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Method of purifying copper electrolytic solution

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ABSTRACT

A method of purifying copper electrolytic solution being circulated in a copper electrorefining system wherein a portion of the solution is withdrawn and is recycled to the system after purification treatment in which hydrosulfide is added to the solution withdrawn to generate only the necessary quantity of hydrogen sulfide gas on the spot and the hydrogen sulfide gas generated is utilized for purification treatment. One process comprises dividing the solution withdrawn into two portions, adding sodium hydrosulfide to the first portion to precipitate and separate metals as sulfides from the first portion, further adding excess sodium hydrosulfide to the first portion for reaction with residual sulfuric acid in the solution to generate hydrogen sulfide gas, contacting the second divided portion with the hydrogen sulfide gas thus produced to precipitate and separate metals in the form of sulfides, and recycling the filtrate to an electrorefining system. There is also provided a process comprising contacting the solution with hydrogen sulfide gas to separate and remove Cu, As, Sb and Bi in the form of sulfides from the solution, dividing the solution into two portions, wherein the first portion is recycled to the electrorefining system, whereas excess sodium hydrosulfide is added to the second portion to separate and recover Ni as nickel sulfide from the solution, while resulting hydrogen sulfide gas is used for contact with solution to be treated.

SPECIFICATION

Method of purifying copper electrolytic solution

BACKGROUND OF THE INVENTION

This invention relates to a method of purifying sulfuric acid-containing copper electrolytic solution being circulated in a copper electrorefining system in which crude copper is electrolytically refined to high purity electrolytic copper, and particularly a method of purifying such copper electrolytic solution being circulated with removal of metals such as copper, arsenic, antimony, bismuth and the like which are gradually built up in the solution and also purifying method by which such metals, especially nickel can be separated and recovered.

In a system for electrorefining crude copper to high purity electrolytic copper, the progress of electrolysis entails gradual buildup of copper, arsenic, antimony, bismuth and the like that have dissolved from the copper anode into the copper electrolytic solution being circulated. The increases in concentrations of the impurity metals such as arsenic, antimony, and bismuth lead to deterioration of the quality of the product copper. Moreover, the presence of excess copper adversely affects the properties of the electrolytic copper produced. With a copper electrorefining system, therefore, it is common practice to purify the electrolytic solution at regular intervals.

A widely used method of purification comprises heating

a copper electrolytic solution to concentrate it and separating and removing copper as copper sulfate from the solution by taking advantage of the differences in the solubilities of the components, causing electrodeposition of the copper, arsenic, antimony, and bismuth remaining in the solution by electrowinning, and finally cooling the solution and separating and recovering nickel as nickel sulfate taking advantage of the solubility difference and returning back to a electrolytic tank the filtrate that has resulted from the separation and recovery of nickel sulfate.

But, this method, which depends on electrowinning for the removal of arsenic, antimony, and bismuth, has the disadvantage of evolving highly toxic arsine gas (As_3H) during electrolysis. An additional demerit is unusually large power consumption involved in the electrowinning.

Japanese Patent Application Kokai No. 57-5884 describes a method of treating a copper electrolytic solution wherein the copper electrolytic solution having subjected to copper electrorefining is first treated to remove copper and then the copper-removed electrolytic solution is heated to no less than 40°C and hydrogen sulfide gas is blown into the solution to a given potential to precipitate the metal values in the solution as sulfides, followed by filtration resulting in the precipitate to be used as raw material for copper refining and the filtrate to be recycled as copper electrolytic solution. Many problems, however, involve in the handling of highly toxic hydrogen sulfide gas in a large quantity as indicated in this method. That is, this method necessitates the transport and storage of highly toxic, high-priced hydrogen sulfide gas in a large quantity and does not assure safe operation which

means that this method is not commercially feasible.

Clearly it would be advantageous if a less hazardous technology for purifying a copper electrolytic solution being circulated in a copper electrorefining system could be devised. Specifically, the new technology should avoid the separation of arsenic, antimony and bismuth by electrowinning which evolves highly toxic arsine gas. It should also obviate the need to transport and store highly toxic expensive hydrogen sulfide gas in large quantities.

SUMMARY OF THE INVENTION

This invention includes the precipitation and separation of arsenic, antimony and bismuth as sulfides. This is accomplished by blowing hydrogen sulfide gas into an electrolytic solution to precipitate and remove these metals as sulfides.

As a result of perceiving the fact that copper electrolytic solution contains sulphuric acid, a new method has been hit upon wherein low priced sodium hydrosulfide (NaHS) is added to a copper electrolytic solution containing sulphuric acid to generate only the necessary amount of high-priced hydrogen sulfide

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(H_2S) gas on the spot, which is to be blown into a copper electrolytic solution to be treated so as to contribute to the separation reaction. Thus, by using low-priced sodium hydrosulfide to generate high-priced hydrogen sulfide gas only in the necessary amount on the spot, namely then and there, an electrolytic solution may be treated efficiently and safely.

