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(54) **PROCESS FOR OPTIMIZING THE PROCESS OF COPPER ELECTRO-WINNING AND ELECTRO-REFINING BY SUPERIMPOSING A SINUSSOIDAL CURRENT OVER A CONTINUOUS CURRENT**

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(57) **ABSTRACT**

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This invention discloses a process of the electro-winning of metals, in particular copper, is done in a strongly acidic aqueous solution (~180 gpl H<sub>2</sub>SO<sub>4</sub>), with permanent cathodes of stainless steel or Cu starting sheets, and Pb—Ca—Sn anodes, in tradition electrolysis cells to obtain copper cathodes wherein in the electrolytic cells, a sinusoidal current is super-imposed over the continuous current in order to produce high-purity electrolytic copper. This invention also discloses the electro-refining process of metals, in particular copper, is done in a strongly acidic aqueous solution (~180 gpl H<sub>2</sub>SO<sub>4</sub>), with permanent cathodes of stainless steel or Cu starting sheets, and anodes of impure copper from founding, in traditional electrolysis cells in order to obtain copper cathodes wherein in the electrolytic cells, a sinusoidal current is super-imposed over the continuous current in order to produce high-purity electrolytic copper.

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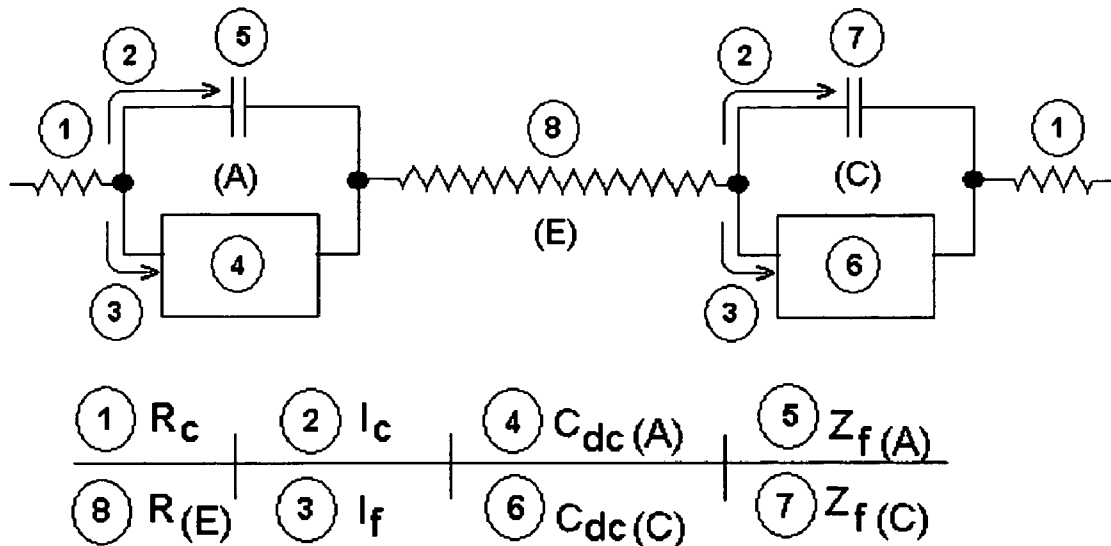


