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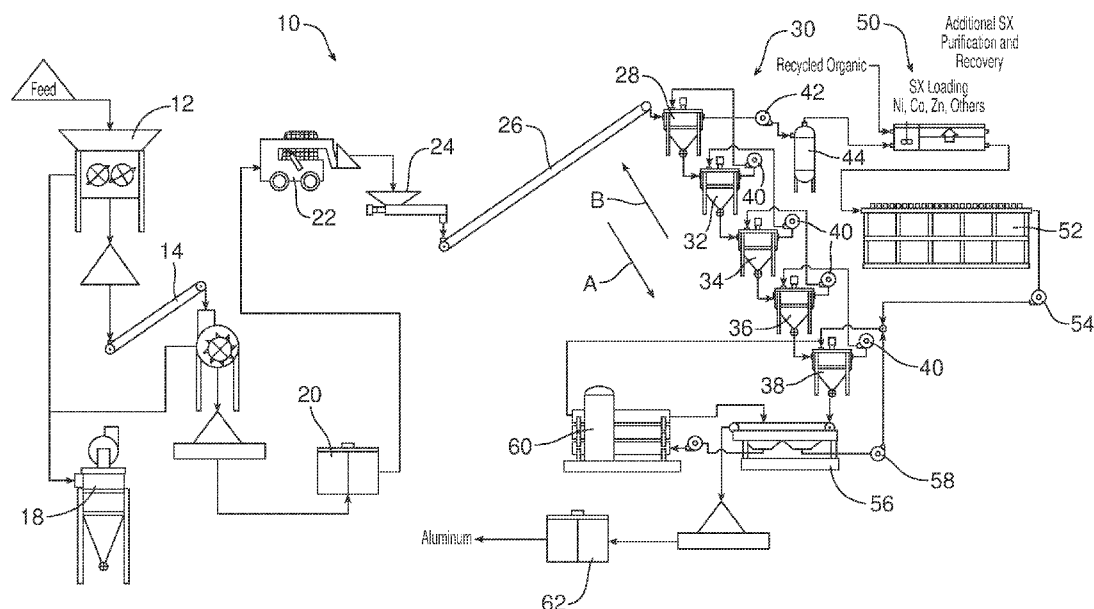
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(54) Title: EXTRACTION OF COPPER FROM A FEED MATERIAL FOR THE PRODUCTION OF METALLIC COPPER

FIG. 2



(57) Abstract: A method of recovering copper from a feed material includes steps of: leaching the feed material with a lixiviant adapted to leach the copper from a feed material feed stream in a leaching circuit having a plurality of leaching vessels V_1, V_n in series, establishing a countercurrent flow in the leaching circuit, simultaneously grinding the feed material in the feed material feed stream during the leaching in at least one of the plurality of leaching vessels and recovering the copper from the lixiviant.

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**EXTRACTION OF COPPER
FROM A FEED MATERIAL FOR THE PRODUCTION OF METALLIC COPPER**

RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application Serial No. 63/398,695, filed on August 17, 2022, which is hereby incorporated by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with government support under grant number 2044719 awarded by the National Science Foundation. The government has certain rights in the invention.

TECHNICAL FIELD

[0003] This document relates generally to the extraction of copper and other elements from feed and waste materials for the production of metallic copper and, more particularly, to a new and improved method for that purpose.

BACKGROUND

[0004] Copper is a soft, malleable and ductile metal that exhibits very high thermal and electrical conductivity. Copper has a wide range of uses, including, but not necessarily limited to

use as a conductor of heat, use as a conductor of electricity, use as a building material, use as coinage, use in marine hardware, use as a constituent of various metal alloys (e.g. brass, bronze), use in strain gauges and thermocouples for temperature measurement, and use in integrated computer chips, printed circuit boards and other electronic products.

[0005] Copper demand is increasing. As such, copper has increasing commercial value and its recovery from waste materials is increasing in importance. This document relates to a new and improved method of recovering copper from waste materials and producing copper metal.

SUMMARY

[0006] In accordance with the purposes and benefits described herein, a new and improved method is provided for recovering copper, from a feed material. That method comprises, consists of or consists essentially of: (a) leaching the feed material with a lixiviant adapted to leach the copper from a feed material feed stream in a leaching circuit having a plurality of leaching vessels V_1, V_n in series, (b) establishing a countercurrent flow in the leaching circuit by delivering the feed material feed stream to the leaching vessel V_1 and moving the feed material feed stream through the leaching circuit in a first direction toward leaching vessel V_n and delivering the lixiviant to the leaching vessel V_n and moving the lixiviant through the leaching circuit in a second direction toward leaching vessel V_1 , (c) and optionally grinding simultaneously the feed material in the feed material feed stream during the leaching in at least one of the plurality of leaching vessels, and (d) recovering the copper from the lixiviant.

