US 20170058414A1

(19) **United States**

(12) **Patent Application Publication**

SIMPSON ALVAREZ

(10) **Pub. No.: US 2017/0058414 A1**

(43) **Pub. Date: Mar. 2, 2017**

(54) INSERTABLE ELECTRODE DEVICE THAT DOES NOT GENERATE ACID MIST OR OTHER GASES, AND METHOD

(71) Applicants: **Victor ARAYA BORQUEZ**, Santiago (CL); **Marco CORTES PANTOJA**, Santiago (CL); **Jaime Roberto SIMPSON ALVAREZ**, Santiago (CL)

(72) Inventor: **Jaime Roberto SIMPSON ALVAREZ**, Santiago (CL)

(21) Appl. No.: **15/307,994**

(22) PCT Filed: **Apr. 24, 2015**

(86) PCT No.: **PCT/CL2015/000027**

§ 371 (c)(1),
(2) Date: **Oct. 31, 2016**

(30) **Foreign Application Priority Data**

Apr. 30, 2014 (CL) 1133-2014

Publication Classification

(51) **Int. Cl.**

C25C 7/02	(2006.01)
C25C 7/04	(2006.01)
C25C 1/12	(2006.01)

(52) **U.S. Cl.**
CPC ***C25C 7/02*** (2013.01); ***C25C 1/12*** (2013.01); ***C25C 7/04*** (2013.01)

(57) ABSTRACT

The invention relates to an insertable electrode device (DEI) for metal electrowinning processes, said device being non-polluting since it does not generate acid mist or other gases. The principle is based on an oxidation half-cell reaction occurring inside the DEI, together with the reduction half-cell that occurs in the metal electrowinning cell using same. The DEI does not generate gases and therefore does not emit acid mist into the environment. The DEI replaces current anodes and permits oxidation reactions to occur below the energy threshold of electrolysis of water, thereby preventing the electro-generation of gaseous oxygen, which is the main cause of acid mist. The DEI comprises a peripheral frame, ion exchange membranes, a strategic electrode that is a strategic semiconductor or conductor (CSE), an inlet duct and outlet duct, a horizontal conductive rod, vertical electrical conducting bars, handles or clamps, a strategic electrolyte, a distributing rod, a discharge rod, and circulation inlet holes and circulation outlet holes.

