

[54] COPPER ELECTROWINNING PROCESS

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

[58] Field of Search **204/108, 275, 237, 239**

[56] **References Cited**

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[57] **ABSTRACT**

A process and apparatus for electrowinning a high purity copper from an aqueous pregnant liquor acid electrolyte at high efficiency, and high current density in the presence of impurities. Electrolyte is circulated through an external loop system and upwardly between the anodes and cathodes. SO₂, iron, and acid are added to the electrolyte in the external loop to maintain an SO₂ concentration of at least 0.01g/l, an iron concentration of at least 1g/l, and an acid concentration of at least 5g/l as the electrolyte enters the tank. Preferred processes use iron and sulfur dioxide in the electrolyte and carbon electrodes.

7 Claims, 4 Drawing Figures

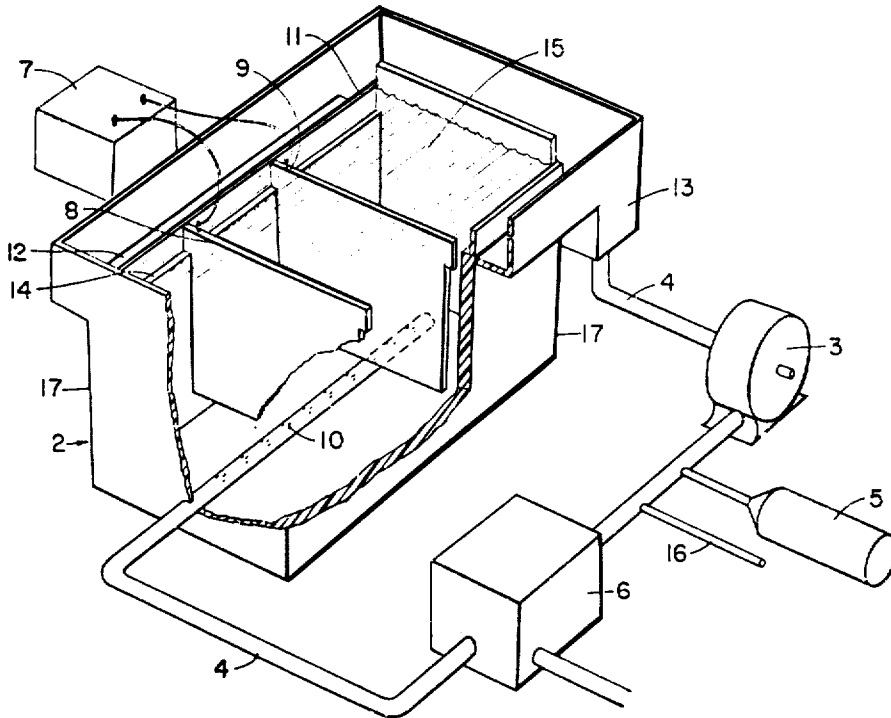


FIG. 1

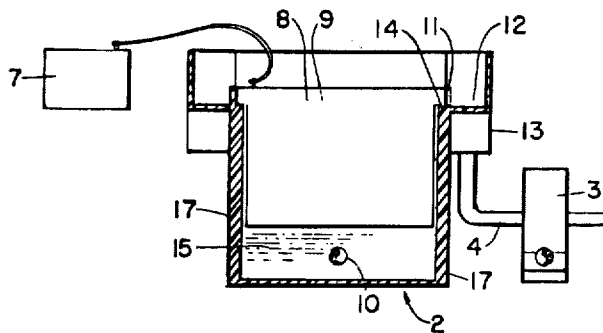


FIG. 2

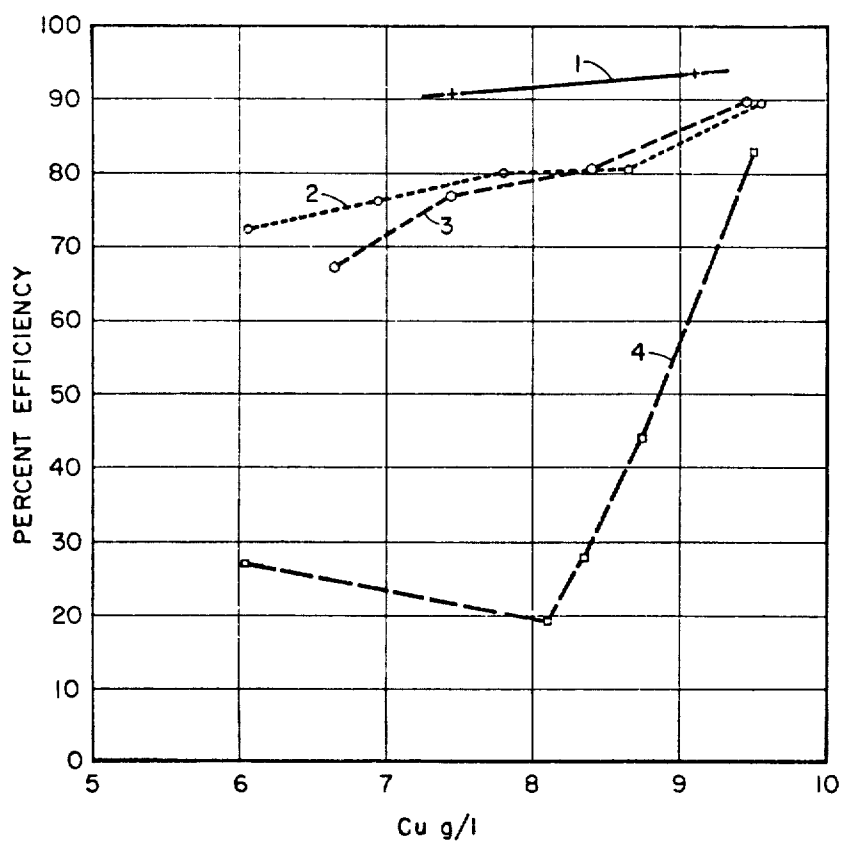


FIG. 3

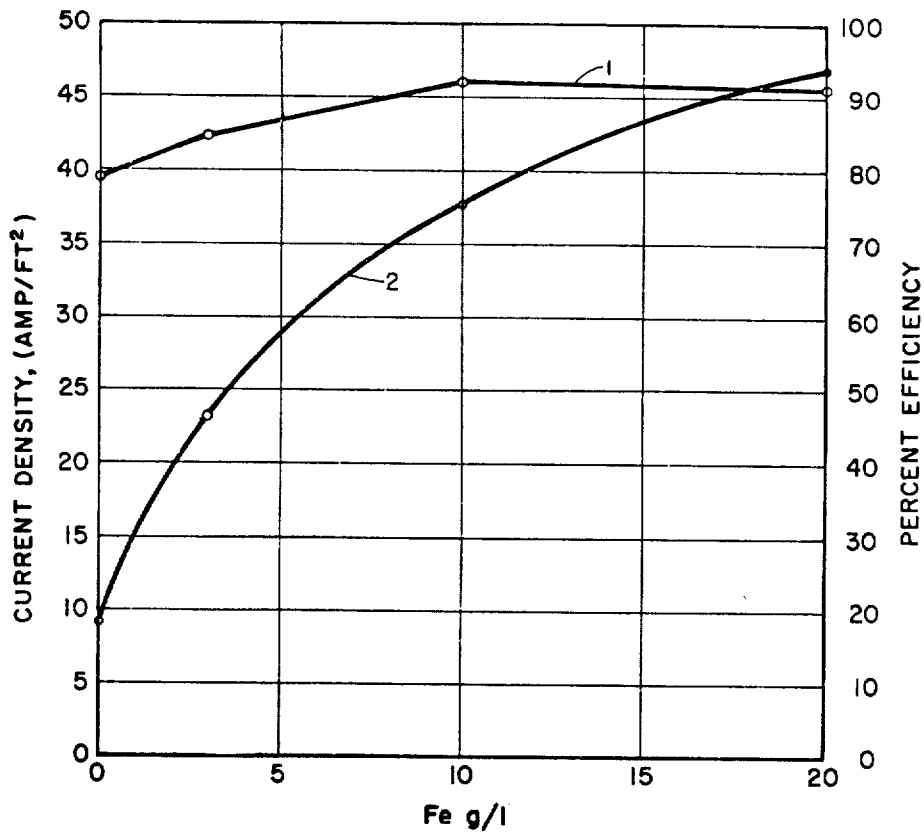


FIG. 4

COPPER ELECTROWINNING PROCESS

The process and apparatus of this invention relates to electrolytic recovery of copper, to electrowinning high purity copper from an aqueous liquor and especially to electrowinning at high efficiency, and high current density from a liquor with low copper concentration in the presence of impurities.

Electrolysis of copper has been used as an analytical technique, for refining copper and for recovering copper from concentrated solvent in extraction processes. This latter recovery process is related to electrowinning which is the separation of a metal from a solution by electrolysis. Typical electrolytic processes are described in Chemical Abstracts 52-8791G, 66-61198, and 67-78397; in *Electrochimica Acta*, 10, pp. 513-27 (1965) in U.S. Pat. No. 1,133,059 to Perreux-Lloyd; in "Electrolytic Copper Refining," by