[0007] In at least some embodiments of the method, the method further includes using an ammonia-based lixiviant. Still further, the method may further include using copper (II) (Cu(II)) as an oxidizer and the reagent. The method may also include conducting the leaching under anaerobic conditions. In at least some of the many possible embodiments of the method, the method includes using electrowinning in the recovering of the copper metal from the lixiviant.

[0008] In at least one particularly useful embodiment, the method includes positively applying a grinding action to the feed material in the feed material feed stream. The applying of the grinding action may be by agitating the feed material feed stream and the lixiviant in at least one leaching vessel. The applying of the grinding action may be by stirring the feed material feed stream and the lixiviant in at least one leaching vessel. The applying of the grinding action may be by rotating

at least one leaching vessel in order to tumble the feed material feed stream and the lixiviant in the at least one leaching vessel, Still further, the applying of the grinding action may be by any combination of these three approaches noted above.

[0009] The method may include providing a grinding media, adapted for grinding the feed material, in at least one leaching vessel. For purposes of this document, “grinding media” refers to any media sufficient to cause cleavage, attrition or erosion beyond what self-contacting of the feed material would produce. The method may further include selecting the grinding media from a non-limiting group of materials consisting of ceramics, stones (a non-limiting example is zircon), metals, plastics, thermoset (epoxy) resins, or heterogenous (multiphase), and combinations thereof.

[0010] In accordance with yet another aspect, the method may further include completing the electrowinning using an electrowinning cell including (a) a cathode, (b) an anode, and (c) optionally a diaphragm surrounding the cathode and defining a cathode compartment within the diaphragm. In such an embodiment, the method may include injecting pregnant leaching solution from the leaching circuit into the cathode compartment defined within the diaphragm. Still further, the method may include using a diaphragm made from a material selected from a group consisting of nylon, polypropylene or combinations thereof. In yet another embodiment, flow with the cell may be such that no diaphragm is utilized.

[0011] In accordance with yet another embodiment, the method may include completing the electrowinning using an electrowinning cell including (a) a cathode, (b) an anode, and (c) a diaphragm surrounding the anode and defining an anode compartment within the diaphragm. In such an embodiment, the method may include injecting pregnant leaching solution from the leaching circuit into a cathode compartment defined outside the diaphragm. Still further, the method may include using a diaphragm made from a material selected from a group consisting of nylon, polypropylene or combinations thereof.

[0012] In accordance with still another aspect, the method may include recovering residual electrolyte following copper leaching. More specifically, the recovering of the residual ammonia may include (a) washing the electrolyte with ammonia while preventing copper precipitation, (b) recovering the ammonia and captured copper from the remaining liquid and (c) heating the

remaining liquid to evaporate and recover residual ammonia. Ammonia washing may also be accomplished in a counter-current manner.

[0013] In accordance with yet another aspect, an ammonia recovery process may include (a) washing the electrolyte with water or steam to remove residual ammonia, (b) recovering the water and or steam and ammonia captured from the remaining solid/liquid stream and (c) heating the remaining liquid to evaporate and recover residual ammonia. Water washing may also be accomplished in a counter-current manner.

[0014] In at least one embodiment, the method includes leaching base metals other than copper from the feed material and recovering the other base metals from the lixiviant.

[0015] Embodiments of the method may include completing the electrowinning using an anode made from a first material selected from a first group consisting of stainless steel, 316 stainless steel, 316L stainless steel, titanium, platinized titanium, titanium coated with mixed metal oxide, graphite and combinations thereof and using a cathode made from a second material selected from a second group of materials consisting of stainless steel, 316 stainless steel, 316L stainless steel, titanium, platinized titanium and combinations thereof.

[0016] At least some embodiments of the method may include (a) maintaining the lixiviant at a pH of between about 5 and 13.5, (b) maintaining the current density during the electrowinning between about 50 and about 1500 A/m² to induce plating of the copper rather than the generation of copper(I) and (c) maintaining an Eh between about 0.0 and about -400 mv versus Ag/AgCL reference electrode to maintain Cu(II) as dominant Cu ion in the lixiviant.

[0017] In at least some of the many possible embodiments, the method may include (a) maintaining the lixiviant at a pH of between about 10 and 13.5, (b) maintaining the current density during the electrowinning between about 50 and about 1500 A/m² to induce plating of the copper rather than the generation of copper(I) and (c) maintaining an Eh between about 0.0 and about -400 mv versus Ag/AgCL reference electrode to maintain Cu(II) as dominant Cu ion in the lixiviant.

[0018] In the following description, there are shown and described several different embodiments of the new and improved method of recovering copper from a feed material and producing metallic copper. As it should be realized, the method is capable of other, different embodiments and its several details are capable of modification in various, obvious aspects all without departing from the method as set forth and described in the following claims. Accordingly, the drawings and descriptions should be regarded as illustrative in nature and not as restrictive.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

[0019] The accompanying drawing figures incorporated herein and forming a part of the patent specification, illustrate several aspects of the method for recovering copper from a feed material and producing metallic copper and serve to explain certain principles thereof.