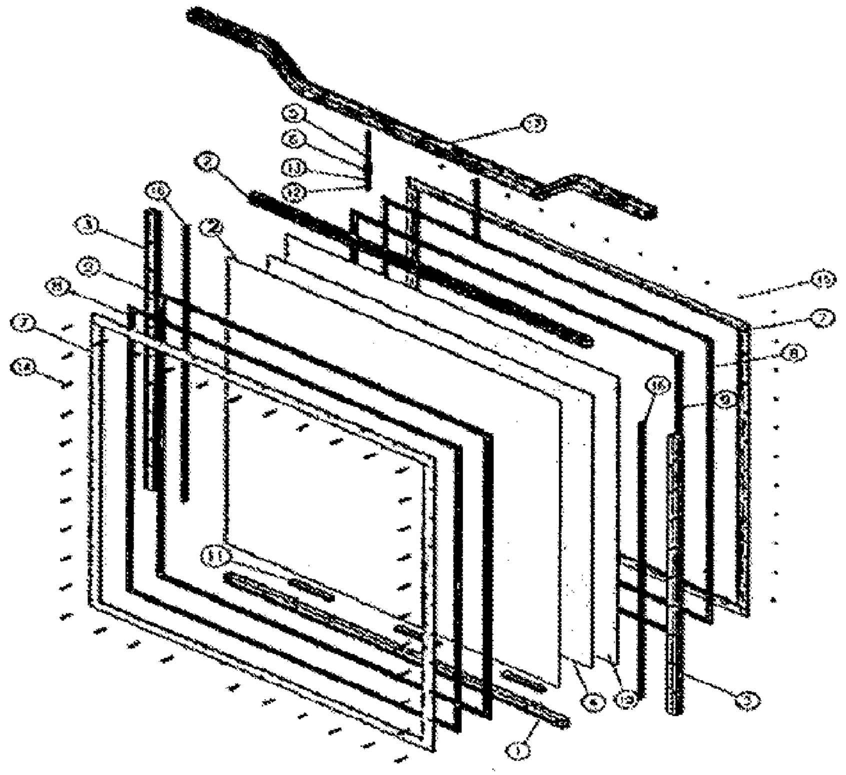


FIG. 1

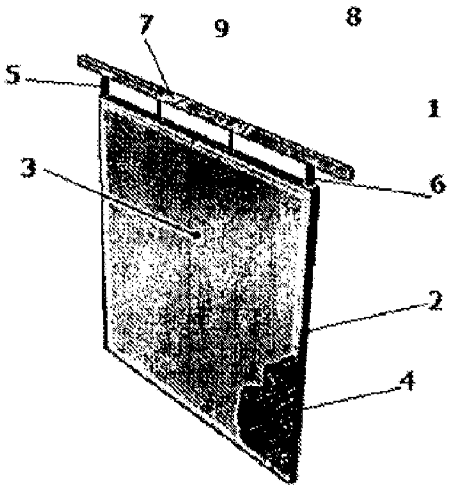


FIG. 2

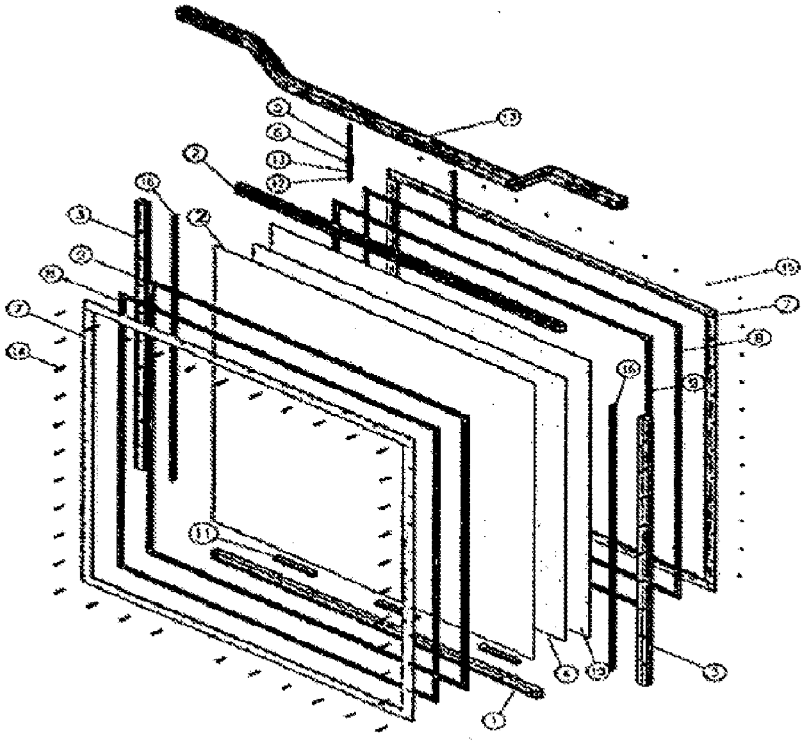


FIG. 3

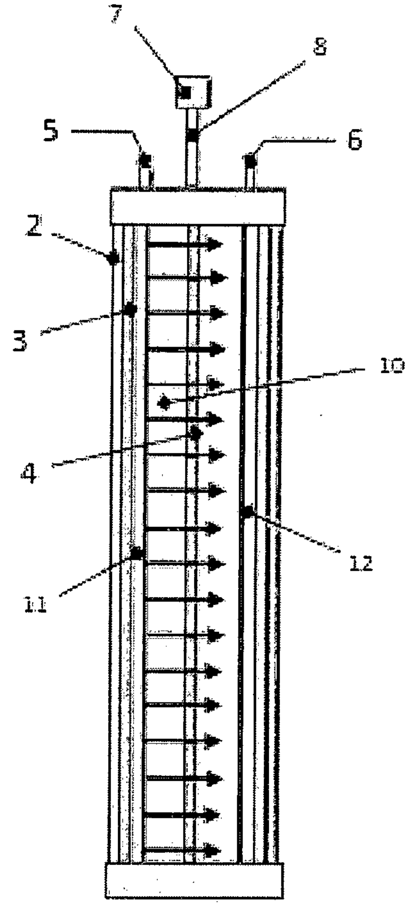


FIG. 4

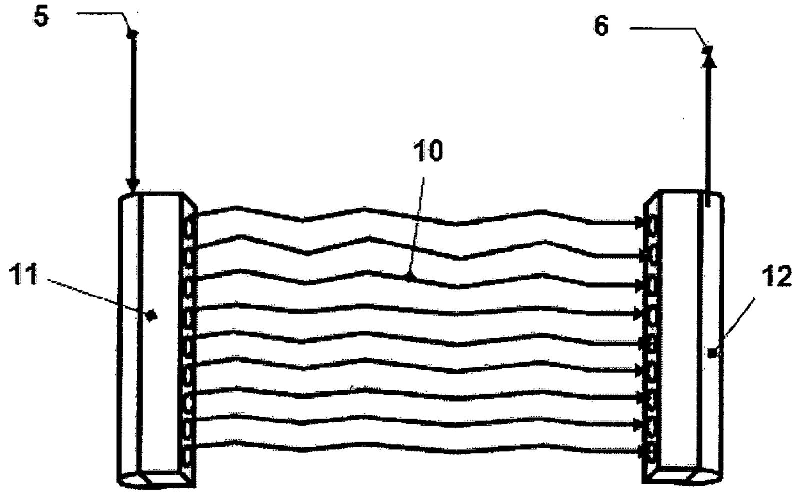


FIG. 5

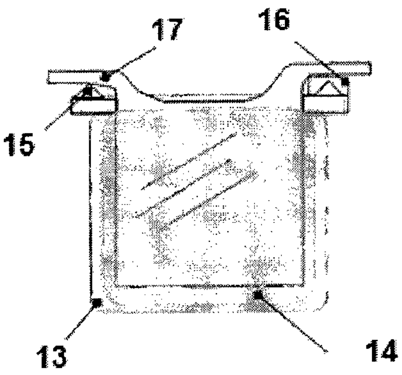


FIG. 6

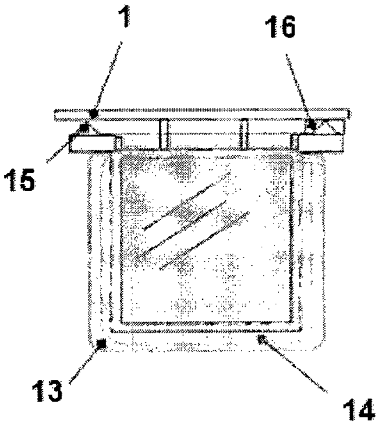


FIG. 7

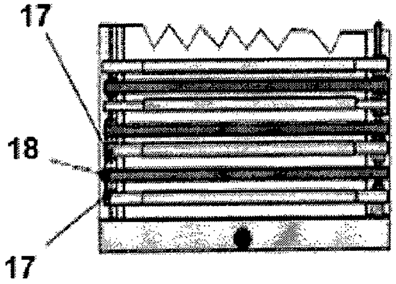
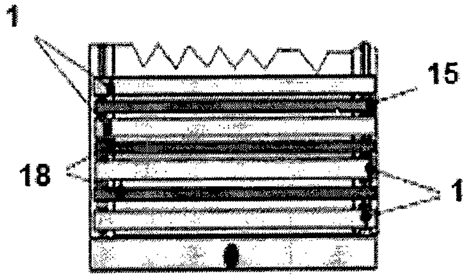


FIG. 8



INSERTABLE ELECTRODE DEVICE THAT DOES NOT GENERATE ACID MIST OR OTHER GASES, AND METHOD

FIELD OF APPLICATION

[0001] The present patent of invention discloses an insertable electrode device (IED) for metal electrowinning processes, to solve the problem of pollution generated by existing processes, as it does not generate acid mist or other gases. The principle is based on that within the (IED) an oxidation half-cell reaction occurs which is complemented with the reduction half-cell which occurs in the metal electrowinning cell that uses it. The (IED) does not generate gases and consequently no acid mist is emitted to the environment. The insertable electrode device (IED) replaces the existing anodes and permits oxidation reactions to occur below the energy threshold of the electrolytic decomposition of water, thus preventing the electro generation of gaseous oxygen, which is the main cause of acid mist.