Actually, it has been found that this method may be usably conducted by dividing an electrolytic solution withdrawn from an electrorefining system into two portions, adding sodium hydrosulfide to the first portion of the solution to separate and remove copper, arsenic, antimony, and bismuth in the form of sulfides from the first solution, further adding excess sodium hydrosulfide for reaction with residual sulfuric acid in the solution to generate hydrogen sulfide gas, and contacting the second solution with the gas thus produced and separating and removing copper, arsenic, antimony, and bismuth in the form of sulfides from the second solution and recycling the filtrate from the second solution to the electrorefining system.

Under the above background, this invention, in its first aspect, provides a method of purifying copper electrolytic solution being circulated in a copper electrorefining system wherein a portion of the electrolytic solution is withdrawn from the system and is recycled to the system after having been subjected to purification treatment for preventing the buildup of impurities in the copper electrolytic solution characterized in that sodium hydrosulfide is added to the copper electrolytic solution to generate only the necessary amount of hydrogen sulfide gas on the spot and the hydrogen

sulfide gas generated is utilized for purification treatment.

This invention also provides a method of purifying copper electrolytic solution being circulated in a copper electrorefining system wherein a portion of the electrolytic solution is withdrawn from the system and is recycled to the system after having been subjected to purification treatment for preventing the buildup of impurities in the copper electrolytic solution comprising dividing the electrolytic solution withdrawn into two portions, adding sodium hydrosulfide to the first divided portion of the solution to precipitate and separate metals such as copper, arsenic, antimony, and bismuth in the form of sulfides from the first solution, further adding excess sodium hydrosulfide to the first divided portion of the solution for reaction with residual sulfuric acid in the solution to generate hydrogen sulfide gas, and contacting the second divided portion of the solution with the hydrogen sulfide gas thus produced to precipitate and separate metals such as copper, arsenic, antimony, and bismuth in the form of sulfides from the second solution and recycling the filtrate from the second solution to an electrolytic system. it is advantageous that slaked lime or calcium carbonate is added to the first divided portion of the solution to which sodium hydrosulfide was added for its reaction with free sulfuric acid to form and precipitate gypsum, and then the solution from which the gypsum has been removed is adjust ed to pH 8 to 10 by the addition of sodium carbonate or caustic soda, so that impurities such as nickel, iron, etc. which could not have removed to the full are separated and removed as neutralized precipitate.

It is preferable to divide the copper electrolytic solution after having recovered almost copper from the electrolytic solution withdrawn by electrowinning. It is better to passing the copper electrolytic solution through an ion exchange resin to allow a portion of antimony and/or bismuth to adsorb on the resin for separation before recover-almost copper in the electrolytic solution withdrawn by electrowinning. It is also recommended to heat the electrolytic solution to evaporate water and to precipitate and separate copper as copper sulfate.

However, in the above method, as copper, arsenic, antimony, and bismuth are separated and removed in the form of sulfides from the first divided portion of the solution by the addition of sodium hydrosulfide, part of the nickel content too is separated and removed as nickel sulfide. While nickel is an impurity from the viewpoint of purification, nickel is a valuable metal and its high rate separation and recovery as nickel sulfide from the system is desirable.

In view of the above, the research has been further continued for its object to provide a method whereby nickel can be separated and recovered at a high rate from the copper electrolytic solution being circulated in a copper electrorefining system for the production of high purity electrolytic copper from crude copper.

As the result,

(1) Contacting a copper electrolytic solution with hydrogen sulfide gas separates and removes copper, arsenic, antimony, and bismuth in the form of sulfides from the solution, but nickel remains unremoved; and

(2) When sodium hydrosulfide is added to the copper electro-

.lytic solution after the separation and removal of copper, arsenic, antimony, and bismuth as sulfides, the nickel that can be separated and recovered as nickel sulfide, although its proportion is not so large, includes little impurities excepting sulfur, and so the recovered nickel sulfide, once freed from excess sulfur, would generally have a high enough quality level to be directly put on the market as a final product.

Then, this invention provides, in its second aspect, a method of purifying copper electrolytic solution being circulated in a copper electrorefining system wherein a portion of the electrolytic solution is withdrawn from the system and is recycled to the system after having been subjected to purification treatment for preventing the buildup of impurities in the copper electrolytic solution comprising contacting the copper electrolytic solution with hydrogen sulfide gas to separate and remove copper, arsenic, antimony, and bismuth in the form of sulfides from the solution, and then dividing the solution into two portions, wherein the first portion of the solution is recycled to the electrorefining system, whereas excess sodium hydrosulfide is added to the second portion of the solution to separate and recover nickel as nickel sulfide from the solution, while resulting hydrogen sulfide gas is utilized for contact with the copper electrolytic solution to be treated next.

It is also possible, after the separation and recovery of nickel as nickel sulfide by the addition of sodium hydrosulfide, to add slaked lime or calcium carbonate to the copper electrolytic solution for reaction with sulfuric acid in the solution to form gypsum and separate and remove the

gypsum from the solution, and thereafter add sodium carbonate or caustic soda and separate and recover residual nickel as nickel carbonate or nickel hydroxide, respectively, from the solution.

As in the first method, a part of copper may be separated and recovered from the copper electrolytic solution by electrowinning or thermal concentration of the solution prior to the separation and removal of copper, arsenic, antimony, and bismuth in the form of sulfides from the electrolytic solution through the contact of the solution with hydrogen sulfide gas. The procedure brings the advantage of reducing the consumption of sodium hydrosulfide and hydrogen sulfide gas and also decreasing the amounts of the sulfides such as of copper formed.