[0020] Figure 1 is an Eh-pH diagram for a Cu-NH₃-H₂O system at 298°K.

[0021] Figure 2 is a schematic diagram of one possible embodiment of an apparatus for performing the method.

[0022] Figure 3 is a detailed schematic illustration of one possible design of a leaching vessel useful in the apparatus illustrated in Figure 2.

[0023] Figure 4 is a detailed schematic illustration of another possible design of a leaching vessel useful in the apparatus illustrated in Figure 2.

[0024] Figure 5 is a detailed schematic illustration of yet another possible design of a leaching vessel useful in the apparatus illustrated in Figure 2.

[0025] Figure 6 is a detailed schematic illustration of one possible embodiment of electrowinning cell useful in the apparatus of Figure 2.

[0026] Figure 7 is a detailed schematic illustration of another possible embodiment of electrowinning cell useful in the apparatus of Figure 2.

[0027] Figure 8 is a schematic illustration of one possible embodiment of a novel waste material washing circuit for the apparatus of Figure 2.

[0028] Figure 9 is a schematic illustration of one possible embodiment of an ammonia and water recovery circuit for the apparatus of Figure 2.

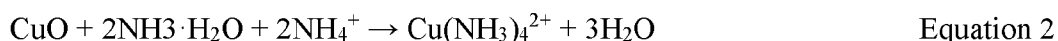
[0029] Reference will now be made in detail to the present preferred embodiments of the method, examples of which are illustrated in the accompanying drawing figures.

DETAILED DESCRIPTION

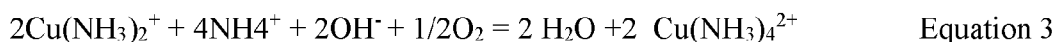
[0030] The new and improved method for recovering copper may best be understood from the following description relating to the recovery of copper and production of metallic copper from a starting or feed material. For purposes of this document, “feed material” refers to any copper bearing man-made material or naturally occurring mineral including waste materials. Non-limiting examples of man-made materials include: E-Waste, integrated computer chips, printed circuit boards, circuit boards, copper wires, copper motors, copper clad aluminum from wires or transformers, copper aluminum radiators, solar panels, fine mixed metal particles from size reduction and shredding operations, fine mixed metal particles from size separation operations, copper tubing both plumbing and for heat transfer.

[0031] Those skilled in the art will recognize that there are a number of methods suitable to provide feedstock to the process by means of pre-treatment if desired or required. Non limiting examples of pretreatment may include in part or in combination: size reduction, density separation, air density separation techniques, eddy current separation, magnetic separation, electrostatic sorting, sensor sorting, flotation, and precipitation.

[0032] The method includes the step of leaching the feed material with an ammonia-based lixiviant. In ammonia leaching, ammonia (NH₃ in forms of NH₄OH) is dissolved in water and used as the lixiviant with or without supporting ammonium salts which may include but are not limited to: (NH₄)₂SO₄, NH₄Cl, NH₄NO₃, (NH₄)₂CO₃ and NH₄HCO₃. Further, to prepare a lixiviant or for leaching, possible combinations of copper compounds such as CuSO₄, CuO, Cu₂O may be added to the lixiviant. The dominant species in a Metal-NH₃-H₂O system are NH₃, NH₄⁺, H⁺, OH⁻ and corresponding anions. The corresponding metal species are complexed with the existing NH₃ and OH⁻ ions and corresponding anions. In an embodiment, the leaching of Cu by ammonia/ammonium solution can be divided into two steps: 1) the oxidation of Cu⁰ to Cu²⁺ by oxidant such as O₂, O₂ via air, H₂O₂, or Fe³⁺, and the formation of CuO; 2) the dissolution of CuO in ammonia/ammonium solution and the generation of soluble copper-ammonia complex.



[0033] An additional oxidation mechanism may be:



[0034] In one possible embodiment for the leaching of copper with Cu(II) as an oxidizer may be accomplished by the following overall reaction, and by extension other base metals, the major reactions are described as follows:



Further written as half cell reactions the reduction of various amine species is as follows:



[0035] Metal ions which are soluble in an ammonia lixiviant of this nature may include but are not limited to: Zn, Mg, Mn, Ni, Co, Sn, Sb, Pg, Ag.