[0002] The (IED) is designed to act as an anode in metal electrowinning processes, particularly to replace the anodic reaction corresponding to the electrolytic decomposition of water

$$\left(H_2O = 2H^+ + \frac{1}{2}O_2 + 2\overline{e}\ E_{0,25^\circ\ C.} = -1,23V_{ENH,25^\circ\ C.}\right)$$

with the oxidation of ferrous ion to ferric ion ($Fe^{2+}=Fe^{3+}+\overline{e}\ E_{0.25^\circ\ C.}=-0.77V_{ENH,25^\circ\ C.}$) or to replace any anodic reaction with a reaction of lower energy requirement and which does not generate gases of any type which are emitted to the environment in the form of acid mist.

[0003] The (IED) is an electrode device insertable as a contained monolithic unit or cartridge. The (IED) is mainly constituted by an outer polymeric framework which acts as a container, lateral membranes and solution inlet and outlet ducts within the device. Inside the (IED) a conductive or semiconductive material is included, which we will call a strategic conductor or semiconductor (SCS), which is immersed in an electrolyte with suitable ions for a particular application, which flows from the inlet ducts toward the outlet ducts.

[0004] The (SCS) inside the device is connected to an external conductive bar located on top of the container of the device. This conductive bar must be designed to withstand the weight of the container as a whole as device and to contact the (SCS) located inside with the system that carries the electric power of the plant. The width of the (IED) enables to locate it in electrolytic cells without making any modifications to the geometries industrially used.

[0005] The (IED) replaces traditional anodes used in metal electrowinning processes (mainly lead alloys or other conductive or semi conductive electrodes), i.e. as with the anodes currently used in the electrowinning processes, the (IED) is mounted in the electrolytic container contacting it with the lateral electric conductors corresponding to the positive pole and isolating the electrical contact at the negative pole, immersing it in the electrolyte containing the metal of interest usually known as rich electrolyte (RE), inside the container.

[0006] The field of application of the (IED) is in the mining industry, specifically in the process of electrowinning of metals such as copper, nickel, cadmium, gold, silver, zinc, cobalt and many more.

[0007] Today in general the electrolytic decomposition of water used and in this regard a lot of resources have been consumed in the problem of acid mist in quantification, research, control and mitigation of the problem, necessarily inviting us however to reflect on the amount of “less visible” resources such as corrosion of structures, equipment, electronic cards, damage in anodes and cathodes of the same process and, most importantly but sometimes even the more difficult to measure, the expenditure on health and safety for people, damage to the environment, increase of the carbon footprint due to poor energy efficiency, which if added to growing global environmental demands, undoubtedly takes us to conclude that electrowinning processes using the electro decomposition water as the anodic reaction should in the near future, and inexorably, cease to operate. The (IED) constitutes a solution to the prior art problem of this process.

[0008] The (IED) further allows to efficiently process solutions coming directly from leaching, without concentrating the element of interest via solvent extraction, ion exchange or activated carbon, because the membranes within do this work. That is, the (IED) can replace the systems of concentration of solutions.

[0009] It can also be applied effectively in the treatment of effluents with heavy metal content from various industries, in the electrolyte recirculation in production systems or in special electroplating treatments.

[0010] The main comparative advantage is that the (IED) of the invention can operate without emission of acid mist and therefore the problems in the facility associated with this matter (pollution, corrosion, increased consumption of water, etc.) are not present. An electrowinning cell operating with the (IED) achieves better energy efficiency with a very low specific consumption of energy compared to the conventional one and similar current efficiencies. There is no acid mist because no water is electrolytically decomposed and consequently there is a saving of water.

[0011] As an example of field of application for the case of copper, the process of electrowinning (EO) is currently carried out in rectangular concrete polymer tanks called “conventional electrolytic cells or containers” (CEC), inside of which metal plates are arranged immersed in a solution rich in copper in an acidic environment. These plates are alternately anode and cathode.

[0012] In most operations the traditional method uses permanent cathodes of 316L stainless steel ear equivalent. All the plates are electrically connected in parallel in an electrolytic cell so as to form a circuit through which a continuous electrical current is circulated from anode to cathode,

[0013] The dissolved metal, such as copper in +2 oxidation state (Cu^{2+}), migrates to the cathode which is negatively polarized, electro-depositing itself on the surface thereof as metallic copper.

[0014] Once the deposition cycle of the metal of interest ends, as of the time when cathodes without the deposition enter the cells (for example, five to seven days in the case of copper), harvesting the same takes place, these being washed and then brought to the stripping machines of the sheets of metal deposited on both sides or, in cases where powder or some special deposits occur, scraped or separated, the cathode then being used again for a new cycle.

[0015] In conventional electrolysis cells (CEC), the reaction occurring at the anode is the electrolytic decomposition of water:

$$H_2O = 2H^+ + \frac{1}{2}O_2 + 2\overline{e}.$$

Use of this anodic reaction requires a high cell voltage and consequently high power consumption. The generation of oxygen produced by the decomposition of water is the root cause of the emission of acid mist in the electrowinning building.

[0016] The so-called acid mist is caused by the electro generation of small bubbles of oxygen on the surface of the anode which emerge to the surface of the electrolyte, bursting and emitting a set of micro electrolyte particles which are spatially distributed throughout the electrolytic polluting the working environment and the environment surrounding the plant, creating risks for people, flora, fauna and the environment in general. This acid mist corrodes equipment, electrodes and structures, forcing to take operational measures to mitigate these emissions. The law requires the control of the acid concentration inside the building and has set it at 0.8 ppm/m^3 of air at sea level, but this value decreases depending on the altitude of the site, for example at 3000 meters above sea level it requires 0.53 ppm/m^3. Copper mining has high economic budgets directed to comply with existing regulations but it is quite possible that in the near future environmental requirements increase.

[0017] The problems associated with the use of the current anodic reaction include the following:

[0018] Acid mist generation

[0019] Increased water consumption

[0020] High specific consumption of energy

[0021] An energy threshold for oxidation of water

[0022] Low faradic current efficiency

[0023] Use of lead-based nodes

[0024] The (IED) applied in this case solves these problems associated with the existing procedure, not generating either gases or acid mist. The field of application is mainly in the mining industry but it is not exclusive of other applications and industrial uses.

STATE OF THE ART

[0025] Currently the procedure used for electrowinning of metals is based on the reaction of electrolytic decomposition of water, which, as it electro-generates gaseous oxygen, produces the acid mist emission to the environment and all the side effects this causes. This procedure used today shows clearly a problem of the art.