The term "copper electrolytic solution" is used to comprehensively mean a copper electrolytic solution as withdrawn from an electrorefining system and the copper electrolytic solution from a part of copper has been separated and recovered in advance by electrowinning.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

Fig. 1 is a flow sheet of a process for purification of a copper electrolytic solution according to the first aspect of this invention.

Fig. 2 is a flow sheet of a process for purification of a copper electrolytic solution while recovering nickel according to the second aspect of this invention.

DETAILED DESCRIPTION OF THE INVENTION

In copper electrorefining, the concentration of copper

in the electrolytic solution gradually increases since the quantity of copper dissolved from an anode is generally larger than that of copper deposited on a cathode. The increase of copper concentration beyond a predetermined level prevents the optimum electrorefining. On the other hand, arsenic, antimony, bismuth, iron and the like included in the copper anode dissolved into the electrolytic solution. When these impurity ions build up beyond a certain level, they precipitate on the cathode to lower the grade of the electrolytic copper produced. Further, nickel functions to rise electrolytic voltage and antimony exhibits adverse actions such as floating due to hydrolysis. For the reasons, it becomes important to conduct the purification of copper electrolytic solution being circulated in a copper electrorefining system wherein a portion of the electrolytic solution is withdrawn from the electrolytic tank and is recycled to the tank after having been subjected to purification treatment.

Fig. 1 is a flow sheet of a process for purification of a copper electrolytic solution according to the first aspect of this invention. An electrolytic solution from an electrorefining factory (which is herein indicated as a copper electrolytic solution from which a part of copper has been separated and recovered by electrowinning step, but this step may be omitted.) is divided into two portions. The first divided portion of the solution (solution I) is passed to a sodium hydrosulfide adding tank while on the other hand second divided portion of the solution (solution II) is passed to reaction tank. In the sodium hydrosulfide adding tank, an industrial grade of sodium hydrosulfide is added to

the solution I to precipitate and separate metals such as copper, arsenic, antimony, and bismuth in the form of sulfides (sulfide I) from the solution I, and excess industrial grade of sodium hydrosulfide is further added to the solution I for reaction with residual sulfuric acid in the solution I to generate hydrogen sulfide gas. The hydrogen sulfide gas generated is passed to the reaction tank containing the solution II to precipitate and separate metals such as copper, arsenic, antimony, and bismuth in the form of sulfides (sulfide II) from the solution II and the filtrate from the solution II is recycled to an electrolytic system. Further, it is advantageous that in a neutralization equipment, slaked lime or calcium carbonate is added to the first divided portion of the solution (solution I) to which sodium hydrosulfide was added for its reaction with free sulfuric acid to form and precipitate gypsum, and then the solution from which the gypsum has been removed is adjusted to pH 8 to 10 by the addition of an alkali agent such as sodium carbonate or caustic soda, so that impurities such as nickel, iron, etc. which could not have removed to the full are separated and removed as neutralized precipitate. The precipitate is send to the refining process as a byproduct, whereas the filtrate is drained off.

The division volume ratio of the first divided portion of the solution (solution I) to the second divided portion of the solution (solution II) from which recycling electrolytic solution is to be produced may range from 1:2 to 1:10. When the volume of the solution II is too much, the quantity of the recycling electrolytic solution becomes insufficient. When the volume of the solution II is excessive, the necessary

amount of hydrogen sulfide gas can not be produced. The electrolytic solution from which copper has removed treatment typically contains, all per liter, about 5 to 20 grams copper, about 1 to 10 g arsenic, about 0.1 to 1 g antimony, about 0.05 to 1.0 g bismuth, about 5 to 20 g nickel, and about 150 to 300 g free sulfuric acid. According to the quantities of impurities involved, the necessary amount of hydrogen sulfide gas is decided from which the division ratio can be decided.

Since the hydrogen sulfide gas is generated in the sodium hydrosulfide adding tank by allowing to react low-priced sodium hydrosulfide with sulfuric acid remaining in the solution only in the necessary quantity and is directly passed to the reaction tank, there becomes no necessity for transporting and storing high-priced hydrogen sulfide gas in large quantity, and safe operation can be carried out. It is preferable that the sodium hydrosulfide adding tank and the reaction tank are mounted side by side.

Since copper constitutes the largest metallic content in a copper electrolytic solution, direct contact of the solution with sodium hydrosulfide produces much copper sulfide which is to be returned back to the copper refining process. Therefore, it is preferable to remove copper before the sulfide precipitation treatment with sodium hydrosulfide. As the method of the preliminary separation and recovery of copper, the electrowinning process by which electrolytic copper having more than 99% purity is obtainable and concentration process under heating for separation as copper sulfate are suitable. In the case where the electrowinning is adopted, in order to enhance the purity of the electrolytic copper to be obtained, it is found that the electrowinning

is preceded by pretreatment of the copper electrolytic solution with an ion exchange resin to remove antimony and/or bismuth.

Fig. 2 is a flow sheet of a process for purification of a copper electrolytic solution while recovering nickel according to the second aspect of this invention.