[0036] The Eh-pH diagrams (Pourbaix diagrams) of Cu-NH₃-H₂O system are referenced from the existing literature in order to better illustrate the copper speciation in ammonia/ammonium matrix as shown in Figure 1. According to this diagram, complexes of Cu⁺ and Cu²⁺ with NH₃ are

stable ionic species in neutral and alkaline solutions. In the presence of NH_3 , Cu^+ and Cu^{2+} mainly exists as $\text{Cu}(\text{NH}_3)_2^+$ and $\text{Cu}(\text{NH}_3)_4^{2+}$ in the water stability zone (between two dash lines referenced as (1) for hydrogen evolution and (2) for oxygen evolution). This result indicates that Cu can be theoretically leached out in ammonia/ammonium solution (equation 4 indicated by (4) in Figure 1) and stably remain in solution as complexes with NH_3 . Additionally, the more positive oxidation–reduction potential (ORP) of $\text{Cu}(\text{NH}_3)_4^{2+}/\text{Cu}$ than $\text{Cu}(\text{NH}_3)_2^+/\text{Cu}$ indicates that $\text{Cu}(\text{NH}_3)_4^{2+}$ can serve as an oxidant to oxidize Cu^0 to $\text{Cu}^+/\text{Cu}^{2+}$ in ammonia/ammonium alkaline solution (equation 3 indicated by (3) in Figure 1). Leaching may be accomplished as described in Published U. S. Patent Applications US 2023/0080921 and US 2023/0082450. Another embodiment may be that the liquid proceeds in a counter current manner with the solid phase remaining constant and fixed in the reactor. This is described in U. S. Patent 10,378,081 - METHODS FOR RECOVERING METALS FROM ELECTRONIC WASTE, AND RELATED SYSTEMS. In yet another embodiment the leaching may be accomplished by batch leaching in a single reactor with sufficient residence time and flow patterns that the oxidizer is consumed sufficiently for electrowinning.

[0037] Reference is now made to Figure 2, which schematically illustrates one possible apparatus 10 for conducting the new and improved method for recovering copper from a feed material. As noted above, “feed material” refers to any copper bearing man-made material or naturally occurring mineral. Non-limiting examples of man-made materials include: E-Waste, integrated computer chips, printed circuit boards, circuit boards, copper wires, copper motors, copper clad aluminum from wires or transformers, copper aluminum radiators, solar panels, fine mixed metal particles from size reduction and shredding operations, fine mixed metal particles from size separation operations, copper tubing both plumbing and for heat transfer.

[0038] As shown in Figure 2, the feed material may be fed into a coarse shredder 12 of a type known in the art to be useful for the coarse shredding of such materials. The coarse shredded feed material is then fed by a conveyor 14 or other means to a fine shredder 16 of a type known in the art for the fine shredding of such materials. In one possible embodiment, the copper bearing feed material is shredded to a size of between about 0.010 mm and about 10mm. Any dust that might be generated during the shredding process may be collected at the cyclone 18 for further processing.

[0039] Next, the fine shredded feed material discharged from the fine shredder 16 may be subjected to conditioning in an oven 20 in order to remove combustible materials. The fine shredded feed material is then transferred by a skid steer 22 or other means to a metered feeder 24 of a type known in the art to be useful for the metered feeding of such materials. The metered feed material may then be transferred by a conveyor 26 or other useful means to the first leaching vessel or unit 28 of a leaching circuit, generally designated by reference numeral 30.

[0040] In the illustrated embodiment, the first leaching circuit 30 includes a total of five leaching vessels 28, 32, 34, 36, and 38 that are connected in series and form a counter current leaching arrangement. The feed material feed stream delivered to the first unit 28 is contacted with a lixiviant in the leaching circuit. That lixiviant is particularly adapted to leach copper metal and other base metals from the feed material feed stream while leaving any noble metals behind in the treated feed material feed stream that is ultimately discharged from the leaching circuit 30.

[0041] In one particularly useful embodiment, the feed material feed stream is subjected to ammonia leaching in the leaching circuit 30 to leach the copper and the other base metals from the feed material feed stream. As noted above, ammonia leaching uses ammonium salts (NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$ or NH_4NO_3 or $(\text{NH}_4)_2\text{CO}_3$ or NH_4HCO_3) combined with ammonia (NH_3 in form of NH_4OH) dissolved in water.

[0042] As should be appreciated, the feed material feed stream travels in a first direction (note action arrow A) through the leaching circuit 30 from the first leaching vessel 28, to the second leaching vessel 32, then to the third leaching vessel 34, then to the fourth leaching vessel 36 and then finally to the fifth leaching vessel 38. The first ammonia-based lixiviant travels in a second opposite direction (note action arrow B) in a countercurrent flow to the waste material feed stream from the fifth leaching vessel 38, to the fourth leaching vessel 36, then to the third leaching vessel 34, then to the second leaching vessel 32 and then finally to the first leaching vessel 28. The various pumps 40 move the ammonia-based lixiviant through the leaching vessels 28, 32, 34, 36, 38 of the leaching circuit 30. Following leaching, the ammonia-based lixiviant, pregnant with copper and base metal ions, is transferred from the first leaching vessel 28 by the pump 42 to a filter 44 which captures any remaining particles of the leached feed material feed stream. The filtered, pregnant lixiviant is then transferred to a solvent extraction circuit 50 of a type known in

the art, that is adapted to remove and ultimately recover base metals other than copper from the lixiviant. Those other base metals include, but are not necessarily limited to nickel, chromium, silver, zinc, cobalt, lead, and the like.