[0026] Acid mist in addition to the severe damages that it may cause to the human organism, today mitigated by the use of increasingly sophisticated PPE but also increasingly more uncomfortable for operators, does not prevent serious damage to structures, electronic equipment and machinery inside the building, as well as damages to the rest of the industrial facilities (which also affects people who work there) and surrounding communities, flora and fauna of the surroundings, by the important fraction of this mist that comes out of the electrolytic building, which could eventually contaminate water resources.

[0027] In this respect, the main problem associated with the prior art is the use of the reaction occurring on the anode surface, i.e. the electrolytic decomposition of water:

$$H_2O = 2H^+ + \frac{1}{2}O_2 + 2\overline{e}.$$

[0028] In conventional electrolytic processes, the conductive or semi conductive anode is submerged inside the electrolytic container, so that the electrolytic reactions occurring on the surface are produced with the rich electrolyte (RE), i.e. the anode and the cathode share the same electrolyte.

[0029] Application example: in the case of copper, a water molecule of the rich electrolyte ER reacts on the anode surface where the water is electrolytically decomposed to form two molecules of hydrogen ion and one molecule of gaseous oxygen, which emerges to the surface of the electrolyte contained in the electrolytic cell. There it explodes and ejects a distribution of micro drops of this electrolyte that contaminates the electrolytic house or building with acid mist. Each time this reaction occurs two electrons are released and travel through the electrical circuit negatively polarising the cathode. Cupric ions build up at the cathode, which capture these electrons producing the reduction and consequent precipitation of copper on the cathode surface. The electrical circuit closes up with the transport of ionic charges in the only electrolyte of the system, the anions moving toward the anode and the cations toward the cathode, the conductivity of the only electrolyte constituting in itself an electrical resistance of the system. Equations 1 to 6 represent these reactions on the anodic surface.

[0030] The traditional process of copper electrowinning is carried out with lead alloy anodes, DSA or RGT anodes, immersed in the electrolytic container or cell through which the (RE) circulates and anode-cathode-anode are alternately arranged, trying to maintain a minimum distance between anode and cathode but preventing electrical contact between each other to prevent short circuits. Independent of the type of conductor, the half-cell reactions that occur in this process are as follows:

[0031] Reactions on the surface of the anode (reactions are shown in the direction of oxidation):

$$\text{Main: } H_2O + 2H^+ + \frac{1}{2}O_2 + 2\overline{e} \quad E_{0,25^\circ\,C.} = -1,23V_{ENH} \tag{1}$$

$$\text{Secondary: } 2Cl^- = Cl_2 + 2\overline{e} \quad E_{0,25^\circ\,C.} = 1,36V_{ENH} \tag{2}$$

$$:\ Fe^{2+} = Fe^{3+} + \overline{e} \quad E_{0,25^\circ} = 0,77V_{ENH} \tag{3}$$

[0032] Reactions on the surface of the cathode (the reaction are shown in the direction of reduction):

$$\text{Main: } Cu^{2+} + 2\overline{e} = Cu \quad E_{0,25^\circ\,C.} = 0,34V_{ENH} \tag{4}$$

$$\text{Secondary: } Fe^{3+} + e = Fe^{2+} \quad E_{0,25^\circ\,C.} = 0,77V_{ENH} \tag{5}$$

$$\text{Global reaction: } Cu^{2+} + H_2O = Cu + 2H^+ + \frac{1}{2}O_2 \tag{6}$$

[0033] A fundamental difference offered by the (IED) is that the (IED) has external contact with the rich electrolyte (RE) through ion exchange membranes that make up the wider was of the device, unlike the conventional process in which the anode is directly in contact with (RE). In other words, the (IED) does NOT use the (RE) directly for its electro chemical reactions.

[0034] Today technological solutions have been designed to alleviate the problem of acid mist, applying the following technologies (not mutually exclusive):

[0035] Polypropylene spheres.

[0036] Forced ventilation.

[0037] Use of tensoactives.

[0038] Capture systems, extraction or washing the acid mist.

[0039] Using special epp.

[0040] Using canvas over the cells.

[0041] New technological developments in electrowinning, have been aimed at mitigating or capture the acid mist, differing mainly in the effectiveness of the measure.

[0042] None of the methods used so far in industry eliminates acid mist. However, to control that the process complies with environmental standards, the different existing technological alternatives should be combined but this increases maintenance and increases the operational complexity, thereby increasing the cost of the operation.

[0043] In the prior art, the NAM cell (Application CL/201100617) does not produce acid mist. However it is a new electrolytic cell that replaces the existing ones, unlike the (IED) which only replaces the anode, as an insertable electrode device.

[0044] The boldest developments have reached only the laboratory stage, for example the oxidation of Fe^{2+} to Fe^{3+} has been studied as anode reaction in copper EW. However, using this anodic reaction in conventional EW causes a large drop in the efficiency of the faradic current because part of the current is consumed in reducing Fe^{3+} to Fe^{2+} on the surface of the cathode and subsequently oxidized Fe^{2+} to Fe^{3+} at the anode. Using this couple is always brought up under the target of operating at higher current densities with cell voltages equivalent to the current values, i.e. never focused on eliminating the generation of gaseous oxygen, in fact from the cell voltages shown water should electro decompose parallel to the oxidation of ferrous.

[0045] The insertable electrode device (IED) replaces the existing anodes and can produce oxidation reactions below the energy threshold of the electrolytic decomposition of water, thus preventing the electro generation of gaseous oxygen which is the main cause of acid mist.

BRIEF DESCRIPTION OF THE FIGURES

[0046] FIG. **1** is an isometric view showing the main elements.

[0047] FIG. **2** is an exploded isometric view of the device (IED).

[0048] FIG. **3** is a side cutaway view showing the direction of flow.

[0049] FIG. **4** is a front cutaway view showing elements and flow.

[0050] FIG. **5** is a front cutaway view showing a conventional cell.

[0051] FIG. **6** is a front cutaway view showing the (IED) in a (CEC).

[0052] FIG. **7** is a cutaway plan view of a conventional cell (CEC).

[0053] FIG. **8** is a cutaway plan view of the (IED) as an anode in the (CEC).

DETAILED DESCRIPTION OF THE INVENTION

[0054] The insertable electrode device (IED) (**1**) of the invention is shaped and confined as a housing or cartridge acting as a container and it is a basic movable monolithic unit insertable and removable in the electrolytic cells for metal extraction.