(1) Preliminary recovery of copper by electrowinning

Similarly to the case of Fig. 1, a part of copper is separated and recovered in advance from a copper electrolytic solution by electrowinning. In this way, electrolytic copper with a purity of 99 % or more can be obtained. Since copper constitutes the largest metallic content in a copper electrolytic solution, direct contact of the solution with hydrogen sulfide gas produces much copper sulfide along with other sulfides. The process involves large hydrogen sulfide gas consumption and sulfide production. These are advantageously lessened by the preliminary separation and recovery of copper by electrowinning. The electrowinning is also herein preferably preceded by pretreatment of the copper electrolytic solution with an ion exchange resin. It prevents the contamination with impurities such as antimony and bismuth and accordingly enhances the purity of the resulting electrolytic copper to a greater advantage.

After the treatment the electrolytic solution typically contains, all per liter, about 5 to 20 grams copper, about 1 to 10 g arsenic, about 0.1 to 1 g antimony, about 0.05 to 1.0 g bismuth, about 5 to 20 g nickel, and about 150 to 300 g free sulfuric acid.

Alternatively, the copper electrolytic solution may be concentrated with heat so that the copper content can partly

be separated and recovered as copper sulfate in advance.

(2) Removal of copper, arsenic, antimony, and bismuth

The copper electrolytic solution from which part of copper has been separated and removed in the step (1) above is then brought in contact with hydrogen sulfide gas for reactions with copper, arsenic, antimony, and bismuth in the electrolytic solution. The reaction products formed and precipitated as sulfides are separated and removed by a conventional filtration technique from the solution. The quantity of hydrogen sulfide gas to be used depends on the arsenic and other impurity contents. Usually it is larger than the theoretical quantity required for the formation of the sulfides by about 0.1 to 5 %. The nickel content in the sulfides thus separated is zero or infinitely close to zero.

(3) Division of the copper electrolytic solution

The filtrate that has resulted from the separation and removal of copper and the like as sulfides is divided into two liquid portions; the first solution (filtrate 1) and the second solution (filtrate 2). The first solution (filtrate 1) is freed from the copper, arsenic, antimony, and other contents and adjusted in composition to suit for copper electrorefining as it has passed through the steps (1) and (2), and is recycled as a purified solution t o the copper electrorefining process. Actually, the copper, arsenic, and antimony concentrations in the solution thus purified are less than 0.1 g each per liter.

The second solution (filtrate 2) is furnished for the recovery of nickel. The ratio of the first solution (filtrate 1) to the second solution (filtrate 2), which will be described in detail later, desirably ranges from about 2:1

to about 5:1 in view of the fact that they are required in actual operation to produce only the necessary amount of hydrogen sulfide gas.

(4) Generation and utilization of hydrogen sulfide gas as well as Formation and recovery of nickel sulfide

The addition of sodium hydrosulfide to the second solution (filtrate 2) causes its reaction with residual sulfuric acid to generate hydrogen sulfide gas, which in turn is recovered for utilization in the step (1). Thus hydrogen sulfide gas which is the highly toxic gas can be produced only in the necessary amount on the spot with a great convenience for handling. The quantity of hydrogen sulfide gas needed is predetermined, and sodium hydrosulfide is added to the second solution (filtrate 2) to an excess just necessary for the generation of the gas. As the hydrogen sulfide gas is generated the addition of sodium hydrosulfide to the second solution (filtrate 2), about 5 to 30 % by weight of nickel in the solution is produced as nickel sulfide and recovered from the solution. The nickel sulfide so recovered is almost free from impurities excepting sulfur and is useful in itself as a nickel raw material.

(5) Formation and recovery of nickel carbonate or nickel hydroxide

The second solution (filtrate 3) from which nickel has been separated and recovered as nickel sulfide by passage through the step (4) above, is first adjusted to a pH of about 1.5 to 2.5 by the addition of slaked lime or calcium carbonate for its reaction with free sulfuric acid remaining in the solution to form and precipitate gypsum. The gypsum that has precipitated is separated and removed in a

conventional way.

The solution (filtrate 4) from which the gypsum has been removed is adjusted to pH 8 to 10 or thereabouts by the addition of sodium carbonate or caustic soda, so that the nickel remaining in the solution is precipitated in the form of nickel carbonate or nickel hydroxide, respectively. The nickel carbonate or nickel hydroxide thus produced is conventionally separated and recovered. The nickel purity is about 35 to 45 %. The solution after the nickel recovery is drained off.

Example 1

A copper electrolytic solution (30 m^3) containing 45 g copper per liter was treated by a known electrowinning process, and 450 kg of electrolytic copper I with a purity of 99.9 % and 606 kg of electrolytic copper II with a purity of 99 % were separated and recovered. The solution after the electrolysis contained, all per liter, 10 g copper, 5 g arsenic, 0.4 g antimony, 0.1 g bismuth, 15 g nickel, and 244 g free sulfuric acid.