Eichrodt and Schloen in A. Butts edition of *Copper - The Science and Technology of the Metal, Its Alloys and Compounds*, ACS Monograph 122, Reinhold Publ. Corp. NY, 1959, and in *Extractive Metallurgy of Copper, Nickel and Cobalt*, Interscience Publ., N.Y. 1961. These processes generally require high copper concentrations, intermediate purification steps or low impurity concentration.

Electrolytic recovery has been used to recover copper from copper sulfate-sulfuric acid extraction solvents following acid or salt leaching and extraction purification. With these processes impurities, such as iron, cobalt, molybdenum, certain sulfur compounds and other compounds, result in low purity copper. Impurities and low copper concentration results in low purity copper, low efficiency and a low current density (i.e. low capacity) process, thereby making electrowinning of such electrolytes impractical.

Various purification or remedial steps have been used to reduce these problems. These steps include use of diaphragm cells, copper cementation, stripping impurities prior to electrolysis, reduction and precipitation of impurities and combinations of conventional purification steps. None of these remedies have been a cure-all and each generally results in a complex or expensive addition to a copper recovery process.

Even with these remedial steps the copper recovered has low purity and must be electrorefined to meet quality specifications such as those set out by ASTM Designations B5-43, B115-43, B170-70, B193-65, B224-70, B216-49, B442-67 and Part 32 of ASTM standards generally. As used herein and as defined by ASTM high purity refers to copper analyzing more than 99.95% by weight copper or better than Grade 2 oxygen-free electrolytic copper as set forth in ASTM B170-70. Practically, a purity of about 99.97% copper is required in industry for high purity copper and Grade 1 copper requires a minimum analysis of 99.99% copper.