FIGURE 1

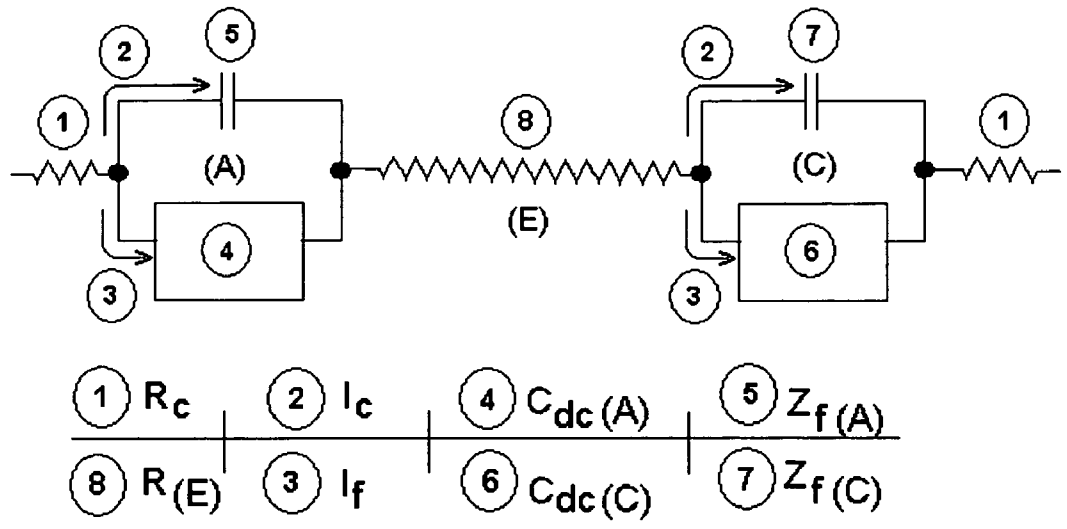


FIGURE 2

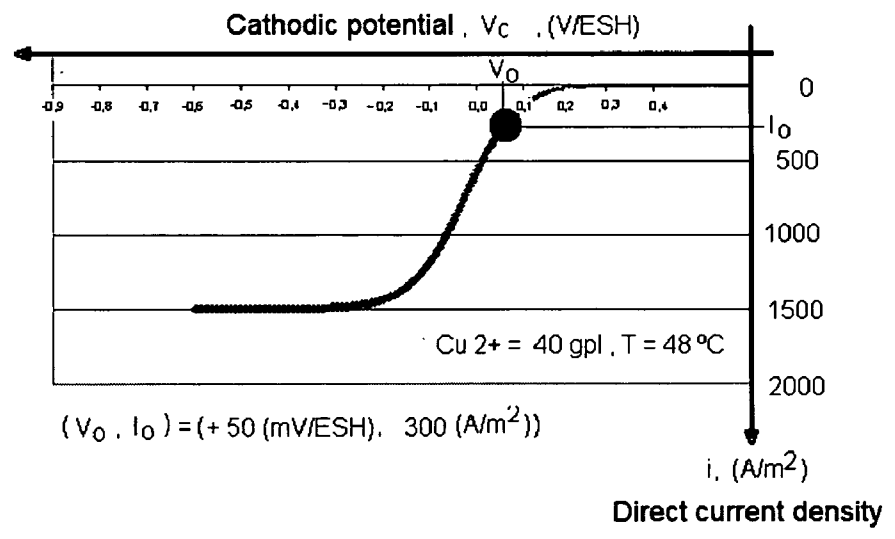


FIGURE 3

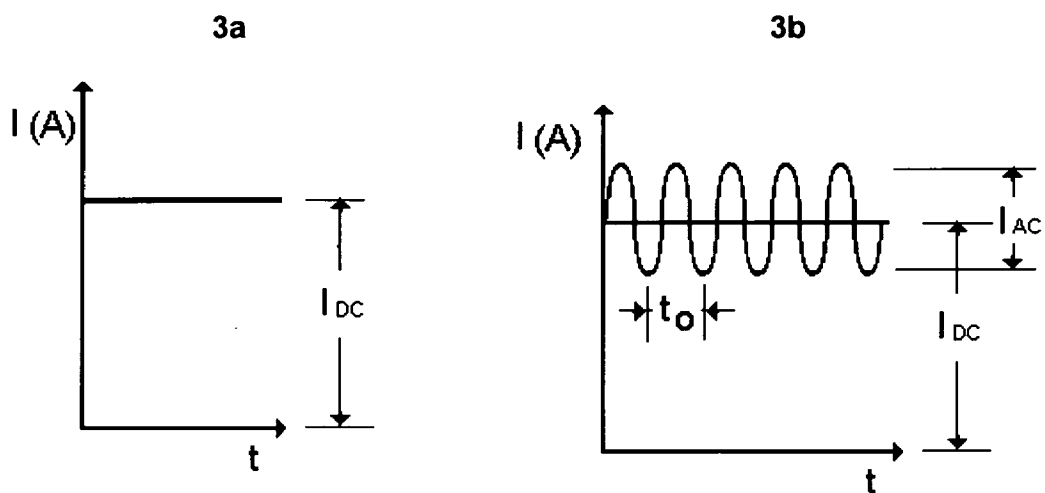


FIGURE 4

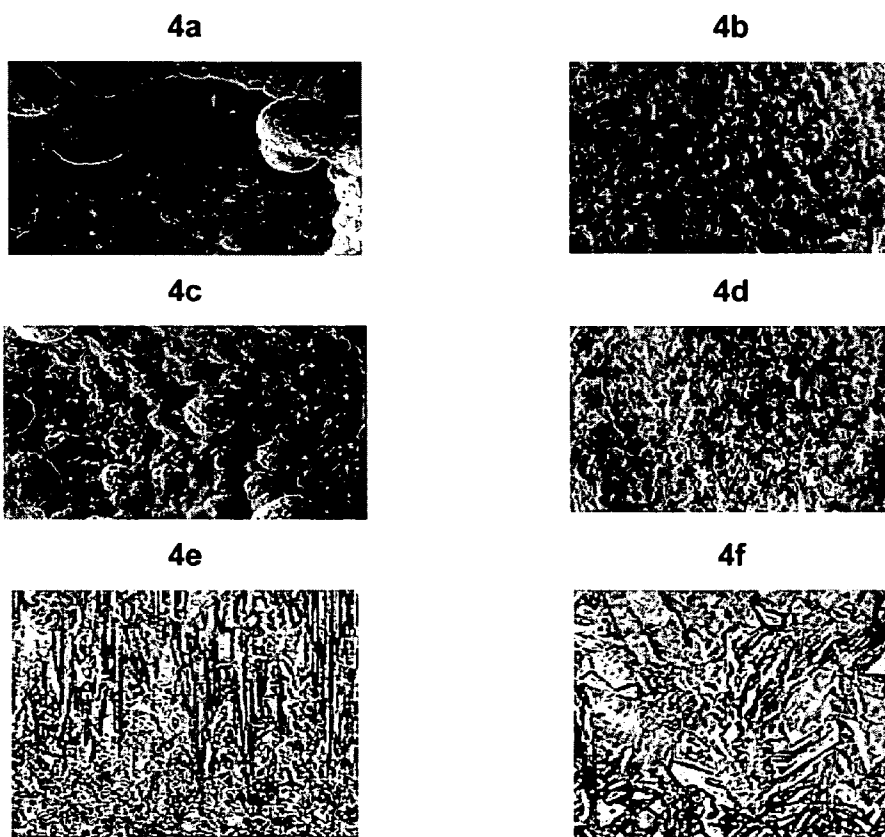
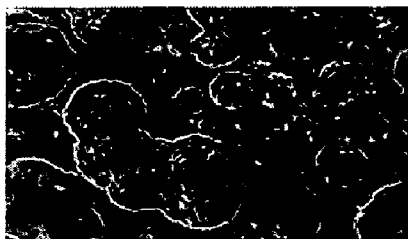
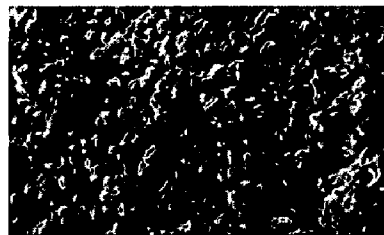


FIGURE 5

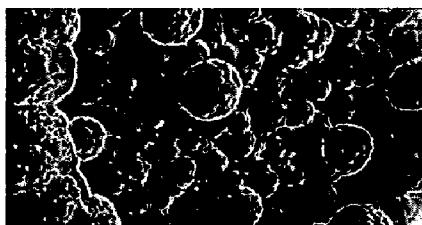
5a



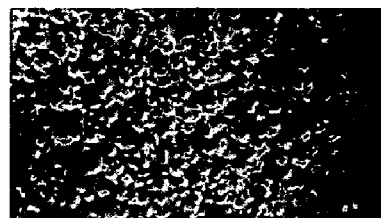
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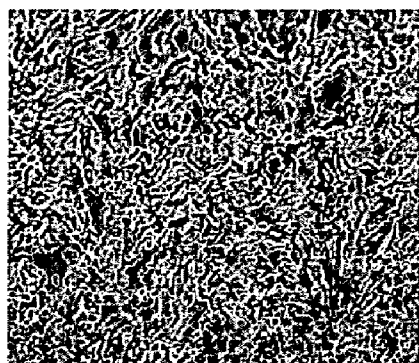
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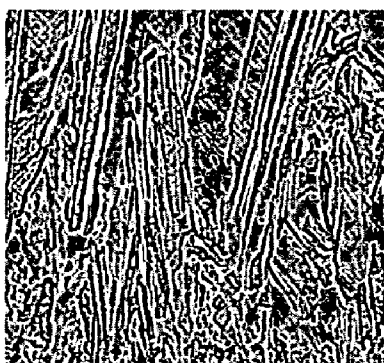
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5e

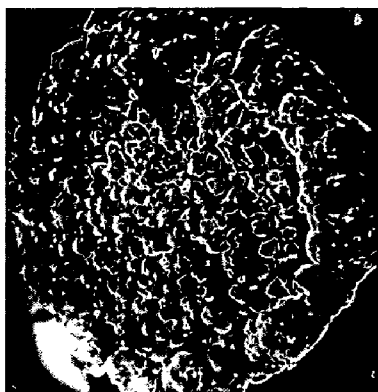


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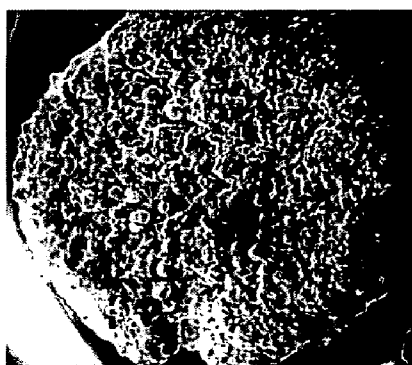


**FIGURE 6**

6a



6b



6c

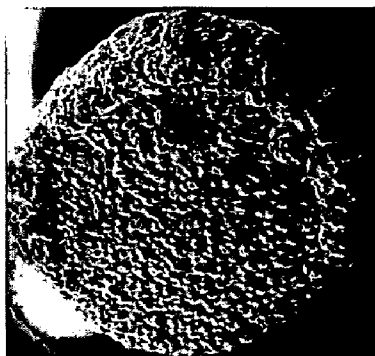
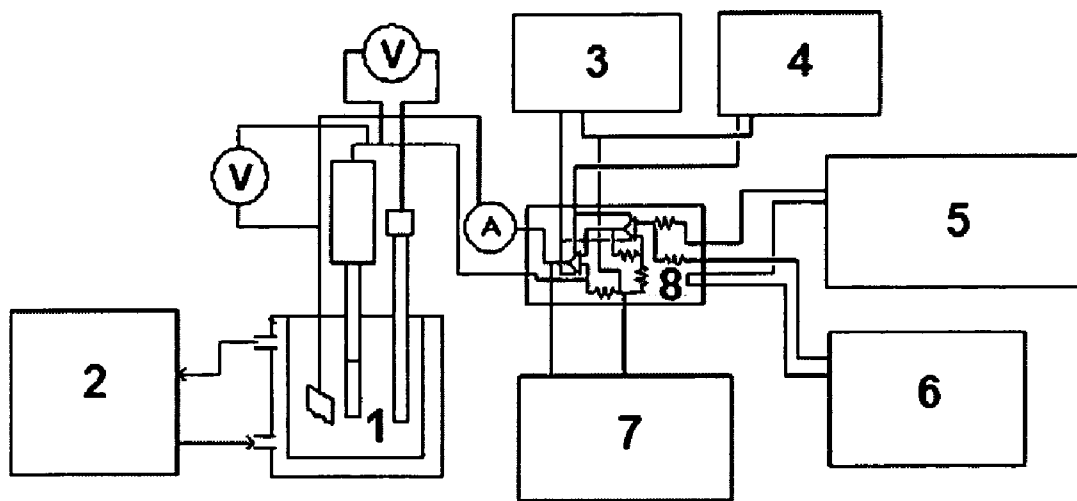


FIGURE 7



**PROCESS FOR OPTIMIZING THE PROCESS OF  
COPPER ELECTRO-WINNING AND  
ELECTRO-REFINING BY SUPERIMPOSING A  
SINUSSOIDAL CURRENT OVER A CONTINUOUS  
CURRENT**

**OBJECT OF THE INVENTION**

[0001] The present invention optimizes the processes of metal electro-winning and electro-refining (in particular copper) by superimposing a sinusoidal current over a continuous current.