The electrolytic solution was divided into two portions; the solution I (2/9, namely 6.7 m^3) and the solution II (7/9, namely 23.3 m^3). 500 kg of industrial sodium hydrosulfide containing about 25 % NaSH was added to the solution I to form and precipitate sulfide I. Next, 2050 kg of industrial sodium hydrosulfide was added at the rate of about 10 kg per minute and allowed to react with sulfuric acid in the solution to generate hydrogen sulfide gas. This hydrogen sulfide gas was conducted to the solution II, and its contact reaction with the solution formed and precipitated sulfide II. The sulfide II was filtered, separated, recovered, and dried in the usual manner. The remaining filtrate (i.e., the electrolytic solution to be recycled) contained at most 0.1 g each of copper, arsenic, antimony, and bismuth, meaning that it was now clean.

The solution I after the generation of hydrogen sulfide gas was, after removing a very small quantity of hydrogen sulfide remaining in the solution, filtered to recover sulfide in the usual manner and next was adjusted to pH 2 for neutralization by the addition of 1280 kg calcium carbonate, so that its reaction with remaining free sulfuric acid in the

solution formed and precipitated gypsum. The precipitated gypsum was separated and removed by the usual method. The amount of gypsum when dried was 2210 kg. Following the removal of the gypsum, the filtrate was neutralized to pH 9 by the addition of 125 kg sodium carbonate. Remaining nickel in the solution was thus precipitated in the form of nickel carbonate. Thereafter the nickel carbonate was conventionally filtered, separated, recovered, and dried.

In the treatment procedure described above, the quantities of the treating solution, the products in the individual steps, and the solution after treatment were as shown in Table 1.

Table 1

	Q'ty	Cu		Ni		As		Sb	
In	m^3	g/l	kg	g/l	kg	g/l	kg	g/l	kg
Electrolytic solution	30	45	1350	15	450	5	150	0.5	15
Out	kg	%	kg	%	kg	%	kg	%	kg
Electrolytic copper I	450	99.9	450						
Electrolytic copper II	606	99	600						
Sulfide I	237	28.3	67	17.0	40	14.3	34	1.4	3
Sulfide II	608	38.3	233	0	0	19.1	116	1.9	12
Nickel carbonate	151	0	0	40	60	0	0	0	0
Electrolytic solution recycled*	23.3	0	0	15	350	0	0	0	0

* in units of m^3 and g/l.

EXAMPLE 2

(1) Preliminary recovery of copper by electrowinning

A copper electrolytic solution (30 m^3) containing 45 g copper per liter was treated by a known electrowinning process, and 450 kg of electrolytic copper 1 having a purity of 99.9 % and 606 kg of electrolytic copper 2 having a purity of 99 % were separately recovered. The solution after the electrolysis contained, all per liter, 10 g copper, 5 g arsenic, 0.4 g antimony, 0.1 g bismuth, 15 g nickel, and 244 g free sulfuric acid.

(2) Removal of copper, arsenic, antimony, and bismuth

With the introduction of 225 m^3 hydrogen sulfide gas into the electrolytic solution after the electrolysis, a contact reaction was effected between the solution and the gas to form and precipitate a sulfide 1. The precipitate was separated and removed by a conventional filtration technique. Sulfide 1 was substantially free from nickel. The resulting filtrate was clean, with the copper, arsenic, antimony, and bismuth concentrations of but 0.1 g or less each per liter.

(3) Division of the copper electrolytic solution

From the filtrate, a portion of 23.3 m^3 was separated off as a purified solution (filtrate 1) for recycling to electrorefining process.

(4) Generation and utilization of hydrogen sulfide gas as well as Formation and recovery of nickel sulfide

To the remaining 6.7 m^3 portion of the filtrate was added 2470 kg of industrial sodium hydrosulfide containing about 25 % NaSH at the rate of about 10 kg per minute to react free sulfuric acid remaining in the solution to generate 225m^3 hydrogen sulfide gas. The hydrogen sulfide gas

generated was passed to the step 2 and utilized to precipitate copper, arsenic, antimony, and bismuth. This addition of sodium hydrosulfide resulted the precipitation of a portion of nickel in the solution as nickel sulfide. After removing a very small quantity of hydrogen sulfide remaining in the solution, the nickel sulfide was separated and recovered by usual method. The nickel sulfide after drying was 80 kg.

(5) Formation and recovery of nickel carbonate or nickel hydroxide

The solution (filtrate 3) from which the hydrogen sulfide gas has been generated and recovered was first adjusted to pH 2 by the addition of 1270 kg calcium carbonate for its reaction with free sulfuric acid remaining in the solution to form and precipitate gypsum. The gypsum that precipitated was separated and removed in a conventional way. The amount of gypsum upon drying was 2180 kg. Following the removal of the gypsum, the solution (filtrate 4) was adjusted to pH 9 for neutralization by the addition of 161 kg sodium carbonate, so that the nickel remaining in the solution was precipitated in the form of nickel carbonate. The nickel carbonate thus formed was conventionally separated by filtration and recovered. The nickel carbonate when dried amounted to 200 kg, and the purity of nickel was 40 %.

Throughout the treatment procedure described above, the quantities of the treating solution, the products in the individual steps, and the solution after treatment were as shown in Table 2.

