.** The method of claim 35, wherein said conditioning step further comprises blending at least a portion of said metal-bearing solution with at least a portion of one or more metal-bearing streams to achieve a copper concentration of from about 15 grams/liter to about 80 grams/liter in said metal-bearing solution.

**35.** The method of claim 23, further comprising separating said product slurry into a liquor component and a solid component prior to step (d), and wherein said recycling step (d) comprises recycling said solid component to leaching step (c).

**36.** The method of claim 23, wherein said conditioning step comprises separating at least a portion of said residue from said metal-bearing solution in said product slurry, and further comprises using at least a portion of said residue as a seeding agent in leaching step (c).

**37.** A method of recovering copper from a metal-bearing material, comprising the steps of:

- (a) providing a feed stream comprising a metal-bearing material;
- (b) subjecting at least a portion of said feed stream to controlled, super-fine grinding;
- (c) leaching at least a portion of said inlet stream in an oxidizing environment at an elevated temperature and pressure to yield a product slurry comprising a metal-bearing solution and a residue;
- (d) conditioning said product slurry without the use of solvent/solution extraction techniques to yield a metal-bearing solution suitable for electrowinning;
- (e) recycling at least a portion of said product slurry to said leaching step;
- (f) electrowinning copper from said metal-bearing solution to yield cathode copper and a metal-bearing lean electrolyte stream;
- (g) recycling a portion of said lean electrolyte stream to said leaching stage; and
- (h) processing a portion of said lean electrolyte stream using solvent/solution extraction techniques.

**38.** The method of claim 39, wherein said step of providing a feed stream comprising a metal-bearing material comprises providing a feed stream comprising a copper-bearing sulfide ore, concentrate, or precipitate.

**39.** The method of claim 39, wherein said step of providing a feed stream comprising a metal-bearing material comprises providing a feed stream comprising a metal-bearing material and a solution stream comprising copper and acid.

**40.** The method of claim 39, wherein said step of subjecting at least a portion of said feed stream to controlled, super-fine grinding comprises reducing the particle size of said feed stream such that substantially all of the particles in said feed stream react substantially completely during pressure leaching.

**41.** The method of claim 39, wherein said step of subjecting at least a portion of said feed stream to controlled, super-fine grinding comprises reducing the particle size of said feed stream to a P98 of less than about 25 microns.

**42.** The method of claim 39, wherein said leaching step comprises leaching at least a portion of said feed stream in a pressure leaching vessel at a temperature of from about 140° C. to about 180° C. and at a total operating pressure of from about 50 psi to about 750 psi.

**43.** The method of claim 39, wherein said conditioning step comprises subjecting at least a portion of said product slurry to solid-liquid separation, wherein at least a portion of said metal-bearing solution is separated from said residue.

**44.** The method of claim 45, wherein said conditioning step further comprises blending at least a portion of said metal-bearing solution with at least a portion of one or more metal-bearing streams to achieve a copper concentration of from about 15 grams/liter to about 80 grams/liter in said metal-bearing solution.

**45.** The method of claim 39, wherein said conditioning step comprises separating at least a portion of said residue from said metal-bearing solution in said product slurry, and further comprises using at least a portion of said residue as a seeding agent in leaching step (c).

**46.** A method of recovering copper from a metal-bearing material, comprising the steps of:

- (a) providing a feed stream comprising a metal-bearing material;
- (b) subjecting at least a portion of said feed stream to controlled, super-fine grinding;
- (c) leaching at least a portion of said inlet stream in an oxidizing environment at an elevated temperature and pressure to yield a product slurry comprising a metal-bearing solution and a residue;
- (d) conditioning said product slurry without the use of solvent/solution extraction techniques to yield a metal-bearing solution suitable for electrowinning;
- (e) electrowinning copper from said metal-bearing solution to yield cathode copper and a metal-bearing lean electrolyte stream; and
- (f) processing a portion of said lean electrolyte stream using solvent/solution extraction techniques.

**47.** The method of claim 48, wherein said step of providing a feed stream comprising a metal-bearing material comprises providing a feed stream comprising a copper-bearing sulfide ore, concentrate, or precipitate.

**48.** The method of claim 48, wherein said step of providing a feed stream comprising a metal-bearing material comprises providing a feed stream comprising a metal-bearing material and a solution stream comprising copper and acid.

**49.** The method of claim 48, wherein said leaching step comprises leaching at least a portion of said feed stream in a pressure leaching vessel at a temperature of from about 140° C. to about 180° C. and at a total operating pressure of from about 50 psi to about 750 psi.

**50.** The method of claim 48, wherein said conditioning step comprises subjecting at least a portion of said product slurry to solid-liquid separation, wherein at least a portion of said metal-bearing solution is separated from said residue.

**51.** The method of claim 48, wherein said conditioning step further comprises blending at least a portion of said metal-bearing solution with at least a portion of one or more metal-bearing streams to achieve a copper concentration of from about 15 grams/liter to about 80 grams/liter in said metal-bearing solution.

**52.** The method of claim 48, further comprising the step of recycling a portion of said lean electrolyte stream from said electrowinning step (e) or a portion of said product slurry from said leaching step (c) to said leaching step (c).

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