[0002] This invention consists of superimposing a sinusoidal current over the continuous current presently used for operations. This improves the processes of electro-winning (EW) and electro-refining (ER) of metals, particularly copper. Depending on the amplitude and frequency selected for the sinusoidal signal, the alternative current component exercises a specific action on the electrochemical double layer of the electrodes [(+) anodes and (-) cathodes] in the electrolysis cell. The electrochemical double layer is charged and discharged during the sinusoidal cycles on both internal and external Helmholtz planes and the diffuse layer, noticeably improving the movement and displacement of the ionic species that are generated or consumed at the electrode/electrolyte interface. From a phenomenological point of view, the use of superimposed current signals makes the double layer and the diffuse layer behave like a true hydraulic pump, forcing ionic flows to and from the electrodes in a zone that is inaccessible when using forced convection (electrolyte flow to cells). During the use of continuous current signals, only the concentration gradients, assisted by the solution temperature, generate movement by diffusion of the determinant ions for the electrochemical reactions and the chemical reactions that take place around the electrodes.

[0003] We have proven experimentally that the superimposition of a sinusoidal current signal (amplitude 400-600 A/m<sup>2</sup>; frequency 1,000-10,000 Hz) over the continuous current acts on the electrochemical double layer, enormously benefiting the electrolysis processes, especially the electro-winning and electro-refining of copper. This new technique allows the use of higher DC current densities in conventional copper EW and ER cells (>300 A/m<sup>2</sup>), the equivalent of an increase in production equal to the installed capacity of an industrial plant. Moreover, the invention improves the physical-chemical cathode quality, the electrochemical corrosion behaviour of the Pb—Ca—Sn anodes, and the electrochemical passivation behaviour of the Cu anodes in the ER electrolysis cells. Consequently, additives are not required to even out the crystalline growth, nor are they necessary for anodic corrosion.

**BACKGROUND**

Description of the Knowledge of the Material

[0004] The Copper Electro-Winning (EW) Process

[0005] Copper has been recovered industrially and commercially from Cu<sup>2+</sup> solutions using the combined LX-SX-EW process for some 30 years. This technique has sustained increased copper production thanks to the technical feasibility of purifying and concentrating Cu<sup>2+</sup> solutions with extraction technology using solvents (SX). High-purity cathodes are produced in the EW tank-house. This global process has the added advantages of low capital and operational costs.

[0006] The chemical quality of the copper cathodes obtained through LX-SX-EW reaches a degree of purity of “five nines” (99.999%), with extremely low levels of impurities (e.g., sulphur, lead, oxygen, iron, hydrogen, carbon). In general, cathode production at most LX-SX-EW plants is over 90% “high-grade”, or superior in quality to Grade A as defined by the London Metal Exchange (LME).

[0007] At present, the Chilean copper production capacity through LX-SX-EW exceeds 3.0 million metric tons per year.

[0008] The objective of copper electro-winning plants is to produce the greatest number of high chemical and physical purity metal cathodes, with the lowest possible specific energy consumption. The plants rely on external electrical energy, and production is determined based on the level of the imposed continuous DC current. This process is carried out in a strongly acidic aqueous solution (~180 gpl H<sub>2</sub>SO<sub>4</sub>), with permanent stainless steel cathodes or Cu starting sheets and Pb—Ca—Sn anodes. The main electrochemical reactions are given in Table 1.

TABLE 1

Main electrochemical reactions in the EW of Cu	
REACTIONS	V° (Volts/SHE)
<u>On the cathode:</u>	
Cu <sup>2+</sup> + 2e <sup>-</sup> = Cu	0.34
<u>On the anode:</u>	
H <sub>2</sub> O = ½O <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup>	1.23

[0009] Table 2 indicates the secondary electrochemical reactions that can also occur on the electrodes. Since the cell potential is between 1.8 and 2.2 V, from a thermodynamic point of view, practically all the reactions indicated in Tables 1 and 2 can take place on the electrodes.

TABLE 2

Secondary reactions in the EW of Cu	
REACTIONS	V° (Volts/ESH)
<u>On the cathode:</u>	
2H <sup>+</sup> + 2e <sup>-</sup> = H <sub>2</sub>	0.00
<u>On the anode:</u>	
Pb + SO <sup>4-</sup> = PbSO <sub>4</sub> + 2e <sup>-</sup>	-0.36
Pb <sup>2+</sup> + 2H <sub>2</sub> O = PbO <sub>2</sub> + 4H <sup>+</sup> + 2e <sup>-</sup>	1.46
Mn <sup>2+</sup> + 4H <sub>2</sub> O = MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup> + 5e <sup>-</sup>	1.51
2Cl <sup>-</sup> = Cl <sub>2</sub> + 2e <sup>-</sup>	1.36
Co <sup>2+</sup> = Co <sup>3+</sup> + e <sup>-</sup>	1.82

[0010] In order to reconcile cathode production with chemical quality, copper EW plants operate with electrical DC current density levels that oscillate, by design, around 300 A/m<sup>2</sup>, with 92-94% current efficiency, and with specific energy consumptions of 1,700-2,000 kWh/ton. Some operational variables can be manipulated externally, including the concentration of cupric ions in the solution entering the cells, the electrolyte temperature, and the electrolyte flow into the cell; these should be established in function of the imposed DC current and the desired chemical quality. The variable ranges are as follows:

- 1) Current density: 160-350 A/m<sup>2</sup>, continuous, DC,
- 2) Flow of electrolytes to cell: 240-340 l/min/cell,
- 3) Electrolyte distribution: conventional or bottom of cell/manifold,
- 4) Cathode-cathode distance: 100-120 mm,
- 5) Cathodic cycle: 5-7 days,
- 6) Temperature: 40-50° C.,
- 7) Laminated Pb—Ca—Sn anodes: 6-7.5 or 9 mm,
- 8) Permanent stainless steel cathodes: 316 L, 3-3.3 mm,
- 9) Additives: “guar-gum”, FeSO<sub>4</sub>, and CoSO<sub>4</sub>.

#### [0011] The Copper Electro-Refining (ER) Process

[0012] Copper electro-refining (ER) is an electrochemical process for obtaining high purity copper cathodes corresponding to the last stage in the treatment of sulphide copper ores.

[0013] In Chile, more than 40% of cathodic copper is obtained by ER, specifically in the Codelco Chile refineries (Chuquicamata and Salvador Divisions) and in the Ventanas electrolytic copper refinery, belonging to the company Empresa Nacional de Minería (ENAMI; National Mining Company).

[0014] This process combines the electrochemical dissolution of impure copper anodes (97-98%) with copper reduction in order to produce high purity cathodes (% Cu>99.99+).

[0015] In general, these copper refineries operate within a density current (DC) range of 200-350 A/m<sup>2</sup>, with voltage drops of 0.25-0.30 VDC. The copper concentration in the solution varies between 40 and 60 gr/lit. The sulphuric acid concentration in most ER plants fluctuates between 170 and 220 gr/lit, for electrolyte temperatures of 50-70° C. In copper refineries, the electrolyte flow generally varies between 15 and 30 (lit/min/cell).