[0055] The (IED) (**1**) allows to vary its configuration of shape and dimensions as a mobile unitary container to adapt it to the shape and dimensions of the cell in which it will be used. The (IED) (**1**) considers and allows the possibility of giving it different volumetric shapes, e.g. it can be rectangular, cylindrical and may even have special geometries as required by a given specific application.

[0056] FIG. **1** shows the cartridge or container which as a unit forms the device (IED) (**1**), which has a polymeric structure which constitutes a peripheral frame (**2**) which gives it the structural strength and ensures the water tightness of the assembly, preventing leakage of solutions from inside to outside or vice versa, wherein the peripheral frame (**2**) works in conjunction with side wails which are formed by a ion exchange membranes (**3**) located on both sides of the cartridge, wherein a strategic electrode (**4**) that is a strategic conductive or semiconductive material (SCS) is located in the inner cavity that these ion exchange membranes (**3**) form. At the top left portion of the cartridge (**1**) there is located an inlet duct (**5**) and on the right an outlet duct (**6**), wherein a horizontal conductive bar (**7**) is electrically connected with the strategic electrode (**4**), through vertical conductive bars (**8**), wherein handles or clamps (**9**) allow to insert or remove the (IED) (**1**).

[0057] FIG. **2** shows in isometric exploded view the insertable electrode device (IED) (**1**), showing that the device as cartridge is configured and confined by containment walls which are surfaces or ion exchange membranes (**3**). These membranes are supported by the peripheral frame (**2**) which includes two peripheral seals on both sides. The peripheral frame (**2**) is formed based on polymers resistant to corrosive environment, this structure allows to vary the volumetric shape as required, depending on the aqueous medium containing the metal to electro-win. It shows the horizontal conductive bar (**7**), the inlet (**5**) and outlet (**6**) ducts. It also indicates the position of the vertical conductive bars (**8**) and through which a conductive electrolyte (**10**) flows which is an electrolyte with suitable ions for a particular application, which flows from the inlet ducts (**5**) to the outlet duct (**6**).

[0058] FIG. **3** shows in side cutaway view how inside the insertable electrode device (IED) (**1**) a strategic electrode (**4**) is located which can be configured or provided with the condition of mass electrode, mesh electrode or plate electrode. The strategic electrode's materials (**4**) may be conductors or semiconductors (metals, graphite, graphene, iridium oxide coated metals, tantalum or ruthenium). It indicates the position of a distributor bar (**11**) connected to the inlet duct (**5**) and the position of a discharge bar (**12**) connected to the outlet duct (**6**) and the direction of circulation of the conductive electrolyte (**10**).

[0059] FIG. **4** shows the direction of circulation of the conductive electrolyte (**10**) wherein entry is through the inlet duct (**5**) and it is distributed perpendicular and horizontally by the distribution bar (**11**) from which circulation is towards the discharge bar (**12**) which is connected to the outlet duct (**6**), wherein both bars have circulation inlet bores or ducts (**13**) allowing passage of the conductive electrolyte (**10**). The conductive electrolyte (**10**) is called strategic electrolyte and it is an aqueous medium containing the ion pair to be used for the half cell anodic reaction and which in the case of copper will be the Fe (II)/Fe (III) couple.

[0060] The circulation of the conductive electrolyte (**10**) within the cartridge (**1**) forming the (IED) (**1**) is carried out through circulation outlet ducts (**14**), wherein the entry of the fluid is injected through the inlet connector or duct (**5**), wherein the fluid entering does it at constant pressure and descends vertically, distributing perpendicularly and horizontally on the entire inner surface of the cartridge (**1**) because of the distribution bar (**11**), the pressure of the fluid allowing it to be captured evenly by the discharge bar (**12**) to discharge it from the (IED) (**1**) through the outlet duct (**6**).

[0061] FIG. **5** shows in front cutaway view a conventional electrowinning or electrolytic cell (CEC), indicating the positive polarity connector (**15**) and the capping board (**16**) which permits to isolate the anode from the contact with negative polarity.

[0062] FIG. **6** shows in front cutaway view a conventional electrowinning or electrolytic cell (CEC) and the cartridge or device (IED) located inside. The (IED) at the top has a horizontal conductive bar (**7**) which is electrically connected with the strategic electrode (**4**) by means of vertical conductive bars (**8**) which further allow to physically hold the cartridge as a whole. The (IED) must be in electrical contact with the conductive bars with positive polarity (**15**) of the conventional cells, by means of the support of the horizontal conductive bar (**7**) of the device. This horizontal conductive bar (**7**) must rest on the capping board (**16**) that allows to electrically isolate the negative pole of the conductive bars or base (**15**) of the cells. The connection between the vertical conductive bars (**8**) and the horizontal conductive bar (**7**) is by means of a system of clamps or handles (**9**).

[0063] The (IED) remains in electrical contact with the conductive bars with positive polarity (**15**) of the conventional cells, CEC, by supporting the horizontal conductive bar (**7**) of the device. This horizontal conductive bar (**7**) must rests on the capping board (**16**) that allows to electrically isolate the negative pole of the conductive bars or base (**15**) of the cells (CEC). The connection between the vertical conductive bars (**8**) and the horizontal conductive bar (**7**) is by means of clamps or handles (**9**).

[0064] FIG. **7** shows a cutaway plan view of a conventional electrolytic cell (CEC) and the arrangement of the traditional cathode (**18**) and traditional anodes (**17**) and the conductive bars or base with positive polarity (**15**) of the cells (CEC).

[0065] FIG. **6** shows a cutaway plan view of a conventional electrolytic cell (CEC) and the arrangement of the traditional cathode (**19**) and the location of the insertable electrode device (IED) or cartridge, wherein in the case of copper electrowinning the (IED) or cartridge considers a maximum thickness for proper insertion as a device within a conventional electrolytic cell, without changing the original design of the traditional cathode (**19**), which allows variation ranges between 10 to 15 millimeters approximately between the anode (**17**) to anode (**17**) or cartridge to cartridge centers. The (IED) or cartridge acts as an insertable and removable anode inside a conventional electrowinning cell (CEC).

[0066] Procedure and Method of Operation of the IED

[0067] The insertable electrode device (IED) (**1**) replaces the existing anodes (**17**) and can produce oxidation reactions below the energy threshold of the electrolytic decomposition of water, thus avoiding the prior art problem resulting from the electro generation of gaseous oxygen which is the main cause of acid mist.