An electrowinning process and apparatus has been discovered which combines several functions into one simple system for recovering and producing copper in one step with an unexpectedly high purity copper with high efficiency and low cost and which will operate at unexpectedly low copper concentration electrolyte. This process will also operate using an aqueous acid leach pregnant liquor as an electrolyte without removing certain impurities. The process utilizes a particular combination of features and operating ranges and

makes continuous electrowinning of even low copper concentration solutions, such as less than about 10 gram per liter (g/l), practical.

This electrolysis process with several particular variations produces high purity copper with high efficiency and current density. This process is very insensitive to many copper leaching and electrolysis impurities such as iron and associated compounds. Thus, the necessity of highly selective extraction, precipitation, and other refining agents prior to electrowinning are less critical. The process also makes possible the use of less expensive anode materials, such as carbon. At the same time, this process practically eliminates copper contamination at the cathode by anode metals and electrolyte metallic impurities. Particularly unexpected is the fact that this process makes electrowinning practical even at low copper concentrations. This process makes it possible to recover substantially all of the copper from an electrolyte at high efficiency and purity, e.g. down to less than about 0.1 g/l.

By this invention, there is provided a process for electrolysis by which coherent copper of high purity can be produced with high efficiency from an aqueous pregnant liquor electrolyte containing copper derived from acid leaching a copper ore, said process comprising circulating said electrolyte through an electrolytic system containing an electrowinning tank which contains the electrolyte and electrodes at least one electrode being a cathode and at least one electrode being an anode with the electrodes being immersed in said electrolyte and connected with a means for supplying electrical current so that electrical potential can be impressed between said anode and cathode electrodes through said electrolyte; said electrolytic system having a temperature control means, an SO₂ injection means and an electrolyte circulation means; said electrolyte being derived from an aqueous acid leach liquor with an adjusted concentration of SO₂; said electrolytic system having means for circulating electrolyte between said electrodes; maintaining the temperature of said electrolyte above about 70°F; adjusting and maintaining a concentration of SO₂ of at least about 0.01 gram per liter in said electrolyte as the electrolyte enters said electrowinning tank; impressing an electrical voltage of at least 0.4 volts between said anode and cathode electrodes through said electrolyte so that sulfuric acid is formed at the anode and copper is deposited at the cathode; and recovering a coherent high-purity copper product at the cathode.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a perspective sketch of an electrolysis system showing components in symbolic form.

FIG. 2 is a cross-section view of the electrowinning tank in FIG. 1.

FIG. 3 is a graph of efficiency v. copper concentration in electrolyte showing efficiency for electrolytes with four different iron concentrations without SO₂.

FIG. 4 is a graph of current density and efficiency plotted against iron concentration in electrolyte with SO₂.

A preferred copper electrolysis process of this invention is the electrowinning of copper from "pregnant liquor" electrolyte; that is, electrolysis from electrolyte containing copper ions and many other ions such as iron, aluminum, and oxygen, which normally reduce efficiency and product purity.

Pregnant liquor as used herein refers to an electrolyte containing copper ions which has been derived from acid leaching a copper ore. Generally, this leach liquor must be processed by selective extraction or chemical purification to remove the impurities such as iron, aluminum, and molybdenum. With the process of this invention complete, removal of all of these other metals is not essential.

In fact, a preferred application of the process of this invention can be used for electrowinning copper at high efficiency and high current density with low copper concentration and other impurities present. In this process, iron is used in the electrolyte, and a residual concentration of sulfur dioxide (SO_2) is maintained in the electrolyte. The iron and SO_2 concentrations must be adjusted in the electrolyte to maintain high current density and high product purity. The external electrolyte circulating loop preferably circulates the electrolyte through a distributor means in said electrowinning tank which circulates said electrolyte uniformly and upwardly between said electrodes by jetting the electrolyte. The electrolyte is preferably jetted by nozzles with a minimum fluid velocity of the electrolyte at the nozzle of at least about 150 feet per second with a volume calculated to completely displace said electrolyte in an electrolysis solvent of the electrowinning tank in the vicinity of said electrodes once every five minutes.

A preferred process of this invention uses inexpensive conductive material such as carbon which is normally decomposed by oxidation in conventional copper electrolysis. Other conventional conductive materials, such as metals and alloys including lead, platinum, mercury, iron, silver, gold, tin, chromium, zinc, aluminum, magnesium, antimony, silicon, and mixtures thereof, can be used for the electrodes. The carbon material used for anodes is preferably selected from carbon black, coke, or graphite. Titanium and the above metals and combinations thereof can be used for the anode. Normally, a relatively inert conductive material is preferred for the anode to prevent contamination of recovered copper. Impurities (such as cations other than copper) that have an electrochemical plating potential near or below copper in the electrochemical series, must be avoided, removed, or inhibited, or these impurities will be reduced at the cathode and contaminate the copper. Effect of these impurities can be avoided by conventional means. The cathode for the process of this invention is normally copper since high purity copper is the product desired, but another conductive material can be used and the copper removed from this material.