[0016] In order to regulate the crystalline growth on the cathodes, chemical agents are added during the ER of copper. The most common additives in this process are Thiourea, glue, Avitone, and chlorhydric acid, all soluble in the acid electrolyte and dosed in concentrations on the order of ppm or gr/ton of copper produced.

[0017] The projections of most new refineries call for permanent cathode technology that can operate at high current densities (>250 A/m<sup>2</sup>). Nonetheless, these plants must maintain high operational standards in order to assure that the physical and chemical quality of the cathodes is adequate:

[0018] Good physical shape of anodes and cathodes, without loss of verticality or plenitude, and with an adequate chemical composition,

[0019] Electrolysis cells that allow good electrolyte circulation,

[0020] Adequate purification process for the solutions,

[0021] Good state of the electrical contacts between the electrodes and the equipotential bars,

[0022] Rigorous control of current leaks and short-circuits.

#### Anodic Impurities

[0023] In the copper electro-refining process, the chemical quality of the commercial cathodes is largely conditioned by the impurities in the anodes from founding. Impurities (e.g., selenium, tellurium, bismuth, antimony, arsenic, etc.) are incorporated into the electrolyte as dissolved species, colloids, or solids that remain in the solution or are gradually incorporated onto the anodic slime that is deposited at the bottom of the cell.

[0024] Under normal operating conditions, arsenic enters the electrolyte as As(III) and is oxidised to As(V) by dissolved oxygen. The affect of the As(III) present in the electrolyte on the cathodic process is not negative; rather, the arsenic prevents the formation of floating slime to the degree that it is found incorporated into the electrolyte in excess with respect to the other impurities, in particular, antimony and bismuth. The antimony on the anode normally hydrolyzes to Sb<sub>2</sub>O<sub>3</sub> and, given an excess of As(V), is able to form compounds of the type As<sub>2</sub>O<sub>5</sub>\*Sb<sub>2</sub>O<sub>3</sub>.

[0025] Both these species have been reported as colloidal types, with low densities and a clear tendency to remain suspended in the solution, constituting one of the most important sources of cathodic contamination. Other compounds reported in the literature that are likely to contaminate the copper cathode are Cu<sub>3</sub>As, 3Cu<sub>2</sub>O\*4NiO\*As<sub>2</sub>O<sub>5</sub>, and 3Cu<sub>2</sub>O\*4NiO\*Sb<sub>2</sub>O<sub>3</sub>. This last compound, denominated “kupferglimer”, does not dissolve chemically or electrochemically, and is one of the main species giving rise to floating slime.

[0026] Industrial experience indicates that the impurities found in commercial cathodes come mostly from the incorporation, by occlusion, of the anodic bar and the electrolyte and, to a much lesser degree, by the co-deposition of the electrolytes of these species.

#### Copper Cathode Reduction

[0027] The industrial process of copper cathode reduction uses a continuous electrical current and involves electrochemical reactions that take place at the electrode-solution interface over both the cathodes and anodes.

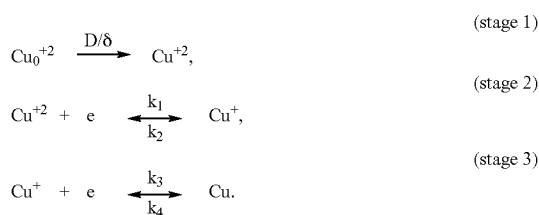
[0028] The simplest way to represent the electrode processes in an electrolysis cell is through an electrical circuit equivalent to that shown in FIG. 1. The equivalent electrical circuit considers three elements (Rs, C<sub>dc</sub>, Z<sub>f</sub>) from the cathodic and anodic sides.

[0029] The faradic impedance is proper to each electrode process. In general, it is necessary to rely on phenomenological models to characterize the kinetic or the velocity of the reaction. This is generally obtained by establishing reaction schemes.

#### Electrochemical Kinetics of the Cathodic Reaction

[0030] Whether by EW or ER of copper in industrial plants, one of the most recurrent mechanisms for characterizing the cathodic reaction of copper over a substrate of copper, titanium, or stainless steel, is the following:





[0031] In this case, 3 kinetic stages make up the reaction leading from the reactive ( $\text{Cu}^{+2}$ ) to the product (metallic Cu on the cathode): the transport of cupric ions by diffusion (stage 1) and two successive mono-electronic stages of electron transfer (stages 2 and 3).

[0032] In industrial plants operating under a stationary regimen with continuous CD current signals, the mathematical model that characterizes the reaction scheme is as follows:

$$\frac{i_f}{F} = \frac{2 * (k_2 * k_4 * e^{2*bnV} - k_1 * k_3 * [\text{Cu}_0^{+2}])}{k_2 * e^{(1+\beta_2)*bnV} + k_3 * e^{\beta_1*bnV} + \frac{k_3 * k_1}{D/\delta}}$$

where:

$k_1$ =kinetic constant of the first ionic exchange, direct, (cm/s);

$k_2$ =kinetic constant of the first ionic exchange, inverse, (cm/s);

$k_3$ =kinetic constant of the first ionic exchange, direct, (cm/s);

$k_4$ =kinetic constant of the first ionic exchange, inverse, (mol/cm<sup>2</sup>/s);

$\beta_1$  and  $\beta_2$ =charge transfer coefficients, a-dimensional;

$[\text{Cu}^{+2}_0]$ = $\text{Cu}^{+2}_0$  concentration, (g/cm<sup>3</sup>).

$$b = \frac{F}{R * T} \text{ (Volts}^{-1}\text{)}$$

where:

R=universal constant of the gases, (cal/mol/°K);

F=Faraday constant, (cb/eq);

T=absolute temperature, (°K);

V=electrode potential, (Volts);

D= $\text{Cu}^{+2}$  diffusion coefficient, (cm<sup>2</sup>/s);

$\delta$ =thickness of the limit layer, (cm);

$i_f$ =faradic current, (A/cm<sup>2</sup>).

[0033] Table 3 presents the characteristic values of the model's parameters, validated on laboratory and industrial scales, for the kinetic of the copper cathode reduction reaction. The data obtained suggest that when the cathodic

super-potential values are low (near equilibrium), the kinetic of the copper cathode reduction is controlled by a mixed regimen of charge transfer (stage 2) and diffusion (stage 1); the mechanism is typified as a slow kinetic.

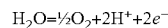
TABLE 3

Values of the constants from the copper cathode reduction model		
Constant	Numerical value	Unit of measurement
$k_1$	$3.46 * 10^{-6}$	cm/s
$k_2$	$1.42 * 10^{-8}$	cm/s
$k_3$	$5.82 * 10^{+6}$	cm/s
$k_4$	$3.49 * 10^{-2}$	mol/cm <sup>2</sup> * s
D/ $\delta$	$1.24 * 10^{-3}$	cm/s
$\beta_1$	0.5	—
$\beta_2$	0.5	—
$V_0$	+50	mV/ESH
R	1.987	cal/mol * ° K
F	96495	cb/eq

[0034] FIG. 2 shows the characteristic stationary  $i=f(V)$  of copper cathode reduction and the current imposed for industrial copper EW and/or ER operations through the point of functioning ( $V_0$ ,  $I_0$ ) on the curve  $i=f(V)$ . In order to assure that the chemical quality of the cathodes is good, this point ( $V_0$ ,  $I_0$ ) should be located in a kinetic control zone due to charge transfers, taking care with the production indicators.

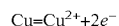
Electrochemical Kinetics of the Anodic Reaction

[0035] In the EW of Cu, the main anodic reaction is water oxidation, as indicated in Table 1. Since the oxidation of the water over the Pb—Ca—Sn anode is slow, its kinetic is controlled by the charge or electron transfer stages.