[0043] The ammonia-based lixiviant, with the copper ions retained and the other base metal ions extracted, is then transferred to an electrowinning cell 52 of the type disclosed in, for example, Published U.S. Patent Application No. 2023/0082450 entitled “Electrowinning Cells for The Segregation of the Cathodic and Anodic Compartments”. There, copper metal is recovered from the ammonia-based lixiviant on the cathodes of the electrowinning cells making up the electrowinning cell 52.

[0044] During the electrowinning process, Cu^{2+} ions are generated in the lixiviant. These Cu^{2+} ions are used as an oxidant in the leaching of the copper and the other base metals from the feed material feed stream in the leaching circuit 30. The lixiviant, minus the now recovered copper metal and the Cu^{2+} ions generated during electrowinning, is returned to the leaching vessel 38 of the leaching circuit 30 by the pump 54. Preferably, the Cu^{2+} ion concentration in the lixiviant of the leaching circuit 30 is maintained between about 0.0001 M and about 1.6 M to enhance the leaching efficiency of the circuit. The Cu^{2+} ion concentration may be adjusted by controlling the rate of the metered feeding of feed material to the circuit 30, the lixiviant flow rate, between stage solid transfer rate or the electric current in the electrowinning cell.

[0045] The treated feed material feed stream is delivered from the last reactor vessel 38 of the leaching circuit 30 to a belt filter wash 56 (or other solid/liquid separators and conveyances of a type known in the art) where the majority of the lixiviant remaining on the treated waste stream is recovered and returned by the pump 58 to the unit 38 of the leaching circuit 30. A portion of the lixiviant is discharged to the reverse osmosis unit 60 to recover ammonia that is returned to the leaching unit 38. The optional oven 62 functions to remove any residual water from the remaining feed material.

[0046] The treated feed material feed stream with some remaining lixiviant, including Cu^{2+} ions, may then be transferred by conveyor or other means to a second leaching circuit (not shown) where it is contacted with a second lixiviant as described in, for example, Published U. S. Patent Application No. 2023/0080921. The Cu^{2+} ion concentration in the second lixiviant is preferably

maintained between about 0.0001 M and about 0.1 M in the second lixiviant in order to provide sufficient oxidization to efficiently leach the at least one noble metal (e.g. gold) from the treated feed material stream. If desired, additional oxidizer for leaching may be provided by sparging oxygen through the second lixiviant.

[0047] The previously described apparatus illustrated in Figure 2 is useful in a method of recovering copper from a feed material that includes steps of (a) leaching the feed material with an ammonia-based lixiviant adapted to leach the copper from a feed material feed stream in a leaching circuit having a plurality of leaching vessels V_1 , V_n in series (illustrated as vessels 28, 32, 34, 36 and 38 in the illustrated embodiment) and (b) establishing a countercurrent flow in the leaching circuit by delivering the feed material feed stream to the leaching vessel V_1 and moving the feed material feed stream through the leaching circuit in a first direction toward leaching vessel V_n and delivering the lixiviant to the leaching vessel V_n and moving the lixiviant through the leaching circuit in a second direction toward leaching vessel V_1 .

[0048] The recovery of copper powder is favored by: (a) maintaining the lixiviant at a pH of between about 5 and 13.5 and more typically at a pH of between about 10 and about 13.5, (b) maintaining the current density during electrowinning between about 50 and about 1500 A/m² to induce the plating of copper rather than the generation of copper(I) and (c) maintaining an Eh between about 0.0 and about -400 mv versus Ag/AgCL reference electrode to maintain Cu(II) as the dominant Cu ion in the lixiviant.

[0049] SIMULTANEOUS GRINDING AND LEACHING OF THE FEED MATERIAL

[0050] In accordance with an additional aspect, the method includes the step of simultaneously grinding the feed material in the feed material feed stream during the leaching in at least one of the plurality of leaching vessels 28, 32, 34, 36, 38. Toward this end, at least one of the leaching vessels 28, 32, 34, 36, 38 may be of the type illustrated in Figures 3, 4 or 5 which may be arranged in series and/or parallel, singly or in counter current, or operated with liquid only flowing in counter current to solids which remain in the vessel.

[0051] As illustrated in Figure 3, a grinding media, adapted for grinding the feed material, is provided in the leaching vessel 100. That grinding material may comprise, for non-limiting

example, ceramics, stones (a non-limiting example is zircon), metals, plastics, thermoset (epoxy) resins, or heterogenous (multiphase), and combinations thereof. The grinding material is in contact with the liquid in the leaching vessel 100 so that when the liquid is agitated or stirred using the mechanical mixer 102 (note drive motor 104, drive shaft 106 and mixing paddles 108 connected to the drive shaft), the grinding material grinds against the feed material better exposing the copper (or other metals) for more efficient leaching. In this embodiment, the drive shaft 106 is on the axis of symmetry of the cylindrical shaped vessel which also extends along a vertical axis. Agitator speeds may range from, for example about 0.001 to about 3,500 rpm.