Conventional methods and materials can be used to construct the electrowinning tank or electrolysis cell, to supply and control the electrical current, to agitate the electrolyte, and to control temperature of the electrolyte. The tank or cell confines the electrolyte in the region of the electrodes. It separates, supports and maintains spacing of the electrodes and other appurtenant equipment so that the electrical current passes through the electrolyte. Agitation is preferably provided by circulating the electrolyte through a loop including the tank and other equipment, such as heating coil, reservoir, and sampling means. Such external circulation provides excellent control of electrolyte temperature, reagent concentrations, and agitation in the cell. Other methods of agitation can be used and will be obvious to one skilled in the art in view of this disclo-

sure. A preferred circulation system uses a distributor conduit in the electrowinning tank relatively perpendicular to and below substantially parallel plate electrodes so that the electrolyte flows upwardly between the electrodes. With this system, electrolyte can exit the electrolysis zone by overflowing from the electrowinning or electrolysis zone, preferably overflowing along the entire length of the longitudinal sides of the zone. The circulation system can be internal or enclosed within the tank. Parallel walls of insulating materials can conveniently be used to define the sides of the electrolysis zone, form an overflow weir, and support the electrodes. A preferred distributor can be formed of cylindrical pipe or conduit having nozzles, preferably at least three, located at intervals along the conduit between each pair of electrodes so that the electrolyte flows or jets from the distributor between each pair of electrodes at a velocity sufficient to agitate electrolyte in the electrolysis zone, prevent chemical polarization and reduce electrical polarization resistance. The nozzles can be sized, shaped, and spaced on the conduit to give the desired velocity and degree of agitation required as set forth herein. The distributor or distributor means can be any type of conduit or flow control means to be sure the electrolyte flows relatively uniformly along the length of the electrowinning tank. This is necessary to provide a relatively uniform flow and agitation upwardly between each pair of adjacent electrodes to prevent polarization. An external loop circulation means is preferred because it permits close control of the electrolyte temperature and concentrations as well as providing agitation between electrodes. Internal agitation, such as a propeller, thermal siphon or mechanical agitator, can be used and the electrolyte flow within the cell can be in any direction as long as the flow or circulation provides the agitation and mixing necessary to prevent polarization and provide adequate control of the electrolyte concentrations and temperature.

A preferred system or apparatus for electrowinning the unique high purity copper of this invention comprises an electrowinning tank which contains the electrolyte, electrodes, at least one electrode being an anode and at least one electrode being a cathode, and an electrolyte distributor means located beneath said electrodes; said electrodes being supported by parallel vertical side walls extending lengthwise of said electrowinning tank and being substantially perpendicular to said electrodes with the electrolyte flowing into said tank through said distributor means upward between said electrodes and from said tank at the top of said sidewalls at a rate which is substantially uniform along said walls into a circulation means collection and reservoir system and then into an external circulation loop and circulation means; said circulation loop having a reagent injection means and a temperature control means; said electrodes in said electrowinning tank having a D.C. electric current supply means capable of impressing a voltage sufficient to reduce copper ions between said anode and cathode electrodes through said electrolyte in said tank. The D.C. current supply means should supply a relatively constant but adjustable voltage to the electrodes.

Unique features of the process of this invention are the composition and temperature of the electrolyte. A residual concentration of sulfur dioxide (SO_2) is essential; this residual concentration should be at least about

0.01 g/l in the electrolysis cell as indicated by any standard test method. A potentiometric dichromate titration method is preferred using calomel and platinum electrodes with a potential of about -75° millivolts (mv) as the end point to indicate SO_2 concentration. Optimum concentration for a particular system can be readily determined and maintained with minimum experimentation by one skilled in the art in view of this disclosure.

The SO_2 concentration of the electrolyte can be controlled by several methods. With the preferred external circulation loop, SO_2 can be injected into the electrolyte practically anywhere in the loop. The SO_2 can be a gas, a liquid or dissolved in electrolyte stored in a reservoir. Electrolyte can be analyzed to determine the SO_2 concentration and SO_2 concentration adjusted accordingly. With minimum experimentation in view of this disclosure, one skilled in the art can predict the rate of SO_2 consumption and add SO_2 accordingly with very few actual tests. The SO_2 consumption can also be predicted in view of this disclosure with minimum experimentation by monitoring other process rates, e.g. electrical power consumption, electrowinning time, etc. The other chemical reagents used in electrowinning and even the concentration of iron used in a preferred process can be controlled by these methods; although, as with iron, the reagent may not be consumed directly by electrowinning. The process produces sulfuric acid which can be recycled to an ore leaching operation.

In a preferred process, an iron concentration of at least 3.0 g/l is maintained in the electrolyte. High iron concentration makes possible high current density. Most "pregnant liquor" electrolytes contain iron, but iron can be adjusted to maintain the desired iron concentration in the electrolyte if needed or desired.

The electrolyte used in the process of this invention are aqueous acidic electrolytes. As used herein, aqueous means that the electrolyte contains a substantial portion of water. Organic, inorganic, or non-aqueous components can also be present. These aqueous electrolytes are preferably acidic and can contain about 5–100 grams per liter (g/l) of acid. More or less, acid can be used, and the process of this invention is practical with low acid electrolytes. An acid concentration of about at least 5 g/l is preferred. Sulfuric acid is the acid normally used for the electrolyte, and it is the acid preferred for this invention. Salts and acids other than sulfuric can be in the electrolyte as long as they do not interfere with the electrowinning process. These acids include mineral acids such as HCl , H_3PO_4 , HNO_3 etc. and organic acids such as acetic, oxalic, etc. These acids and salts can be used as a buffer, to prevent side reactions or for other purposes not directly related to electrowinning. With sulfuric acid, two moles of sulfuric acid are produced for each mole of copper recovered at the cathode where prior art process only produced one mole of acid. Thus, the process of this invention produces twice as much sulfuric acid and consumes SO_2 which is normally in air polluting byproduct of sulfide ore processing.