[0068] The (IED) is designed to act as an anode in metal electrowinning processes, particularly to replace the anodic reaction corresponding to the electrolytic decomposition of water

$$\left(\mathrm{H_2O} = 2\mathrm{H}^+ + \frac{1}{2}\mathrm{O}_2 + 2\overline{e} \quad E_{0,25^\circ\,C.} = -1,23V_{ENH,25^\circ\,C.}\right)$$

by oxidation of the ferrous to ferric ion ($\mathrm{Fe}^{2+}=\mathrm{Fe}^{3+}+\bar{\mathrm{e}}\ \mathrm{E}_{0.25^\circ\,C.}=-0.77\mathrm{V}_{ENH,25^\circ\,C.}$) or for replacement of any anodic reaction with a reaction or lower energy requirement and which does not generate gases of any type to be emitted to the environment as acid mist.

[0069] Inside the (IED) a conductive or semiconductive material (SCS) is included which is the strategic electrode (**4**), which is immersed in an electrolyte with suitable ions for a particular application, which flows from the inlet ducts (**5**) to the outlet ducts (**6**).

[0070] The membrane (**3**) is a polymeric material with electrically charged fixed groups inside. If the functional groups are positive, it is a cationic exchange membrane (**3**) and if the groups are negative, it corresponds to an anion exchange membrane (**3**).

[0071] The importance of the membranes (**3**) is to maintain a physical separation between the rich electrolyte (RE), which contains the metal to be recovered, and the fluid flowing into the (IED), but enabling to maintain the electrical conductivity between the (RE) and the fluid circulating inside the (IED) thanks to selective ion exchange in a single direction, from the RE into the (IED). The fluid flowing inside the (IED), of conductive properties and containing a suitable redox couple, is called strategic electrolyte (SE).

[0072] The (SCS) within the device is connected to a horizontal conductive bar (**7**) external to the (CEC), located on top of the container device. This horizontal conductive bar (**7**) must be designed to support the weight of the container as a whole as a device or cartridge and to contact the (SCS) located inside with the system that carries the electric power of the plant. The geometry of the (IED) allows to piece it in the existing industrial cells, keeping the amount of cathodes of each cell and without any changes in the geometry of the existing cells.

[0073] The (IED) or cartridge replaces traditional anodes used in metal electrowinning processes (mainly lead alloys or other conductive or semi conductive electrodes), i.e. as with the anodes currently used in the electrowinning processes, the (IED) is mounted in the electrolytic container, contacting the lateral electric conductors corresponding to the positive pole and isolating the electrical contact at the negative pole, immersed in the electrolyte containing the metal of interest usually known as rich electrolyte (RE), within the container. The walls which correspond to the membranes must remain submerged in the outer electrolyte containing the metal to be recovered.

[0074] A cathode is located between two cartridges or units of (IED), so in an electrolytic cell there will always exist n+1 cartridges (**1**) or (IED) for each n cathodes. This is very similar to the existing situation. For that reason no changes are to be made to the existing electrolytic cells nor to the electrical conductors nor to the electrical insulators. No modifications to the lifting and material displacement equipment in the electrolytic building are considered, either.

[0075] For example in the case of copper, where a solution rich in ferrous sulfate can be used as (SE), the sequence of the process will occur as follows: inside the (IED) a ferrous ion contained in the (SE) is contacted with the (SSC) located inside the (IED) housing, electrolytically reacting on the surface of the (SCS), wherein the electrolytic transformation of ferrous ion to ferric ion occurs so that the (SE) leaving the (IED) has a high content of ferric ion. The conversion reaction of ferrous ion to ferric ion involves the loss of electrons which are carried by the electrical conductors to the cathode, negatively polarizing it. The reduction of cupric ion occurs at the cathode, which captures electrons deposited as metallic copper.

[0076] When the oxidation reactions within the (IED) and the reduction of cupric ion occurs, it results in an imbalance of positive charges within the (IED) and negative charges in the ER which is offset by the selective passage of anions through the exchange membranes (**3**) from the (RE) into the (IED). In this example, the main ion that is transferred is the SO_4^{2-} ion. Here other differences appear with existing systems: the electrical conductivities involved are now the corresponding to the (RE), the conductivity in the membrane (**3**) and the conductivity in the SE, all being resistances of the system.

[0077] The reaction of ferrous ion to ferric ion occurs at an energy threshold much lower than the electrolytic decomposition of water and, because of this, it does not produce acid mist because it does not generate micro bubbles of gaseous oxygen emerging and burst at the surface of electrolyte, which are responsible for the emission of acid mist.

[0078] Reactions on the (SCS) Surface Inside the (IED):

$$\text{Main: } Fe^{2+}=Fe^{3+}+\bar{e}\ E_{0.25^\circ\ C.}=-0.77\,V_{ENH,25^\circ\ C.} \tag{7}$$

Secondary: None

[0079] Equilibrium on the Surface of the Membrane:

$$\gamma_{SO_4{}^{2-}{}_{SE}}[SO_4{}^{2-}]_{SE}=K\gamma_{SO_4{}^{2-}{}_{RE}}[SO_4{}^{2-}]_{RE} \tag{8}$$

[0080] Reactions on the Surface of the Cathode:

$$\text{Main: } Cu^{2+}+2e\bar{e}=Cu\ E_{0.25^\circ\ C.}=0.34\,V_{ENH,25^\circ\ C.} \tag{9}$$

$$\text{Secondary: } Fe^{3+}+e=Fe^{2+}\ E_{0.25^\circ}\ C.=0.77\,V_{ENH,25^\circ\ C.} \tag{10}$$

$$\text{Global Reaction: } Cu^{2+}+2Fe^{2+}=Cu+2Fe^{3+} \tag{11}$$

[0081] Mounting the (IED) to replace existing anodes does not affect the number of cathodes considered in a conventional cell. The (IED) does not consider any changes or modifications to the conductors nor the electrolytic cells which it will arranged to carry out the process; it requires the mounting of:

[0082] a recirculation tank with a heat exchanger; and

[0083] an external propelling system with respective piping for conveying the strategic electrolyte (SE) into the (IED).