[0052] Figure 4 illustrates an alternative embodiment wherein the leaching vessel 200 is rotated about the axis A by the drive motor 202 so that the feed material is mechanically mixed up and ground as it tumbles along the wall 204 of the vessel (note that axis A also corresponds to the axis of symmetry of the cylindrically shaped vessel 200 which rests in a horizontal plane). A grinding media, such as described above with respect to the embodiment illustrated in Figure 3, may be added to the leaching vessel 200 to enhance the grinding action provided by the tumbling. Rotation speeds may range from about 0.001 rpm to about a speed sufficient where the centrifugal force forces the materials completely against the outer wall or shell of the vessel.

[0053] The embodiment illustrated in Figure 5 is similar to the embodiment illustrated in Figure 4. In the Figure 5 embodiment, the leaching vessel 300 is also rotated about an axis A by a drive motor 302 so that the feed material is mechanically mixed up and ground as it tumbles along the continuously curved sidewall 304 of the vessel. The difference between the two embodiments is that in the Figure 5 embodiment, the grinding media is a plurality of discrete rods 306, each having a longitudinal axis substantially aligned with the axis of symmetry of the vessel, that roll along the wall 304 crushing and grinding the feed material to expose the copper for more efficient processing. Rotation speeds may range from about 0.001 rpm to about a speed sufficient where the centrifugal force forces the materials completely against the outer wall or shell of the vessel.

[0054] ALTERNATIVE ELECTROWINNING CELL GEOMETRIES

[0055] Figure 6 illustrates a first possible embodiment of an electrowinning cell geometry. As shown in Figure 6, the electrowinning cell 400 includes an anode 402, a cathode 404 and a diaphragm 406 surrounding the cathode and dividing the electrowinning cell into an anode

compartment 408 outside the diaphragm and a cathode compartment 410 inside the diaphragm. The diaphragm 406 may be made from nylon, polypropylene or other suitable membrane material adapted to manage the flow of pregnant lixiviant/electrolyte from the cathode compartment 410 to the anode compartment 408 (note action arrows). The method includes injecting the pregnant lixiviant/electrolyte with the copper ions into the cathode compartment 410 where metallic copper is recovered on the cathode 404. That lixiviant, then passes through the diaphragm 406 into the anode compartment 408 before being discharged from the cell 400.

[0056] Figure 7 illustrates another possible embodiment of an electrowinning cell geometry. As shown in Figure 7, the electrowinning cell 500 includes an anode 502, a cathode 504 and a diaphragm 506 surrounding the anode and dividing the electrowinning cell into an anode compartment 508 inside the diaphragm and a cathode compartment 510 outside the diaphragm. The diaphragm 506 may be made from nylon, polypropylene or other suitable membrane material adapted to manage the flow of pregnant lixiviant/electrolyte from the anode compartment 508 to the cathode compartment 510 (note action arrows). The method includes injecting the lixiviant/electrolyte with the copper ions into the cathode compartment 510 where metallic copper is recovered on the cathode 504. That lixiviant, then passes through the diaphragm 506 into the anode compartment 508 and then is discharged from the cell 500.

[0057] The cathode 404, 504 may be constructed from stainless steel, such as 316 stainless steel or 316L stainless steel, titanium, platinized titanium (to improve conductivity) or other appropriate material. The anode 402, 502 may be constructed from stainless steel, such as 316 stainless steel or 316L stainless steel, titanium, platinized titanium (to improve conductivity), titanium coated with mixed metal oxide, graphite or other appropriate material.

[0058] To affect the production of copper powders, the electrowinning cell 400, 500 may be operated in the following manner. 1) In a way that the current density nears the mass transport limit of the fluid conditions allowing for the production of electrolytic copper. 2) Operation of the leaching circuit in such a way that there is a significant quantity of Cu(II) reporting to EW where the current density nears the mass transport limit of the fluid conditions allowing for the production of electrolytic copper. 3) Operating the leaching circuit near the solubility point of Cu in the lixiviant and allowing a significant quantity of Cu(II) reporting to EW where the current density

nears the mass transport limit of the fluid conditions allowing for the production of electrolytic copper. In these cases, electrolytic copper can be produced. 4) Operating at high pH where at or near the solubility of Cu.

[0059] Variables of importance are concentration of copper, copper oxidation state, local fluid velocity at the cathode, and current density, and pH. Copper powders may be performed in EW cell embodiments with and without a diaphragm.

[0060] Figure 8 illustrates a novel waste material washing circuit 600. The first clarifier unit 602 shows the removal of a portion of the leaching electrolyte. The next two clarifier units 604, 606 show the addition of an ammonia wash to remove any residual copper bearing electrolyte. The reason ammonia is utilized is to prevent copper precipitation from the residual electrolyte. It is arranged countercurrent fashion to assist in washing efficiency. The next two clarifier units 608, 610 utilize steam to heat the remaining liquid to evaporate the ammonia which is captured for recovery. The residual water phase is recovered for further processing. The residual insoluble solids are thus washed of a significant portion of the lixiviant and ammonia.