Temperature of the electrolyte of the process of this invention must be maintained above about at least 70°F and preferably in the range of about 100° – 150°F . Electrolysis efficiency of this process is higher at temperatures near the top of this temperature range.

Components other than those pointed out herein can be present in the electrolyte. Most of the components encountered in acid leaching sulfide copper ores can be tolerated and do not interfere in the process of this invention as they do with prior art process. Unusual components which interfere with SO_2 , iron, or electrolysis can be readily identified in view of this disclosure and must be removed or inhibited.

The source and control of electrical current for electrolysis are conventional with the process of this invention; however, lower voltage can be used than with prior art processes. A voltage sufficient to deposit copper at the cathode or reduce copper ion to atomic copper is required. With this process, the minimum practical voltage is about at least 0.4 volts. Voltage in the range of about 0.5–1.5 volts is preferred. The maximum permissible voltage is determined by impurities and side reactions. For instance, high voltage which causes evolution of oxygen at the anode, evolution of hydrogen at the cathode, formation of copper sulfide, or other undesirable side reactions should be avoided. Chemical component polarization or localized high concentration contribute to these problems; for example, high acid concentration accentuates hydrogen evolution although high acid concentration aids use of high current density. Whether steady direct current (D.C.), pulsating D.C., or any other current form is used, the voltage should be near the optimum range to avoid reduction of other cations. The voltage is preferably maintained substantially constant although it can be adjusted for various electrolytes. For a preferred process current densities of over 40 amperes per square foot of cathode area (amp./ft.²) can be obtained with less than 1.5 volts and an electrolyte having about 10 g/l sulfuric acid and less than 10 g/l copper. Electrode number and spacing are conventional, and optimum values can be readily determined by one skilled in the art in view of this disclosure, and the total electrolysis rate desired. High electrolysis rate can result in electrical polarization or formation of a high electrical resistance barrier which, in effect, lower the effective voltage driving the electrolysis. Likewise, high reaction rate and inadequate agitation can result in chemical polarization or high and low concentration of components required for electrolysis. Polarization should be avoided and can generally be reduced by increasing agitation of the electrolyte. The SO_2 -iron combination of this invention makes it practical to use less expensive materials, such as carbon, for electrodes because oxygen is not evolved and prevents oxygen contamination of deposited copper.

Copper deposited at the cathode is high purity copper which normally adheres to the cathode. With starting cathodes of copper, the entire cathode is copper. If carbon or other material is used, removal of the copper from the cathode will be required to recover only copper. If the copper does not adhere to the cathode, it can be recovered from the electrolyte by conventional methods such as sedimentation or filtration. With the process of this invention, copper having a purity higher than about 99.95 percent by weight can be recovered from electrolyte having less than about 10 g/l copper at an efficiency of better than about 70 percent with recovery of more than about 95 percent of the copper or down to a concentration of about 0.5 g/l. As used herein efficiency refers to the percent of electrical current which actually reduces copper ion at the cathode.

Thus, the process of this invention provides a practical process for recovering copper in high purity with high current density and efficiency in the presence of impurities even at copper concentrations which have previously been too low for practical recovery.

The following examples illustrate the invention; parts, percentages, ratios, and concentrations are by weight unless indicated otherwise.

EXAMPLES

ELECTROLYSIS CELL

An electrolysis system 1 is constructed as shown in FIGS. 1 and 2. The electrowinning tank 2 is constructed of plexiglas having two vertical side walls 17 about 12 inches long, about 5 inches high and spaced about 3 1/4 inch apart to support anode 8 and cathode 9 electrodes while containing electrolyte 15. Electro-

pressed between anode and cathode electrodes through electrolyte in the tank 2. The electrodes at each end of the tank are anodes with cathodes and anodes alternating in sequence along the tank. The sidewalls are preferably slotted to maintain the electrode spacing uniform. Starting cathodes are 0.25 mil thick copper sheet. Anodes are preferably (a) graphite or (b) platinum black.

EXAMPLE 1

Distilled water is mixed with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 98 percent H_2SO_4 to produce electrolyte having the desired concentration of each component. Six samples having 10 g/l copper, 10 g/l H_2SO_4 , and iron concentrations between 0 and 5 g/l are used for plating copper using 1-inch electrode spacing and 1.9-volt D.C. current. Typical values for iron concentration, av-