[0036] The anodic process continuously generates the movement of protons ( $\text{H}^+$ ) from the reaction interface toward the bulk. This plays a fundamental role in the electrochemical passivation behaviour of the Pb—Ca—Sn anode and, consequently, electrode breakdown by corrosion. Thus, the capacity of the anode/electrolyte interface to impede the chemical precipitation of lead sulphate (the compound responsible for the generation of passive zones on the copper electro-winning anodes) depends on the movement of the  $\text{H}^+$  ions from the electrode (where they are generated) toward the solution. Continuous current signals do not impede the accumulation of these cations produced during water oxidation, and only the concentration gradient and electrolyte temperature are responsible for generating the movement of charged species toward or from the electrode. When operating conditions are inadequate (low temperature, inadequate electro-active species concentration, electrolyte flow to a deficient cell), the  $\text{H}^+$  ions move very slowly from the reaction interface toward the bulk, where the chemical precipitation of the lead sulphate is catalyzed over the anode surface. This tends to block the surface sites from the anodic reactions, causing anodic corrosion of the Pb—Ca—Sn electrode. The resulting permanent anode corrosion takes the form of scales that are deposited at the cell bottoms, constituting “lead slime”, which should be removed every 3 or 4 months.

[0037] Otherwise, the main anodic reaction in the ER of Cu is the oxidation of the impure Cu anode that comes from founding (see Table 3). The kinetic of the slow copper oxidation is controlled by the stages of charge transfer and ion diffusion.



[0038] The oxidative process of the anode should impede the accumulation of anions and cations at the anode/electrolyte interface. This increases the possibility of a precipitation of mixed oxides (e.g., of As, Bi, Sb), as these can cause passivation of the refinery anodes, in particular when operating with elevated current densities ( $i>300 \text{ A/m}^2$ ). During copper electro-refining, it is imperative to avoid the phenomenon of anode passivation, which requires that operations in the affected cell sections be stopped, with the consequent losses of production, and metallic efficiency, and energy efficiency in the copper electro-refining process.

Operational Problems Affecting Cu Cathode Production and Quality (Current Technology)

[0039] The most important variables affecting cathode production and quality are the following:

- [0040] Imposed current,
- [0041] Electrolyte temperature,
- [0042] Concentration of ions in the electrolyte,
- [0043] Flow of electrolytes to the cell, and
- [0044] Electrochemical behaviour of the electrodes (cathodes and anodes).

[0045] In the industrial processes of Cu electrolysis, the key to increased production (given the same installed capacity) is increased current density. However, with the current cell designs and technology, indiscriminate increments in current density decrease the physical-chemical quality of the cathodes. As already indicated, copper EW and ER plants generally operate with current levels between 240 and 350  $\text{A/m}^2$ , not being able to surpass 320  $\text{A/m}^2$  in order to safeguard the quality standards of the cathodes.

[0046] An increase of current density in conventional electrolysis cells must consider the following technical and economic aspects:

- [0047] Appropriate technology for increasing the current density without experiencing a deterioration of the process control indicators, most notably the physical-chemical quality of the cathodes, current efficiency, and specific energy consumption;
- [0048] An anode material able to withstand elevated currents without experiencing significant corrosion;
- [0049] Control of the current passage through the intercell electrode/bar contact;
- [0050] Control and removal of acid mist in the EW of Cu;
- [0051] Control and removal of lead slime in the EW of Cu;
- [0052] Control of anodic passivation in the ER of Cu.

Recent Technological Developments

[0053] The most important technological developments for improved electrolysis processes in the electrometallurgy of copper from the point of view of production and cathode quality are the following:

Permanent Cathode Technology

[0054] This technology has been applied worldwide for the last 10 years in copper EW and ER plants, providing important benefits such as operating at greater current densities (up to 350  $\text{A/m}^2$  in some plants) and greater productivity indices.

Intercell Equipotential Bars

[0055] New intercell bar designs such as those used by Asturiana de Cinc in their copper EW plants (Compañía Minera Doña Inés de Collahuasi and CODELCO Norte Planta RT, Chile) have reduced voltage by up to 10 mV/cell with respect to a triangular base design. Considering the parallel-type distribution of the current in the cell electrodes, new bar designs have been patented recently by the companies "Outokumpu" (Finland) and "Optibar" (Chile). These novel designs offer greater control over the current distribution in the electrolysis cells and their inventors find that this improves the control indicators for the productive processes. It should be noted that this invention has not been applied massively in copper electrolysis plants.

Insoluble Anodes in the EW of Cu

[0056] One of the most relevant problems in the copper EW process is related to the material of the anode body and the technology and design of the electrode bar/body union. This physical union between the copper bar and the catalyzing Pb—Ca—Sn plate that makes up the anode body is the site for water oxidation. Several types of anodes have been developed that incorporate oxides of noble metals over the lead surface [ALE anodes (lead anodes covered by oxides of noble metals) and DSA anodes (titanium anodes covered by oxides of titanium and ruthenium)], in order to catalyze better the water oxidation reaction. Another development consists of the so-called MOL (mesh on lead) anodes, made by Eltechsystem Co. (USA). In DEA anodes, a Ti mesh covered by oxides of noble metals such as Ru and/or Ir is placed over the conventional plate of the Pb anode.

[0057] It should be noted that, in general, these developments have not presented encouraging results for large-scale incorporation into the productive copper EW processes due to inadequate designs, elevated costs, and poor adherence of the noble metal oxide films that catalyze the water oxidation reaction.

New Electrolysis Cells

[0058] The most relevant technological innovations in the field have recently resulted in the design of more compact cells for the electro-winning of copper. One such innovation is the EMEW process (an English abbreviation that commercially defines the integral process that encompasses cells, hydraulic systems, piping, rectifiers, electrodes, and mechanical systems for copper cathode harvesting). In the EMEW process, the electro-deposition of copper is done on closed cylindrical cells, with tubular stainless steel cathodes and DSA anodes (titanium anodes covered by titanium and ruthenium oxides). The cell operates at current densities  $>600 \text{ A/m}^2$  and has been used industrially to treat diluted  $\text{Cu}^{2+}$  solutions, resulting in cathodes of high chemical quality and no environmental pollution by acid mist.

#### Control of Acid Mist in Copper EW Plants

[0059] At current densities  $>200 \text{ A/m}^2$ , the generation of acid mist in copper electro-winning cells requires the implementation of appropriate steps for its control. Hoods or ventilated covers placed over the cell and forced air (DESOM process) have given good operational results, as has the addition of tensioactive chemical antifoam agents such as FC 1100 (3M) or small amounts of “quillay” extract ( $<5 \text{ ppm}$ ) to the electrolyte in the copper electro-winning cells.

#### Increased Operating Current in Copper EW Plants

[0060] Two main techniques have been used to increase the operating current density in the copper electro-winning plants:

[0061] Ultrasound vibration, and

[0062] Agitation through the injection of pressurized air (air sparging).

[0063] Of these alternatives, only air sparging at the limit layer of diffusion has shown possibilities for application in the electro-winning of copper, according to the test programs of electrolysis with agitation by air carried out by Kennecott and Inco, amongst others. Air sparging is being developed for larger scales and a reliable air sparging design that allows operating at densities over  $600 \text{ A/m}^2$  is expected to be available in the medium term. This technology should decrease cell voltage in 400-600 mV, with the consequent reduction in the plant's energy consumption. Nevertheless, this technological solution requires alternative anode technology, as the Pb—Ca—Sn anodes cannot withstand  $600 \text{ A/m}^2$  of continuous current density without mechanical and corrosive deterioration in the cells, to the detriment of the cathodic quality.

#### Periodic Current Inversion PRC, in Processes of the ER of Cu

[0064] This technology was developed for the processes of the ER of copper. Even though it is rarely applied in copper electrolytic refineries around the world, this unique technology requires little time for the electrode to change polarity. PRC allows the cells to operate at elevated current densities, and the inversion of the current controls the preferential growth of the cathodic deposits and avoids the formation of a-circular nodules and crystals that cause short-circuits in the electrolysis cells.