[0061] Figure 9 illustrates the ammonia and water recovery circuit 700. A condenser 702 receives vapor phase fluids from several points on the process including the vent 704 from the leaching and washing stage. The condensate is an ammonia/water mixture which is recycled back to the wash stage. Other feeds to this condenser 702 will be described later. The fluid passing through the condenser 702 is then contacted with a vertical packed bed scrubber feed 706 with cold makeup water for further removal of ammonia. The remaining gases (mostly air) is then vented to the atmosphere at 708. The outflow from the adsorption column 706 is feed to a heat exchanger 710 to elevate the temperature and then further heated in an evaporator 712 to drive off the remaining ammonia which is sent back to the condenser 702 for ammonia recovery. The underflow of the evaporator 712 sends the now ammonia free water to a boiler 714. The steam is used in the waste wash process and to directly heat several streams including rinse waters and other streams containing ammonia and copper. The direct contact steam heater 716 brings a copper bearing rinse solution to near boiling, removing the ammonia which is sent to the condenser 702. The liquid phase containing copper and water has now shifted in pH which will cause the copper to precipitate. A clarifier 718 is used with the overflow sent to the heat exchanger 710 and when

cooled to the ammonia adsorption column 706. The precipitate is captured in a filter press 720 and the filtrate also sent to the heat exchanger 710 and then to the adsorption column 706. In this manner the recovery of water and ammonia is maximized.

[0062] It may be said that this document relates to the following items:

1. A method of recovering copper from a feed material, comprising:

leaching the feed material with a lixiviant adapted to leach the copper from a feed material feed stream in a leaching circuit having a plurality of leaching vessels V1, Vn in series;

establishing a countercurrent flow in the leaching circuit by delivering the feed material feed stream to the leaching vessel V1 and moving the feed material feed stream through the leaching circuit in a first direction toward leaching vessel Vn and delivering the lixiviant to the leaching vessel Vn and moving the lixiviant through the leaching circuit in a second direction toward leaching vessel V1; and

recovering the copper from the lixiviant.

2. The method of item 1, further including simultaneously grinding the feed material in the feed material feed stream during the leaching in at least one of the plurality of leaching vessels.

3. The method of item 2, further including using an ammonia-based lixiviant.

4. The method of item 3, further including using copper (II) (Cu(II)) as an oxidizer and the reagent.

5. The method of any of items 1-4, further including using electrowinning in the recovering of the copper metal from the lixiviant.

6. The method of item 5, further including conducting the leaching under anaerobic conditions to encourage generation of copper (II).

7. The method of item 5, further including applying a size reduction to the feed material prior to leaching.

8. The method of item 7, wherein the grinding is by (a) agitating the feed material feed stream and the lixiviant in the at least one leaching vessel, (b) stirring the feed material feed stream and the lixiviant in the at least one leaching vessel, (c) rotating the at least one leaching vessel in order to tumble the feed material feed stream and the lixiviant in the at least one leaching vessel or (d) all

of the above (a)-(c).

9. The method of item 8, further including providing a grinding media, adapted for grinding the feed material, in the at least one leaching vessel.

10. The method of item 9, further including selecting the grinding media from a non-limiting group of materials consisting of ceramics, stones (a non-limiting example is zircon), metals, plastics, thermoset (epoxy) resins, or heterogenous (multiphase), and combinations thereof.

11. The method of item 5, further including completing the electrowinning using an electrowinning cell including (a) a cathode, (b) an anode, and (c) a diaphragm surrounding the cathode and defining a cathode compartment within the diaphragm.

12. The method of item 11, further including injecting pregnant leaching solution from the leaching circuit into the cathode compartment defined within the diaphragm.

13. The method of item 12, further including using a diaphragm made from a material selected from a group consisting of nylon, polypropylene or combinations thereof.

14. The method of item 5, further including completing the electrowinning using an electrowinning cell including (a) a cathode, (b) an anode, and (c) a diaphragm surrounding the anode and defining an anode compartment within the diaphragm.

15. The method of item 14, further including injecting pregnant leaching solution from the leaching circuit into a cathode compartment defined outside the diaphragm.

16. The method of item 15, further including using a diaphragm made from a material selected from a group consisting of nylon, polypropylene or combinations thereof.

17. The method of item 5 including recovering residual copper from electrolyte discharged following the electrowinning.

18. The method of item 17, wherein the recovering of the residual ammonia includes (a) washing the electrolyte with ammonia in countercurrent fashion while preventing copper precipitation, (b) recovering the ammonia and captured copper from remaining liquid and (c) heating the remaining

liquid to evaporate and recover residual ammonia.