TABLE I

Sample	CONC. G/L.			Ave. Cu Conc.	Eff. %	Ave. Cu Conc.	Eff. %	Ave. Cu Conc.	Eff. %	Ave. Cu Conc.	Eff. %	Ave. Cu Conc.	Eff. %
	Cu	Fe	H_2SO_4										
1	10	0	10	9.1	93.6	7.45	90.7						
2	10	0.5	10	9.65	89.5	8.9	85.9	8.1	86.5	7.35	86.7	6.6	84.3
3	10	1.0	10	9.55	89.7	8.65	80.6	7.8	80.0	6.95	76.1	6.05	72.2
4	10	2.0	10	9.45	89.5	8.4	80.6	7.45	77.0	6.65	67.1	5.9	71.7
5	10	3.5	10	9.55	96.7	8.8	53.2	7.2	57.1	7.6	52.7	6.9	57.9
6	10	5.0	10	9.5	83.0	8.75	44.0	8.35	27.0	8.1	19.0	6.05	27.0
7	20	2.0	10	19.55	86.7	18.8	73.8	18.2	65.8	17.4	63.2	16.6	64.2
8	20	5.0	10	19.5	86.0	18.7	52.2	18.15	40.0	17.65	35.2	17.2	40.4

lyte is circulated from the reservoir 13 by circulating means 3 through circulation loop 4 and into the tank 2 so that it overflows the top of the tank at the top of the sides which function as an overflow weir 11 to control the level in the tank. The circulation reservoir is provided with a collection means 12 for the reservoir 13. Electrolyte is pumped into the tank through distribution means 10 which provides relatively free flow of the electrolyte along the length of the tank and uniform upward electrolyte flow between each adjacent pair of electrodes. The distributor means is about 1/2 inch below the electrode plates with three 1/64 inch diameter jets, one vertical and the other two at about 30° from vertical so that the jets agitate the electrolyte uniformly along both sides of each electrode. These jets are spaced about every 1/4 inch along the distributor for maximum number of electrodes with a 1/4 inch spacing and the electrolyte is circulated at about 0.6–1.5 gallon per minute (gpm) for a jet velocity of about 400–800 feet per second (fps).

As electrolyte is pumped from the reservoir 13, which contains about 4 liters, additives such as SO_2 , iron and any other reagents are injected by means 5 and 16 to adjust and maintain the reagent or additive concentrations in the desired ranges. The temperature is also adjusted by temperature control means 6 in the circulation loop 4 so that temperature entering the tank is maintained uniform.

The electrodes 8 and 9 are tee-shaped so that they are supported by the tank sidewalls 17 with about a 3 inch by 3 inch square immersed in the electrolyte. The electrodes are connected to a D.C. electric current supply means 7 so that an electric voltage can be im-

posed across the electrodes and the electrolyte. The average copper concentration, and copper plating efficiency for various intervals are given in Table I and FIG. 3.

FIG. 3 shows the electrowinning efficiency in percent without SO_2 plotted as the ordinate versus the electrolyte copper concentration in g/l for four samples having different concentrations of iron in the electrolyte. The curves are numbered 1 through 4 which correspond to 0, 1, 3 and 5 g/l of iron. These curves show that electrowinning efficiency is adversely affected by iron concentrations above about 2 g/l without SO_2 .

EXAMPLE 2

Several electrolyte samples are prepared as in Example 1 using copper concentration of 10 g/l and H_2SO_4 concentration of 10 g/l. Each sample is electrolyzed to recover the copper at the cathode with a preselected voltage and electrolyte temperature. A portion of the samples are electrolyzed with SO_2 being bubbled directly into the electrolyte for comparison with samples electrolyzed without SO_2 .

Several samples are electrolyzed using carbon anodes without SO_2 at ambient temperature, 120°F and 160°F. At all three temperatures, the anode quickly discolors when SO_2 is not added to the electrolyte. This discoloration is caused by carbon anode decomposition which occurs after only 30 minutes of electrolysis at 160°F. With SO_2 in the electrolyte, the electrolyte is not discolored by carbon anode decomposition.

Several samples containing 10 g/l of iron are electrolyzed with SO_2 at 120°F. These samples produce high current density with low voltage and comparable copper concentration and efficiency.

Typical data for these samples are given in Table 2.

TABLE 2

Sample	SO ₂	Volts	Current Density (Amp./Ft ²)	Temp. °F	Ave. Cu Conc.	Eff. %
1	No	1.9	5.9	Amb.*	9.0	100
2	No	1.9	8.0	Amb.	7.35	98.4
3	No	1.9	8.4	120	8.75	94.7
4	No	1.9	7.35	120	6.65	95.2
5	No	1.9	17.3	160	7.5	87.0
6	No	1.9	24.1	160	3.05	91.3
7	Yes	0.7	7.2	Amb.	9.85	38.5
8	Yes	1.2	14.4	Amb.	8.85	83.0
9	Yes	1.75	21.6	Amb.	6.9	96.1
10	Yes	0.70	7.2	120	9.5	52
11	Yes	0.95	14.4	120	9.1	84
12	Yes	1.35	21.6	120	7.5	93
13	Yes	0.7	7.2	160	9.75	60
14	Yes	1.28	14.4	160	8.85	85
15	Yes	1.50	21.6	160	7.1	91
16**	Yes	0.60	7.2	120	9.8	44
17**	Yes	0.90	14.4	120	9.8	72
18**	Yes	1.13	21.6	120	8.1	85.7

*Ambient temperature

**Iron concentration of 10 g/l

EXAMPLE 3

A sample of electrolyte containing 10 g/l each of copper, H₂SO₄ and iron. Sulfur dioxide is added to this sample as sodium sulfite with an equivalent amount of H₂SO₄. A sample of the electrolyte is withdrawn from the electrolyte stream periodically and titrated periodically with potassium dichromate by a standard method to determine SO₂ concentration. The average copper concentration, voltage, current density, temperature, SO₂ concentration, and efficiency for each period are given in Table 3. The power consumption for plating copper from electrolyte from a copper concentration of 9.59 g/l to 0.12 g/l was 0.372 kw-hr per pound of copper plated at the cathode.