Table 2

	Q'ty	Cu		Ni		As		Sb	
In	m^3	g/l	kg	g/l	kg	g/l	kg	g/l	kg
Electrolytic solution	30	45	1350	15	450	5	150	0.5	15
Out	kg	%	kg	%	kg	%	kg	%	kg
Electrolytic copper 1	450	99.9	450						
Electrolytic copper 2	606	99	600						
Sulfide 1	783	38.3	300	0	0	19.1	150	1.9	15
Sulfide 2	80	0	0	25.0	20	0	0	0	0
Nickel carbonate	200	0	0	40	80	0	0	0	0
Electrolytic solution recycled*	23.3	0	0	15	350	0	0	0	0

* in units of m^3 and g/l.

A comparison between Tables 1 and 2 indicates that according to the method of Example 1 nickel mostly precipitates as a sulfide together with copper, arsenic etc., leaving only a little proportion of nickel for recovery as nickel carbonate, while on the other hand in the method of Example 2, by contrast, permits the recovery of nickel as nickel sulfide and nickel carbonate with an increased quantity.

Example 3 (pretreatment with an ion exchange resin)

A copper electrolytic solution containing, all per liter, 45 g copper, 5 g arsenic, 0.4 g antimony, 0.1 g bismuth, 15 g nickel, and 190 g free sulfuric acid was withdrawn and passed through an ion exchange resin (a product of Miyoshi Resin Co. marketed under the trade designation "EPOROUS MX-2") for partial adsorption of antimony and bismuth from the solution. The solution after the passage through the resin contained 45 g copper, 5 g arsenic, 0.1 g antimony, 0.05 g bismuth, 15 g nickel, and 190 g free sulfuric acid. This solution was treated by electrowinning in the manner described in the step (1) of Example 2. Thanks to the lowered antimony and bismuth concentrations in the solution, 600 kg of electrolytic copper with a purity of 99.9 % and 450 kg of electrolytic copper with a purity of 99 % were obtained.

This invention has succeeded in establishing an industrially feasible method useful as a purifying method of a copper electrolytic solution being circulated in a copper electrorefining system which takes the place of the separation method of arsenic, antimony, and bismuth depending

on electrowinning and evolving highly toxic arsine gas. Since the high-priced hydrogen sulfide gas is produced in the sodium hydrosulfide adding tank only in the necessary amount by allowing to react low-priced sodium hydrosulfide with sulfuric acid remaining in the solution and is directly passed to the reaction tank with easier handling, there becomes no necessity for transporting and storing high-priced hydrogen sulfide gas in large quantity, and safe and efficient operation can be carried out. According to the second flow, nickel may be efficiently recovered as nickel sulfide and nickel carbonate.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of treating a sulfuric acid containing copper electrolytic solution being circulated in a copper electro-refining system wherein a portion of the electrolytic solution is withdrawn from the system and is recycled to the system after having been subjected to purification treatment for preventing the buildup of impurities in the copper electrolytic solution including:

dividing the withdrawn electrolytic solution into first and second solution portions;

adding sodium hydrosulfide to the first solution portion to precipitate and separate metals including copper, arsenic, antimony and bismuth from the first solution portion in the form of sulfides;

further adding excess sodium hydrosulfide to the first solution portion for reaction with residual sulfuric acid in the solution to generate hydrogen sulfide gas;

contacting the second solution portion with the hydrogen sulfide gas thus produced to precipitate and separate metals including copper, arsenic, antimony and bismuth from the second solution portion in the form of sulfides; and

recycling the second solution portion to the electro-refining system.

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2. A method according to claim 1, further including filtering the second solution portion to separate the precipitated sulfides from the second solution portion prior to recycling the second solution portion to the electro-refining system.

3. A method according to claim 1 or claim 2, wherein an alkali agent is added to the first solution portion to which sodium hydrosulfide has been added so that heavy metal impurities are separated and removed from the first solution portion as a neutralised precipitate.

4. A method according to any one of claims 1 to 3, wherein copper is recovered from the withdrawn copper electrolytic solution by electrowinning prior to the step of dividing the electrolytic solution into first and second solution portions.

5. A method according to claim 4, wherein the copper electrolytic solution is passed through an ion exchange resin to allow a portion of the antimony and/or bismuth in the solution to adsorb on the resin for separation prior to recovering copper from the withdrawn electrolytic solution by electrowinning.

6. A method according to any one of claims 1 to 3, wherein the withdrawn copper electrolytic solution is heated to evaporate water and to precipitate and separate copper as copper sulfate prior to the step of dividing the withdrawn electrolytic solution into first and second solution portions.

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7. A method of purifying a sulfuric acid containing copper electrolytic solution being circulated in a copper electrorefining system wherein a portion of the electrolytic solution is withdrawn from the system and is recycled to the system after having been subjected to purification treatment for preventing the build-up of impurities in the copper electrolytic solution, the method including the steps of:

contacting the withdrawn portion of the copper electrolytic solution with hydrogen sulfide gas to separate and remove copper, arsenic, antimony and bismuth from the solution in the form of sulfides;

dividing the solution into first and second solution portions, wherein the first solution portion is recycled to the electrorefining system;

adding excess sodium hydrosulphide to the second solution portion to separate and recover nickel as nickel sulfide therefrom;

wherein the withdrawn portion of the copper electrolytic solution to be treated is contacted in said contacting step with hydrogen sulfide gas generated by the addition of sodium hydrosulfide to the second solution portion.