[0065] Very few copper electrolyte refineries in the world still use this technology in their plants.

#### Use of Super-Imposed DC+AC Current Signals

[0066] This type of super-imposed alternating signal at the continuous level has been used successfully in electroplating processes on sensitized surfaces of materials that are not conductive for currents (e.g., pressed circuit plates, plates for electronic components, or diverse geometric PVC bases metallized for practical and decorative uses in automobiles). These processes seek very fine, smooth electrolytic deposits of copper and chrome that are very adherent to the base surface. In fact, these processes are reported to benefit the super-imposed sinusoidal signal at the continuous level in terms of the quality of the metallic deposit by acting directly on the electrochemical double layer, although no further phenomenological explanations are given.

[0067] On the other hand, information was recently posted on-line regarding an invention patent developed in Europe that concerns the increased useful life of automobile batteries that use lead, lead dioxide, sulphuric acid, and water as principle components. The invention is supported by the development of an electronic component that, coupled to the electrical system of the automobile, allows the battery current to be fed with sinusoids during the charging process. This technology has been shown to improve the useful life of the battery considerably. Although the article does not present the phenomenology of the invention; nevertheless, it can be inferred that the sinusoid-type current signals superimposed over the continuous level allow greater regeneration of the products on the battery plates, by the action of the alternating component on the electrode phenomena.

#### Description of the Proposed Technology

[0068] The technology proposed for the present invention consists of superimposing a sinusoidal AC signal of constant frequency and amplitude over the continuous DC signal and applying this to the processes of electro-winning and electro-refining of metals, in particular copper, as shown in FIG. 3. The amplitude and frequency of the alternating signal depend on the faradic impedance of the cathodic and anodic processes described in FIG. 1.

[0069] The range of the electrical variables applied to the cathodic reduction processes of copper using conventional vs. the proposed technology is presented in Table 4.

TABLE 4

Range of electrical current applied in the cathodic reduction of copper: conventional vs. proposed technology	
Range of electrical current applied in the cathodic reduction of copper. Conventional technology	Range of electrical current applied in the cathodic reduction of copper. Proposed technology
DC: 240–400 $\text{A/m}^2$ (off-set)	DC: 240–600 $\text{A/m}^2$ (off-set) AC: 400–600 $\text{A/m}^2$ (amplitude) Frequency AC: 100 Hz–10000 Hz

#### EXAMPLES

[0070] Crystalline structures and grain morphologies are different in cathodic deposits of copper when using conventional vs. proposed technology.

[0071] The electro-deposits of cathodic copper obtained with the conventional and proposed technology were carried out in double-walled glass electrolysis cells containing the synthetic solution  $\text{Cu}^{2+}=30 \text{ gpl}$  and concentrations of sulphuric acid (180 gpl), without additives to inhibit crystalline growth. These were maintained in a double boiler at  $40^\circ \text{ C}$ . without agitation. A copper cathode and Pb—Ca—Sn anode were used. The differences in the morphology of the copper deposits and in the metalographs are presented in FIGS. 4, 5, and 6.

#### Example 1

[0072] Micrographs and metalographs of the cathodic deposits obtained in the cathodic reduction of copper with an imposed DC current level of  $400 \text{ A/m}^2$  and a sinusoidal signal of  $600 \text{ A/m}^2$  (amplitude) and 1,000 Hz (frequency).

## Comparison of Conventional and Proposed Technology

[0073] The conventional and proposed technologies were analyzed using the micrographs and metalographs of the cathodic deposits obtained under the operating conditions indicated in Table 5, maintaining the physical-chemical conditions and the instrumentation described in the experimental test procedure.

TABLE 5

	Experimental conditions	
	Conventional technology	Proposed technology
Current	DC signal	DC + AC signal
DC level	400 A/m <sup>2</sup>	400 A/m <sup>2</sup>
AC amplitude	—	600 A/m <sup>2</sup>
AC frequency	—	1,000 Hz.
Copper Deposition time	hours	10 hours
Micrographs	20X	20X
Metalographs	200X	200X

## Interpretation of the Results (Example 1)

[0074] The surface quality of the cathodic deposits obtained at 400 A/m<sup>2</sup> with the conventional DC technology is shown in FIGS. 4a and 4c, and their grain morphology in FIG. 4e. The surfaces of these cathodes are characterized by abundant spherical nodules, with preferential growth concentrated on the borders and in the centre of the deposits (FIGS. 4a, 4c). The metalographs indicate (FIG. 4e) fine grains with fibrous and disorganized growth.

[0075] On the other hand, the surface of the cathodes electro-won with DC+AC signals did not present nodules and the preferential growth disappeared, even along the cathode edges, as can be seen in FIGS. 4b and 4d. Moreover, the metalographs (FIG. 4e) indicate coarser grains, with the growth of the crystals beginning at the base of the deposits.

## Example 2

[0076] Micrographs and metalographs of the cathodic deposits obtained in the cathodic copper reduction with an imposed DC current level of 500 A/m<sup>2</sup> and a sinusoidal signal having 600 A/m<sup>2</sup> (amplitude) and 1,000 Hz (frequency).

A Comparison of the Conventional and Proposed Technologies

[0077] Again, in order to compare the two technologies (conventional vs. proposed), micrographs and metalographs were examined for cathodic deposits obtained under the operating conditions indicated in Table 6, and retaining the physical-chemical conditions and the instrumentation described in the experimental procedure of the tests.

TABLE 6

	Experimental conditions	
	Conventional technology	Proposed technology
Current	DC signal	DC + AC signal
DC level	500 A/m <sup>2</sup>	500 A/m <sup>2</sup>

TABLE 6-continued

	Experimental conditions	
	Conventional technology	Proposed technology
AC amplitude	—	600 A/m <sup>2</sup>
AC frequency	—	1,000 Hz.
Copper Deposition time	10 hours	10 hours
Micrographs	20X	20X
Metalographs	200X	200X

## Interpretation of the Results (Example 2)

[0078] The surface quality of the cathodic deposits obtained at 500 A/m<sup>2</sup> with conventional DC technology is shown in FIGS. 5a and 5c. These cathode surfaces present a greater quantity of nodules than were obtained with 400 A/m<sup>2</sup> DC. The size of the nodules is also greater and these are distributed over the entire surface of the deposits, preferentially on the borders. The metalographs (FIG. 5e) show very fine grains and highly disorganized spatial orientations characterized by abundant nucleation and little crystal growth. This reveals the generation of inter-crystalline spaces that should be occupied by the electrolyte and that result in a loss of chemical purity.

[0079] The surface of the electro-won cathodes (500 A/m<sup>2</sup> DC+600 A/m<sup>2</sup> AC; 1,000 Hz) did not present preferential growth. As described in Example 1, nodules were not formed, even when operating at greater continuous current densities (FIGS. 5b, 5d). Furthermore, the metalographs (FIG. 5e) indicate coarse grains with crystal growth oriented from the base of the deposits and an excellent inter-crystalline union that does not show the generation of interstices for electrolyte occlusion, even when operating at elevated current densities. This is one of the greatest advantages of the new technology.

[0080] The greater the crystalline disorganization, the greater the number of interstices or inter-crystalline spaces generated in the copper deposits. This increases the probability of electrolyte occlusion and, therefore, contamination with impurities from the cathode body. Increased crystalline disorganization results in increased cathode impurities and lower chemical quality, with increased penalties for the product on international markets.

## Example 3

[0081] The morphology of the copper cathode deposits obtained with super-imposed current signals.

[0082] This set of tests attempts to show the effect of the amplitude and frequency of the AC signal super-imposed over a DC current of 500 A/m<sup>2</sup>.

[0083] FIGS. 6a, 6b, and 6c show the micrographs of the cathodic deposits obtained when operating with DC+AC signals. In these three cases, an AC signal (variable amplitude between 200 and 600 A/m<sup>2</sup> and variable frequency between 5,000 Hz and 100 Hz) is super-imposed over a continuous current (DC; 500 A/m<sup>2</sup>).