TABLE 3

Time Interval	Ave. Copper Conc. G/L	Current Density (Amp./Ft ²)	Voltage	Temp. °F	SO ₂ Conc. G/L	Eff. %
1	7.32	28.8	0.80	148	5.2	87.5
2	3.86	28.8	0.75	148	2.6	74.7
3	2.31	28.8	0.75	148	1.6	85.1
4	1.19	28.8	0.80	150	6.4	81.2
5	0.48	14.4	0.62	152	4.2	62.8
6	0.19	10.8	0.58	150	—	17.9
7	0.14	7.2	0.50	150	1.0	15.6

EXAMPLE 4

A large portion of "pregnant liquor" electrolyte is mixed as in the previous examples having 10 g/l each of copper, iron, and sulfuric acid. Also, Al₂(SO₄)₃·18-H₂O is added to the electrolyte to give an aluminum concentration of 3.8 g/l. From a separate reservoir electrolyte saturated with SO₂ is added to the electrolyte stream to maintain an average SO₂ concentration of 0.5 g/l. The "pregnant liquor" electrolyte is divided into samples and electrolyzed using a ½-inch electrode spacing at three different temperatures and several voltage settings to determine the effect of temperature and voltage.

At copper concentration below about 3 g/l black Cu₂S deposits form on the cathode. Formation of these spots is eliminated by using voltage below about 0.7 volts.

Typical data for these samples are given in Table 4.

TABLE 4

Sample	Temp. °F	Volts	Ave. Current Density (Am/Ft ²)	Current Density at 5 G/L Cu
1	84(1)	0.8	8.3	10.0(2)
2	84(1)	1.3	18.1	14.3
3	120	0.8	11.8	14.2
4	120	1.3(3)	25.2	25.2
5	150	0.8	15.3	18.3
6	150	1.3(4)	31.9	40.4(4)

(1) Ambient temperature

(2) Estimated; electrolysis is stopped at 8.5 copper concentration because of low current density

(3) Voltage is decreased to 0.95 volts at 2.0 g/l copper concentration

(4) Estimated current density; voltage is decreased to 0.7 volts at 1.5 g/l copper concentration

EXAMPLE 5

A "pregnant liquor" electrolyte is prepared having a 10 g/l concentration of copper and sulfuric acid. The electrolyte is divided into several portions and iron is added for concentrations of 0, 3, 10, and 20 g/l. SO₂ is added to the electrolyte and each portion is electrolyzed at 150°F to recover copper as in Example 4. Typical data for each sample is given in Table 5.

Data for voltages of about 1-1.3 volts are plotted as FIG. 4 showing variation of efficiency in percent (1) and current density (2) in amperes per square foot (amp/ft²) plotted versus iron concentration (Fe g/l) in the electrolyte. These curves show that with SO₂ in the electrolyte current density and efficiency increase with iron concentration.

TABLE 5

Sample No.	Volts	Current Density (Amp/Ft ²)	Ave Cu Conc. (G/L)	Iron Conc. G/L	Eff. Percent
1	1.15	9.2	8.05	0	78.8
2	1.10	9.2	6.85	0	84.9
3	1.3	23.3	6.85	3.0	84.7
4	1.3	22.2	2.2	3.0	68.7
5	0.8	7.1	0.15	3.0	12.7
6	1.3	37.6	7.0	10.0	92.0
7	1.3	39.6	2.95	10.0	70.3
8	0.7	12.0	1.0	10.0	45.4
9	1.3	46.8	7.0	20.0	91.1
10	1.0	32.1	2.85	20.0	63.0
11	0.7	14.2	1.0	20.0	48.9
12	0.6	10.3	0.45	20.0	20.9

EXAMPLE 6

A "pregnant liquor" electrolyte is mixed having concentrations of 10 g/l for copper, iron, and sulfuric acid with 3.8 g/l aluminum. The electrolyte is electrolyzed as in Example 4 using a 1-inch electrode spacing and 5 mil 99.93 percent copper cathode starting sheet. With copper concentration below about 3 g/l, black Cu_2S spots form on the cathode.

A second "pregnant liquor" electrolyte is mixed and electrolyzed as above. The voltage is decreased to about 0.8 volt at copper concentration of about 3 g/l, and no Cu_2S forms on the cathodes.

A third "pregnant liquor" electrolyte is mixed, having concentrations of 1.5 g/l copper and aluminum, 5 g/l sulfuric acid, and 8.3 g/l iron. This electrolyte is electrolyzed at 0.7 volts.

Copper recovered from each electrolysis is analyzed for purity by ASTM Method E-53. The data from each sample is given in Table 6.

TABLE 6

Sample	Voltage	Copper		Purity (Per-cent)	Current Density (Amp/Ft ²)	Eff. %
		Ave.	Lower Limit			
1	1.30	8.65	7.20	99.97	22.7	94.1
2	1.30	5.80	4.40	99.98	25.1	89.8
3	1.18	3.35	2.30	99.97	27.0	84.3
4	1.00	1.65	0.93	99.40	16.7	63.0
5	0.88	0.52	0.12	99.27*	11.0	28.4
6	1.3	8.20	6.20	99.99	26.3	86.4
7	1.3	4.52	2.85	99.96	32.1	80.7
8	0.8	1.85	0.65	99.97	12.4	55.0
9	0.8	0.62	0.19	—	10.3	20.4
10	0.7	0.89	0.28	99.97	4.1	44.6
11	0.7	0.24	0.20	—	4.1	1.5

* Cu_2S_2 formation.