8. A method according to claim 7, wherein after the separation and recovery of nickel as nickel sulfide by the addition of sodium hydrosulfide, slaked lime or

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calcium carbonate is added to the copper electrolytic solution for reaction with sulfuric acid in the solution to form gypsum, the gypsum being separated and removed from the solution, and sodium carbonate or caustic soda being added to the solution to separate and recover residual nickel as nickel carbonate or nickel hydroxide from the solution.

9. A method according to claim 7, wherein a part of the copper in the copper electrolytic solution is separated and recovered from the solution by electrowinning or concentration under heating of the solution prior to the separation and removal of copper, arsenic, antimony and bismuth in the form of sulfides from the electrolytic solution through the contact of the solution with hydrogen sulfide gas.

10. A method of treating a sulfuric acid containing electrolytic copper solution being circulated in a copper electrorefining system, the method including the steps of:

withdrawing a portion of solution from the process;

treating the withdrawn portion of solution to reduce the level of impurities in the system, the treatment step including adding sodium hydrosulfide to the solution to generate an appropriate amount of hydrogen sulfide gas and using the generated hydrogen sulfide gas to precipitate impurity metals as sulfides from the solution; and

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returning the withdrawn portion of solution to the copper electrorefining system.

11. A method of treating a sulfuric acid containing copper electrolytic solution being circulated in a copper electrorefining system substantially as herein described with reference to the embodiment illustrated in Fig.1 or Example 1.

12. A method of treating a sulfuric acid containing copper electrolytic solution being circulated in a copper electrorefining system substantially as herein described with reference to the embodiment illustrated in Fig. 2.

13. A method of treating a sulfuric acid containing copper electrolytic solution being circulated in a copper electrorefining system substantially as herein described in Example 2.

14. A method of treating a sulfuric acid containing copper electrolytic solution being circulated in a copper electrorefining system substantially as herein described with reference to Example 3.

DATED this thirtieth day of November 1999

NIPPON MINING & METALS CO., LTD.

BY

PIZZEYS PATENT AND TRADE MARK ATTORNEYS

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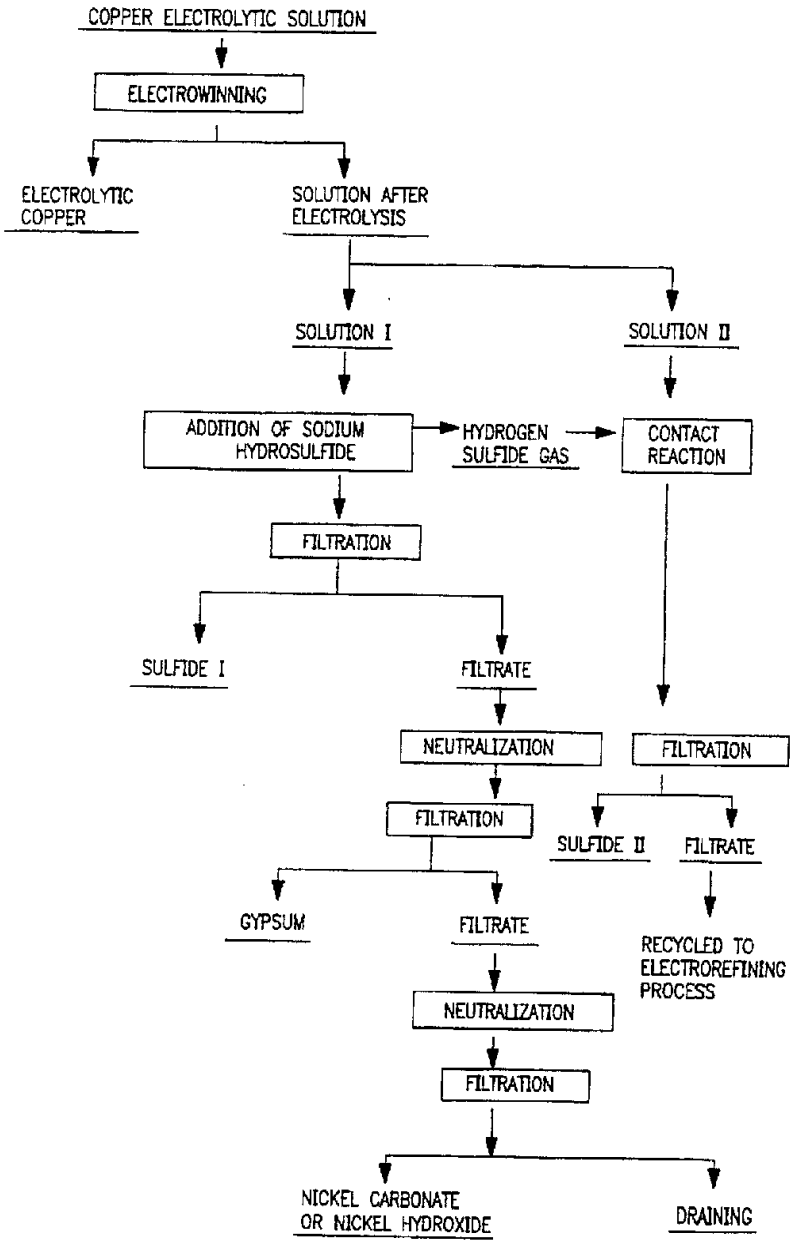