[0084] When working with an AC signal (amplitude 600 A/m<sup>2</sup>, alternating signal frequency 100 Hz), the cathodic deposits obtained had the following characteristics (micrography, FIG. 6a):

[0085] abundant amounts of small-sized nodules, and

[0086] a marked copper ribbon on the cathode borders.

[0087] When working with another AC signal (amplitude 200 A/m<sup>2</sup>, frequency 5,000 Hz), the cathodic deposits obtained had the following characteristics (micrography, FIG. 6b):

[0088] no observed nodulation on the cathode surfaces, and

[0089] little preferential growth on the borders.

[0090] Finally, the last AC signal (amplitude 600 A/m<sup>2</sup>, frequency 5,000 Hz), resulted in cathodic deposits with the following characteristics (micrography, FIG. 6c):

[0091] surface with very even copper deposits and no nodules, and

[0092] no preferential growth on the borders.

[0093] This shows that, in order to improve the surface quality and the crystalline growth of the copper cathodes, it is better to use super-imposed current signals (new technology), in which the frequency of the sinusoidal signal plays a fundamental role. In all the cases studied, the need to operate with AC signals having frequencies over 1,000 Hz was demonstrated. On the other hand, it is necessary to sensitize the amplitude of the AC signal in order to obtain the best results.

#### Figure Descriptions

[0094] FIG. 1: Equivalent electrical circuit in an electrolysis cell

[0095] This circuit considers three elements ( $R_s$ ,  $C_{dc}$ ,  $Z_f$ ) from both the cathodic and anodic sides.  $C_{dc}$  corresponds to a condenser of flat plates that represents the distribution of ions in the double electrochemical layer.  $Z_f$  corresponds to the faradic impedance and represents the electrochemical reaction of the electrode.  $R_s$  represents the equivalent resistance of the inter-electrode electrolytes and  $R_c$  the contact resistances.

(A)=Anode

(C)=Cathode

(E)=Electrolyte

$R_{(C)}$ =Electrical resistance to electric contact, (ohm)

$R_{(E)}$ =Equivalent electrical resistance of the electrolyte, (ohm)

$I_c$ =Capacitive current, (A)

$I_f$ =Faradic or process current, (A)

$C_{dc}$ =Capacity of the double electrochemical layer, [uF]

$Z_{f(A)}$ =Anodic faradic impedance, (Ohm)

$Z_{f(C)}$ =Cathodic faradic impedance, (Ohm)

[0096] FIG. 2: Stationary characteristic  $i=f(V)$  of the cathodic reduction of copper.

[0097] A kinetic curve characteristic of the reduction of copper over a stainless steel cathode is presented. It can be observed that the kinetic is slow based on the equilibrium. In this curve, the coordinate pair ( $V_o, I_o$ ) stands out, equivalent to the point of stationary operations of an electrode from

a plant operating at  $I_o=300$  A/m<sup>2</sup>, and an electrochemical potential of  $V_o=+50$  mV/SHE.

[0098] FIGS. 3a and 3b: Electric current signals used in the copper EW process: conventional vs. proposed technology

[0099] FIG. 3 shows the differences between the electric signals applied in the conventional process (DC; FIG. 3a) and in the technology proposed for patenting (DC+AC; FIG. 3b).

[0100] FIG. 4: Micrographs and metalographs of the cathodic deposits obtained in the cathodic reduction of copper with an imposed DC current level of 400 A/m<sup>2</sup> and a sinusoidal signal of 600 A/m<sup>2</sup> amplitude and 1,000 Hz frequency.

[0101] A comparison of the conventional and proposed technology, according to the experimental conditions given in Example 1.

[0102] FIG. 4 presents 4 micrographs and 2 metalographs of cathode samples obtained in the experimental conditions that are explained in Example 1, with the conventional (DC current signals) and proposed technology (AC+DC current signals). The micrographs of the cathodic deposits were done with Scanning Electronic Microscopy (SEM). The experiments were repeated 10 times and are reproduced in order to compare the morphology of the cathodic deposits.

[0103] FIG. 4a: Micrography 20× Conventional technology, peripheral view of the electrode

[0104] FIG. 4b: Micrography 20× Proposed technology, peripheral view of the electrode

[0105] FIG. 4c: Micrography 20× Conventional technology, central view of the electrode

[0106] FIG. 4d: Micrography 20× Proposed technology, central view of the electrode

[0107] FIG. 4e: Metalography 200× Conventional technology

[0108] FIG. 4f: Metalography 200× Proposed technology

[0109] FIG. 5: Micrographs and metalographs of the cathodic deposits obtained in the cathodic reduction of copper with an imposed DC current level of 500 A/m<sup>2</sup> and a sinusoidal signal of 600 A/m<sup>2</sup> amplitude and 1,000 Hz frequency.

[0110] A comparison of the conventional and proposed technology under the experimental conditions given in Example 2.

[0111] FIG. 5a: Micrography 20× Conventional technology peripheral view of the electrode

[0112] FIG. 5b: Micrography 20× Proposed technology central view of the electrode

[0113] FIG. 5c: Micrography 20× Conventional technology central view of the electrode

[0114] FIG. 5d: Micrography 20× Proposed technology central view of the electrode

[0115] FIG. 5e: Metalography 200× Conventional technology

[0116] FIG. 5f: Metalography 200× Proposed technology

[0117] FIG. 6: Morphology of the cathodic deposits in the cathodic reduction of copper obtained at a DC current level of 500 A/m<sup>2</sup> and with an alternative sinusoidal signal of variable frequency and amplitude, according to the experimental conditions of the general procedure, and those in Example 3.

[0118] FIG. 6a: Micrography 20× Frequency 100 Hz, Amplitude 600 A/m<sup>2</sup>

[0119] FIG. 6b: Micrography 20× Frequency 5,000 Hz, Amplitude 200 A/m<sup>2</sup>

[0120] FIG. 6c: Micrography 20× Frequency 5.000 Hz, Amplitude 600 A/m<sup>2</sup>

[0121] FIG. 7: Experimental set-up used to carry out tests  
Example: Selection of Operational Parameters

#### Copper Concentration

[0122] In copper EW plants, the copper concentration varies between 38 gpl and 45 gpl. However, the experimental tests were done with values lower than 30 gpl. Operating at elevated current densities and at this copper concentration, the effect of using DC and DC+AC signals can be compared more clearly.

#### Acid Concentration

[0123] Normally, the acid concentration varies between 160 gpl and 190 gpl. In this case, the typical value used in the plant (180 gpl) was applied.

#### Temperature

[0124] On average, a constant temperature of 40° C. was used so as not to favour the quality of the copper deposit. It should be noted that an electrolyte at the plant enters the electrolysis cells at a minimum of 45° C., in particular for high current densities DC ( $j > 250$  A/m<sup>2</sup>).

#### Cathodic Cycle

[0125] The copper deposition time was initially set at 5 hours in order to end the experiments with 10 hours of copper electro-deposition, thereby obtaining thicker deposits for the metallographic analyses.

#### Additives

[0126] No additives were used to control the preferential growth of the copper crystals. This was done in order to compare the effect of using DC vs. DC+AC signals on the grain morphology.

#### Electrolyte Flow

[0127] The experimental tests carried out for the present invention were done without electrolyte agitation in order to focus on the crystalline growth and the electrical signals and not mass transport. Strictly speaking, the tests were batches without agitation.

#### DC and AC Current Signal Ranges

[0128] DC signals between 400 A/m<sup>2</sup> and 500 A/m<sup>2</sup> and AC signals between 25 A/m<sup>2</sup> and 600 A/m<sup>2</sup> were used.

#### AC Signal Frequency Range

[0129] The experiments were done with AC frequencies ranging between 100 mHz and 5,000 Hz.