[0084] The mounting procedure (IED) in a conventional cell includes the following steps:

[0085] mounting an (SE) external recirculation tank with a heat exchanger and respective piping;

[0086] de-energising the plant to perform the replacement procedure;

[0087] removing conventional anodes and conventional lead anodes from the cell to intervene;

[0088] mounting the (IED) at positions corresponding to the conventional lead anodes and interleaved between the positions of the conventional cathodes;

[0089] connecting the (SE) external recirculation piping system;

[0090] preparing (SE) solutions in the recirculation tank;

[0091] mounting cathodes in the conventional cell;

[0092] propelling the strategic electrolyte (SE) toward the (IED);

[0093] propelling the rich electrolyte (RE) in the conventional cell; energizing the electrolytic container, setting the current required by the process;

[0094] the (IED) anodes are only removed for maintenance.

[0095] It does not require any arrangement to control the acid mist, such as hoods and scrubbers which are currently used.

[0096] The (IED) allows to electro deposit metals without emitting acid mist to the working environment or the environment surrounding the facilities, so existing acid mist mitigation systems can be eliminated. However, the main objective of the (IED) is to eliminate acid mist emitted from existing electrowinning systems that apply and use the electrolytic decomposition of water, which generates micro oxygen bubbles which emerge to the surface of the electrolytes, where they break open and emit a distribution of micro droplets that pollute the environment. The (IED) eliminates the root of the problem and does not generate acid mist. The energy threshold not to electrolytically decompose water, allows to eliminate the production of gaseous chlorine.

[0097] The number of (IED) units required for a given level of production is calculated by means of Faraday's law, commonly used for these calculations and linking the production of a metal of interest with current density and area of the (IED). In the case of copper, the (IED) must be arranged in cells of 15, 30 or 60 cathodes which exist in market.

[0098] In the case of copper, the (SE) fed is a solution in sulphuric atmosphere in an acidity range between 150 to 180 g/L of sulphuric acid with a total Fe concentration in solution between 50 to 90 g/L, mostly as Fe (II). The operating temperature can be moved from room temperature to 90° C. The (SE) exiting in the (IED) contains 150 to 180 of sulphuric acid with a concentration of total Fe in solution between 50-90 g L, mostly as Fe (III). The operating temperature can be moved from room temperature to 90° C. The flow rate to each (IED) can fluctuate between 1 to 60 L/min.

[0099] The (SCS) may be a conductive or semi conductive material in the form of a plate, mesh, metallic wool or pieces of these materials filling the cavity of the cartridge (**1**), provided they have electrical contact with the top horizontal conductive bar (**7**).

[0100] The selection of the (SCS), the (SE) and the redox couple to be used as well as the most suitable ion exchange membrane (**3**) is performed by laboratory tests which consider performing linear voltammetries in a unit scalable to industrial size and tests in a scalable unit, also at the laboratory, of electrowinning tests where all metallurgical responses that may enable to properly select these materials are measured.

[0101] For example, in the case of copper, using the (SE) described above, with a (SCE) of Ti coated with iridium oxide, cell voltages values between 0.6 to 1.85 V were recorded, range in which no acid mist occurs operating with respective current densities of 250 to 600 A/m^2. These values were validated at pilot level without recording any emission of acid mist. The reactions involved in the selection correspond to those presented in equations 7 through 11.

[0102] Polymeric materials that constitute the structure bearing the (IED) and which tense the membranes must also be tested to ensure chemical resistance.

[0103] The metals that can be recovered with this new technology are zinc, copper, gold, silver, cadmium, nickel, palladium, platinum, cobalt and rhodium, whose half-cell reactions are the reduction of these ionic species to their metallic form, a reaction which necessarily occurs on the negatively polarized surface of the cathode.

[0104] The anodic reaction is any oxidation reaction that in the series of standard potentials is located above the reduction of the metal species and below the water oxidation reaction, not forming any gases. For example, the Fe (II)/Fe (III) couple.

[0105] This change is substantial, because in this way generation acid mist is avoided by the evolution of gases, as with oxygen generated in the electrolytic decomposition of water. Therefore, the anodic reaction using the (IED) technology is below the energy threshold of oxidation of water. This further allows to prevent unwanted oxidation reactions such as electro chlorine generation and preventing in this manner all the problems associated with these reactions.

[0106] According to the electrolytes currently used in the industry in the deposition of copper, that is to say in sulphuric medium, the anion to be transferred into the (IED) (crossing the membrane walls (**3**)), is the SO_4^{2-} ion. The anionic ion exchange membrane (**3**) used in the (IED) only allows the passage of anions, thus the electrolyte rich in copper and other species will keep the cations that compose the same in the same way the cations that form the anolyte. This allows the current efficiency to be very high since no undesired oxide reducing reactions of impurities occur as in the conventional process. The energy threshold will be less than the decomposition of water so the energy requirements are lower; no acid mist is generated and no chlorine oxidizes.

[0107] Having the polarized materials separated with a physical barrier, as the membranes (**3**), contact between the anode and the cathode is prevented and logically the possibility of a short circuit is removed. The lead anode does not offer a good response for couples desired to be used for the change of anodic reaction, therefore lead anodes are not used. Since no lead is used, the (IED) system does not generate anodic dregs, so it does not require stopping the operation (thus improving operational continuity) and there is no generation of hazardous solid waste. Since no removal of dregs or electric insulations is required, it is not necessary to remove them from the cell, except in very special situations.

[0108] The physical barrier of the outer frame of the IED protects the membranes and the (SCS) electrode located inside from accidental bumps when the cathodes are handled during harvesting of the deposited product.

[0109] The change of anodic reaction decreases water consumption, which is expected to drop by about half. For example, in the conventional process one mole of water, an increasingly scarce supply, is consumed for depositing 1 mole of copper. In addition, the water that must be replenished should be first treated to ensure its purity and it must be heated so as not to make sudden changes in temperature. With the addition of the IED, no water is consumed by this concept and only the water that evaporates and the equivalent of system purges must be replaced.

[0110] Less damage to the conductors and contacts is observed associated with this change of reaction, so less maintenance of these and of the plant's structures is required.

[0111] The fact that the (IED) developed is watertight inside and with few solid particles, without dregs, allows to operate with a more aggressive flow condition, improving on transfer, increasing the limiting current density and thus the operating current density, optimally maintaining the physical and chemical surface quality of the final product.

[0112] For copper operation could be performed at current densities far greater than existing processes (between 100 and 600 A/m^2), recording voltages below conventional processes (between 0.6 to 1.8 V, depending on the density of current). It should be noted that in conventional copper processes operating at 300 A/m ^{2} voltages are recorded in the order of 2.0 volts in the best case, If operation was at a density of 600 A/m^2, the cell voltage would exceed 3 volts.