COPPER ELECTROLYTIC SOLUTION
ELECTROWINNING
ELECTROLYTIC COPPER
SOLUTION AFTER ELECTROLYSIS
SOLUTION I
SOLUTION II
ADDITION OF SODIUM HYDROSULFIDE
HYDROGEN SULFIDE GAS
CONTACT REACTION
FILTRATION
SULFIDE I
FILTRATE
NEUTRALIZATION
FILTRATION
FILTRATION
SULFIDE II
FILTRATE
GYPSUM
FILTRATE
RECYCLED TO ELECTROREFINING PROCESS
NEUTRALIZATION
FILTRATION
NICKEL CARBONATE OR NICKEL HYDROXIDE
DRAINING

FIG. 1

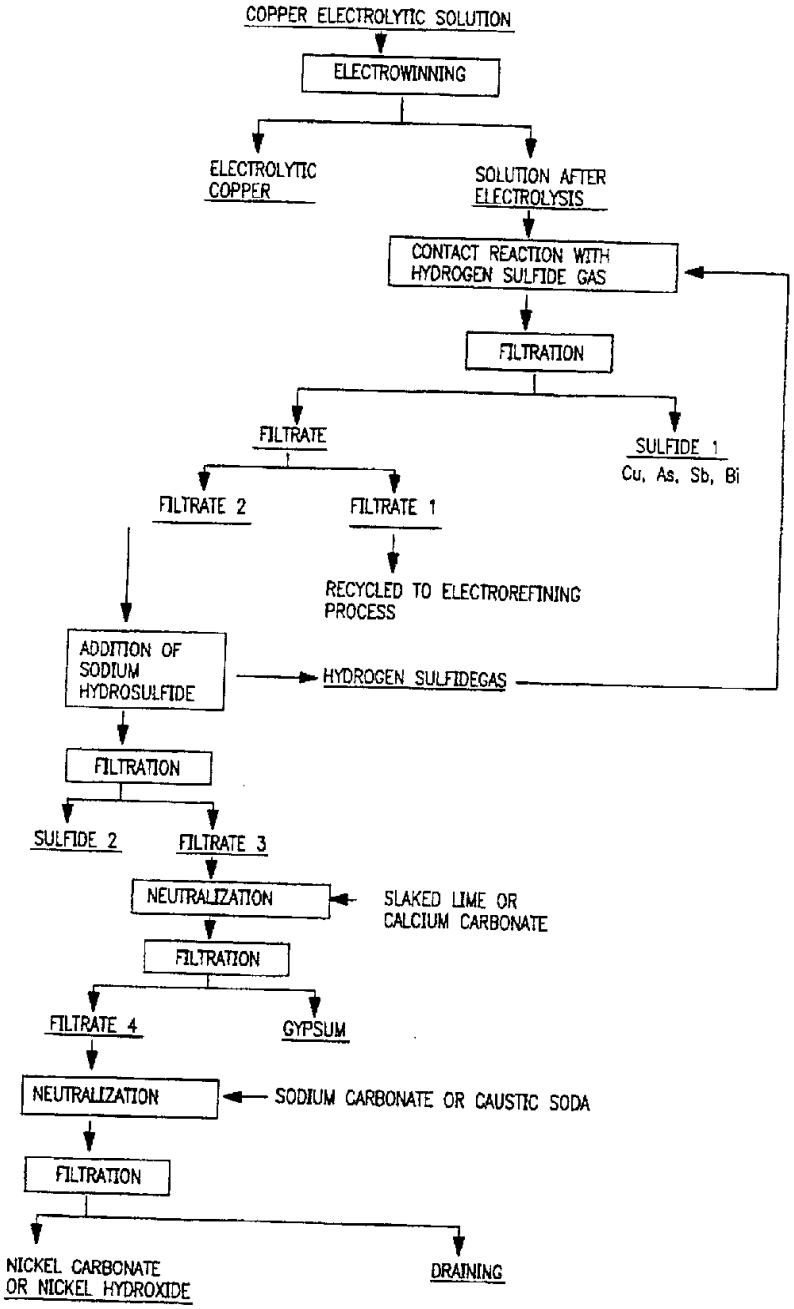

COPPER ELECTROLYTIC SOLUTION
ELECTROWINNING
ELECTROLYTIC COPPER
SOLUTION AFTER ELECTROLYSIS
CONTACT REACTION WITH HYDROGEN SULFIDE GAS
FILTRATION
FILTRATE
SULFIDE 1
Cu, As, Sb, Bi
FILTRATE 2
FILTRATE 1
RECYCLED TO ELECTROREFINING PROCESS
ADDITION OF SODIUM HYDROSULFIDE
HYDROGEN SULFIDEGAS
FILTRATION
SULFIDE 2
FILTRATE 3
NEUTRALIZATION
SLAKED LIME OR CALCIUM CARBONATE
FILTRATION
FILTRATE 4
GYPSUM
NEUTRALIZATION
SODIUM CARBONATE OR CAUSTIC SODA
FILTRATION
NICKEL CARBONATE OR NICKEL HYDROXIDE
DRAINING

FIG. 2