#### Materials and Reactives

##### Reactives

[0130] Sulphuric acid H<sub>2</sub>SO<sub>4</sub>

[0131] Pentahydrated copper sulfate CuSO<sub>4</sub>\*5H<sub>2</sub>O

[0132] Distilled water

##### Cell and Accessory Equipment

[0133] Metrohm Cell

[0134] Reference electrode Ag/AgCl; Reference potential: V=+200 mV/SHE

[0135] Auxiliary electrode

[0136] Thermometer

[0137] Cables

[0138] Heater HAAKE F2 120° C.

##### Cu Test Tubes and Accessory Materials for Conditioning

[0139] Copper wire 2.91 mm diameter

[0140] Synthetic resin in cold Epofix

[0141] Fe-silicate sandpaper

[0142] Alumina

[0143] Polishing disk

##### Electro-Chemical Experiment Set-Up

##### Electro-Chemical Cell

[0144] The cell used is double-walled (Metrohm brand), which requires the recirculation of hot water to maintain the electrolyte temperature at 40° C. The set-up and connexion of the equipment are shown in FIG. 7.

[0145] In FIG. 7, the numbers indicated correspond to:

1=Metrohm cell

2=water heater

3=power source 1

4=power source 2

5=bipotentiostat

6=signal generator

7=oscilloscopy

8=adding circuit of DC+AC signals

V=voltmeter

A=amp meter

##### Electrodes Used

##### Working Electrode

[0146] A copper disk (6.65 mm<sup>2</sup>) mounted on a synthetic resin briquette was used as the working electrode; this was screwed into a conductive support in order to make the electrical connexion.

##### Auxiliary Electrode

[0147] A Pb—Ca—Sn electrode was used as the auxiliary electrode.

## Reference Electrode

[0148] In order to measure cell potential, Ag/AgCl. (Vref: 200 mV/ENH) was used as a reference electrode.

## Experimental Procedure

## Preparation of the Aqueous Solution

[0149] An aqueous solution was prepared with a concentration of 30 gpl of Cu<sup>2+</sup>. For this, 400 ml of distilled water were heated in a glass of precipitate and 117.7 g of CuSO<sub>4</sub>\*5H<sub>2</sub>O were added to this. Later, 65.5 ml of sulphuric acid at 98% were added. This solution was poured into a graduated matrass and left to repose for 2 hours to obtain exactly 1 L.

## Experimental Set-Up

[0150] FIG. 3 is a photograph of the actual set-up used in the laboratory to carry out the tests for this research. The following table details the equipment and instruments used.

TABLE

Description of the experimental set-up	
No. Equipment	Description
1	Electro-chemical double-walled cell, Metrohm
2	Signal generator: contribution for the alternative component, AC
3	Stabilized power source: contribution to the continuous level, DC
4	Additive electronic circuit box, DC + AC
5	Power source, ACM to energize operational amplifier, AOP1, of the box described in 4
6	Power source, ACM to energize the operational amplifier, AOP2, of the box described in 4
7	Water heater-recirculator
8	Multimeter Fluke, used as voltmeter
9	Multimeter Fluke, used as amperimeter

## Experimental Procedure

[0151] 1. 100 ml of electrolyte were added to the cell and heated to 40° C.

[0152] 2. The briquette was mounted with the copper disk on the conductive support later inserted into the cell.

[0153] 3. The auxiliary and reference electrodes were inserted into the cell.

[0154] 4. The electrodes were connected to the circuit.

[0155] 5. The null current potential was measured.

[0156] 6. The power source and signal generator were activated for the tests with a pound signal.

[0157] 7. The selected parameters were established.

[0158] 8. After the copper deposition time, the electrode was removed from the solution.

[0159] 9. The electrode was washed with abundant water.

[0160] 10. The electrode was dried and placed in a desiccator with silica-gel to avoid surface oxidation.

[0161] With the present invention, specifically for the electro-winning of copper, the operating variables that can be manipulated externally (e.g., concentration of cupric ions in the solution entering the cells, electrolyte temperature,

electrolyte flow to the cell) are established in function of the super-imposed DC+AC current. The chemical production and quality of the electro-won copper depend basically on the DC+AC current level imposed on the copper EW process.

[0162] For example, in the copper EW process, it is possible to operate with the solution entering the cell at temperatures below 40° C., having Cu<sup>2+</sup> concentrations lower than 30 gr/l, and with flows lower than 240 l/min/cell. The production and the chemical quality of the cathodes depend fundamentally on the amplitude and frequency of the AC current signal super-imposed over the continuous DC current ( $\geq 300$  A/m<sup>2</sup>).

## ADVANTAGES OF THE PRESENT INVENTION

[0163] 1. Operation at greater continuous current levels.

[0164] 2. Increased copper cathode production in industrial plants with the same installed capacity.

[0165] 3. Improved movement of cupric ions, protons, and other ions in the diffusion layer, toward or from the interface of the electrode/electrolyte reactions. This allows operations with lower electrolyte temperatures, consuming less energy and making the process less costly.

[0166] 4. Orderly growth of the grain structure, which assures a higher quality chemical of the electro-won and/or electro-refined cathodes. This avoids the consumption of additives ("guar-gum" for electro-winning; Thiourea and glue for electro-refining), making the process less costly.

[0167] 5. Improved surface quality of the cathodes and, consequently, decreased risk of formation and growth of nodules and entrapment of impurities. This avoids the consumption of additives ("guar-gum" for electro-winning; Thiourea and glue for electro-refining), making the process less costly.

[0168] 6. Improved transfer of hydrogen ions (H<sup>+</sup>, or protons) in copper electro-winning from the anode/electrolyte reaction interface toward the bulk of the solution, improving the behaviour of the Pb—Ca—Sn anodes in terms of their chemical stability when faced with corrosion and their operation in electrolysis cells. This allows an increased useful life of the Pb—Ca—Sn anodes operating in industrial plants. The resulting achievements avoid the consumption of cobalt sulphate, making the process less costly.

[0169] 7. Decreased production of lead slime in the cells, generating savings in cell maintenance, resulting in less contamination and a less costly process.

1. The process of the electro-winning of metals, in particular copper, is done in a strongly acidic aqueous solution (~180 gpl H<sub>2</sub>SO<sub>4</sub>), with permanent cathodes of stainless steel or Cu starting sheets, and Pb—Ca—Sn anodes, in tradition electrolysis cells to obtain copper cathodes wherein, in the electrolytic cells, a sinusoidal current is super-imposed over the continuous current in order to produce high-purity electrolytic copper.

2. The electro-refining process of metals, in particular copper, is done in a strongly acidic aqueous solution (~180 gpl H<sub>2</sub>SO<sub>4</sub>), with permanent cathodes of stainless steel or Cu starting sheets, and anodes of impure copper from founding,

in traditional electrolysis cells in order to obtain copper cathodes wherein, in the electrolytic cells, a sinusoidal current is super-imposed over the continuous current in order to produce high-purity electrolytic copper.

3. The electro-winning process, according to claim 1, wherein the sinusoidal current applied in the electrolytic cells has an amplitude greater than  $400 \text{ A/m}^2$  and a frequency greater than 1,000 Hz.

4. Electro-refining process according to claim 2, CHARACTERIZED because the sinusoidal current applied in the electrolytic cells has an amplitude greater than  $400 \text{ A/m}^2$  and a frequency greater than 1,000 Hz.

5. Electro-winning process according to claim 1, wherein the solution entering the cells operates with temperatures

lower than  $40^\circ \text{ C.}$ , with  $\text{Cu}^{2+}$  concentrations lower than 30 gr/l, and with flows lower than 240 l/min/cell when the amplitude of the frequency of the super-imposed AC current signal at the continuous current level is  $\text{DC} \geq 300 \text{ A/m}^2$ .

6. Electro-refining of copper according to claim 2, wherein the operating variables that can be manipulated externally (e.g., concentration of cupric ions in the solution exiting the cells, electrolyte temperature, electrolyte flow to the cell) are established in function of the amplitude and frequency of the AC current signal super-imposed over the continuous current level ( $\text{DC} \geq 300 \text{ A/m}^2$ ) imposed on the copper electro-refining process.

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