We claim:

1. A process for efficient electrolysis of an aqueous pregnant liquor electrolyte containing copper producing high purity copper, said process comprising circulating said electrolyte in an external loop electrolyte system from an electrowinning tank which contains the electrolyte and electrodes, at least one electrode being a cathode and at least one electrode being an anode, with the electrodes being immersed in said electrolyte and connected with a means for supplying electrical current so that electrical potential can be impressed between said anode and cathode electrodes through said electrolyte; said tank having parallel side walls substantially perpendicular to said electrodes; circulating said electrolyte through a distributor means in said electrowinning tank uniformly and upwardly between said electrodes overflowing along the entire length of said side walls; maintaining the temperature of said electrolyte above about 70°F with a temperature control means in said external loop; adjusting in said external loop the residual concentration of SO_2 , iron, and acid to maintain a concentration of SO_2 of at least about 0.01 gram per liter of electrolyte as it enters the tank, of iron of at least 1.0 g/l of electrolyte as it enters the tank, and of acid of at least 5 g/l of electrolyte as it enters the tank; impressing an electrical voltage of at least 0.4 volts between said anode and cathode electrodes through said electrolyte forming sulfuric acid at the anode and depositing high purity copper at the cath-

ode; and recovering a coherent high purity copper product.

2. A process of claim 1 wherein said electrolyte is circulated at a rate sufficient to prevent chemical polarization in the vicinity of said anode and cathode electrodes in said electrowinning tank.

3. A process of claim 1 wherein the carbon material of said anode electrode is selected from carbon black, coke or graphite and the metal of said anode electrode is selected from platinum, silver, gold, lead, mercury, tin, iron, chromium, zinc, aluminum, magnesium, antimony, silicon, titanium, and combination thereof.

4. A process of claim 1 for producing a copper product wherein the electrolyte system has an electrowinning tank of rectangular horizontal cross-section wherein the electrodes are substantially rectangular plates suspended in a vertical plane with supporting means at the upper edge of said electrodes which supports the electrodes from vertical tank side-walls which are substantially perpendicular to said electrodes; wherein electrolyte is circulated upwardly into said tank through a distributor means with jets located beneath said electrodes so that the upward electrolyte flow rate is substantially uniform along the side-walls of said tank and the electrolyte leaves said tank near the upper edge of said side-wall at a rate which is substantially uniform along the length of said tank and the electrolyte velocity at said jet is in the range of about 400-800 feet per second.

5. A process of claim 1 for efficient electrolysis by which coherent copper of high purity can be produced with high efficiency and high current density from an aqueous pregnant liquor electrolyte containing copper, said process comprising circulating said electrolyte through an external loop electrolyte system from an electrowinning tank which contains the electrolyte and electrodes, at least one electrode being a cathode and at least one electrode being an anode, with the electrodes being immersed in said electrolyte and connected with a means for supplying electrical current so that electrical potential can be impressed between said anode and cathode electrodes through said electrolyte; said electrolytic system having a temperature control means, an SO_2 injection means and an electrolyte circulation means; said electrolyte being derived from an aqueous acid leach liquor with SO_2 and iron being added; circulating said electrolyte through a distributor means in said electrowinning tank which circulates said electrolyte uniformly and upwardly between said electrodes by jetting said electrolyte between said electrodes from nozzles with a minimum fluid velocity at the nozzle of at least about 150 ft/sec with a volume calculated to completely displace said electrolyte in an electrolysis zone of the electrowinning tank in the vicinity of said electrodes once every 5 minutes; maintaining the temperature of said electrolyte above about 70°F; adjusting the concentration in said loop to maintain a residual concentration of SO_2 of at least about 0.01 g/l, to maintain an iron concentration of at least 1 g/l and to maintain an acid concentration of at least 5 g/l in said electrolyte as it enters said electrowinning tank; impressing an electrical voltage of at least 0.4 volts between said anode and cathode electrodes through said electrolyte forming sulfuric acid at the anode and depositing copper at the cathode; and recovering substantially all of the copper as high purity copper product at the cathode.

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6. In a process for electrowinning by which coherent copper of high purity can be produced with high efficiency from an aqueous pregnant liquor electrolyte, said electrolyte being prepared by acid leaching a copper ore, the improvement comprising circulating said electrolyte through an external loop electrolyte system and upwardly between at least one cathode and at least one anode immersed in said electrolyte; adjusting in said external loop the concentration of SO_2 to maintain residual concentration of at least about 0.01 gram per liter of electrolyte as it enters the tank of iron to maintain a concentration of at least 1.0 g/l of electrolyte as

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it enters the tank and of acid to maintain a concentration of at least 5 g/l of electrolyte as it enters the tank; maintaining an electrical voltage differential between said anode and cathode of at least 0.4 volts, and maintaining the temperature of the electrolyte above about 70°F and recovering a coherent high-purity copper product at the cathode.

7. A process of claim 6 wherein a concentration of iron of about at least 3.0 grams per liter is maintained by adjusting the iron concentration of said electrolyte.

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