[0113] Advantages of the (IED):

- **[0114]** No chlorine gas evolves.
- **[0115]** It allows an operation with higher current densities and consequently lower specific consumption of energy (in the order of 50% lower) which allows to deposit more of the metal per effective deposit area (it will take to less space, fewer cathodes, fewer cells, less impulsion).
- **[0116]** There will be lower consumption of specific energy to reach an equal current density (2100 kWh/ton in the case of copper for the conventional versus 600 kWh/ton for the (IED) to produce the same per unit of area).
- **[0117]** It produces less contamination of the cathode as it has the (SCS) within a housing.
- **[0118]** Greenhouse gases are reduced and it improves current efficiency.
- **[0119]** It does not generate PbO2 anodic dregs as in the case of most conventional copper processes.
- **[0120]** It neither produces nor is any lead contamination on the cathodes as in the case of most conventional copper processes.
- **[0121]** The problem of the manganese remains absolutely controlled.
- **[0122]** In the case of using a ferrous (SE), Fe (III) is generated, which is an essential reagent for leaching of sulfides.
- **[0123]** It improves the quality of cathodes.
- **[0124]** It can eliminate any process of concentration of solution (e.g. extraction by solvent).
- **[0125]** There are no short circuits and it is not necessary to remove dregs from the electrolytic cells.

1. Insertable electrode device (IED), which replaces the traditional anode in metal electrowinning processes, which does riot generate acid mist or other gases, wherein the IED comprises;

- a) a peripheral frame (**2**) arranged on both sides of the device in matching manner and facing each other, each supporting and stabilizing the;
- b) ion exchange membranes (**3**) formed of polymeric material and watertight, with electrically charged fixed groups, wherein contained in between such membranes is a;
- c) strategic electrode which is a strategic conductor or semiconductor SCS (**4**), wherein said elements form a monolithic unit that is the insertable electrode device IED (**1**) or cartridge, and joining of the elements that comprise it is achieved through seals and fastening means, wherein mounting is performed of an;
- d) inlet duct (**5**) and an;
- e) outlet duct (**6**), wherein both pipelines are located at the top of IED device (**1**); wherein the SCS (**4**) contained within the IED (**1**) is connected at the top horizontal portion to a;
- f) horizontal conductive bar (**7**), wherein;
- g) electrically conductive vertical bars (**8**) allow to physically hold the IED (**1**) device that is connected as a whole to a set of;
- h) handles or clamps (**9**) that permit connection between the vertical conductive bars (**8**) and the horizontal conductive bar (**7**), wherein inside the device circulates;
- i) a strategic electrolyte (**10**), which is distributed by a;
- j) distribution bar (**11**) connected to the inlet duct (**5**) and flows towards a;
- k) discharge bar (**12**) connected to the outlet duct (**6**), wherein the strategic electrolyte (**10**) enters pressurized through;
- l) circulation inlet bores (**13**) located on the distribution bar (**11**) and exits through;
- m) circulation outlet bores (**14**) located on the discharge bar (**12**).

2. Insertable electrode device (IED), which replaces the traditional anode in metal electrowinning processes, which does not generate acid mist or other gases, according to claim **1** wherein a strategic electrolyte (**10**) circulates inside the device (IED) (**1**) that is an aqueous medium containing the ion pair to be used for the anodic half-cell reaction, which in the case of copper will be the Fe (II)/Fe (III) couple.

3. Insertable electrode device (IED), which replaces the traditional anode in metal electrowinning processes, which does not generate acid mist or other gases, according to claim **1**, wherein the shape and dimensions of the device (IED) (**1**) are variable as a mobile unitary container to suit the shape and dimensions of the conventional electrolytic cell (CEC) where it will be used; wherein the device considers and allows the possibility of giving it different volumetric shapes.

4. Insertable electrode device (IED) that replaces the traditional anode in metal electrowinning processes, which does not generate acid mist or other gases, according to claim **1**, wherein the IED is of rectangular shape. insertable electrode device (IED) that replaces the traditional anode in metal electrowinning processes, which does not generate acid mist or other gases, according to claim **1**, wherein the IED is of cylindrical shape.

6. Insertable electrode device (IED) that replaces the traditional anode in metal electrowinning processes, which does not generate acid mist or other gases, according to claim **1**, wherein the IED is of a shape with special geometries as required by a given specific application.

7. Insertable electrode device (IED) that replaces the traditional anode in metal electrowinning processes, which does not generate acid mist or other gases, according to claim **1**, wherein the strategic conductor or semiconductor (SCS) (**4**) located inside the insertable electrode device (IED) (**1**) is configured with the condition of mass electrode.

8. Insertable electrode device (IED) that replaces the traditional anode in metal electrowinning processes, which does not generate acid mist or other gases, according to claim **1**, wherein the strategic conductor or semiconductor (SCS) (**4**) located inside the insertable electrode device (IED) (**1**) is a mesh electrode.

9. Insertable electrode device (IED) that replaces the traditional anode in metal electrowinning processes, which does not generate acid mist or other gases, according to claim **1**, wherein the strategic conductor or semiconductor (SCS) (**4**) located inside the insertable electrode device (IED) (**1**) it is a plate electrode.

10. Insertable electrode device (IED) that replaces the traditional anode in metal electrowinning processes, which does not generate acid mist or other gases, according to claim **1**, wherein the material of the strategic conductor or semiconductor (SCS) (**4**) can be metals, graphite, graphene, coated iridium oxide, tantalum or ruthenium metals.

11. Procedure for applying the insertable electrode device (IED) of claim **1**, wherein mounting of the (IED) comprises the following steps;

- a) discharging rich electrolyte (RE) from the conventional cells, withdrawing lead conventional cathodes and anodes;
- b) mounting the (IED) at positions corresponding to conventional lead anodes and interleaved between the positions of the conventional cathodes;
- c) connecting the piping of the (SE) external recirculation system;
- d) preparing (SE) solutions in the recirculation tank;
- e) mounting cathodes in the conventional cell;
- f) propelling the strategic electrolyte (SE) toward the (IED);
- g) propelling the rich electrolyte (RE) in the conventional cell;
- h) energizing the electrolytic container, setting the current required by the process.

* * * * *