19. The method of item 5, further including treating vapor phase fluids generated during the method in an ammonia and water recovery circuit including a condenser, an absorber, an evaporator and a boiler.

20. The method of item 19, including condensing ammonia vapor in the condenser.

21. The method of item 20, including contacting fluids discharged from the condenser with cooling water in the absorber whereby ammonia is absorbed in the water and treated gas is discharged to atmosphere.

22. The method of item 21, including heating outflow from the absorber in the evaporator to drive off remaining ammonia that is returned to the condenser and discharging underflow of ammonia-free water to the boiler.

23. The method of item 22, including boiling the ammonia-free water received from the evaporator and using that steam to heat other streams used during the method.

24. The method of item 5, further including leaching base metals other than copper from the feed material and recovering the other base metals from the lixiviant.

25. The method of item 5, including completing the electrowinning using an anode made from a first material selected from a first group consisting of stainless steel, 316 stainless steel, 316L stainless steel, titanium, platinized titanium, titanium coated with mixed metal oxide, graphite and combinations thereof and using a cathode made from a second material selected from a second group of materials consisting of stainless steel, 316 stainless steel, 316L stainless steel, titanium, platinized titanium and combinations thereof.

26. The method of item 5, including (a) maintaining the lixiviant at a pH of between about 5 and 13.5, (b) maintaining the current density during the electrowinning between about 50 and about 1500 A/m² to induce plating of the copper rather than the generation of copper(I) and (c) maintaining an Eh between about 0.0 and about -400 mv versus Ag/AgCL reference electrode to maintain Cu(II) as dominant Cu ion in the lixiviant.

27. The method of item 5, including (a) maintaining the lixiviant at a pH of between about 10 and 13.5, (b) maintaining the current density during the electrowinning between about 50 and about 1500 A/m² to induce plating of the copper rather than the generation of copper(I) and (c) maintaining an Eh between about 0.0 and about -400 mv versus Ag/AgCL reference electrode to maintain Cu(II) as dominant Cu ion in the lixiviant.

[0063] Each of the following terms written in singular grammatical form: “a”, “an”, and “the”, as used herein, means “at least one”, or “one or more”. Use of the phrase “One or more” herein does not alter this intended meaning of “a”, “an”, or “the”. Accordingly, the terms “a”, “an”, and “the”, as used herein, may also refer to, and encompass, a plurality of the stated entity or object, unless otherwise specifically defined or stated herein, or, unless the context clearly dictates otherwise. For example, the phrase: “a lixiviant”, as used herein, may also refer to, and encompass, a plurality of lixiviants.

[0064] Each of the following terms: “includes”, “including”, “has”, “having”, “comprises”, and “comprising”, and, their linguistic / grammatical variants, derivatives, or/and conjugates, as used herein, means “including, but not limited to”, and is to be taken as specifying the stated component(s), feature(s), characteristic(s), parameter(s), integer(s), or step(s), and does not preclude addition of one or more additional component(s), feature(s), characteristic(s), parameter(s), integer(s), step(s), or groups thereof.

[0065] The phrase “consisting of”, as used herein, is closed-ended and excludes any element, step, or ingredient not specifically mentioned. The phrase “consisting essentially of”, as used herein, is a semi-closed term indicating that an item is limited to the components specified and those that do not materially affect the basic and novel characteristic(s) of what is specified.

[0066] Terms of approximation, such as the terms about, substantially, approximately, etc., as used herein, refers to $\pm 10\%$ of the stated numerical value.

[0067] Although the method of this disclosure has been illustratively described and presented by way of specific exemplary embodiments, and examples thereof, it is evident that many alternatives, modifications, or/and variations, thereof, will be apparent to those skilled in the art.

Accordingly, it is intended that all such alternatives, modifications, or/and variations, fall within the spirit of, and are encompassed by, the broad scope of the appended claims.

What is claimed:

1. A method of recovering copper from a feed material, comprising:
 - leaching the feed material with a lixiviant adapted to leach the copper from a feed material feed stream in a leaching circuit having a plurality of leaching vessels V_1 , V_n in series;
 - establishing a countercurrent flow in the leaching circuit by delivering the feed material feed stream to the leaching vessel V_1 and moving the feed material feed stream through the leaching circuit in a first direction toward leaching vessel V_n and delivering the lixiviant to the leaching vessel V_n and moving the lixiviant through the leaching circuit in a second direction toward leaching vessel V_1 ; and
 - recovering the copper from the lixiviant.
2. The method of claim 1, further including simultaneously grinding the feed material in the feed material feed stream during the leaching in at least one of the plurality of leaching vessels.
3. The method of claim 2, further including using an ammonia-based lixiviant.
4. The method of claim 3, further including using copper (II) (Cu(II)) as an oxidizer and the reagent.
5. The method of any of claims 1-4, further including using electrowinning in the recovering of the copper metal from the lixiviant.
6. The method of claim 5, further including conducting the leaching under anaerobic conditions to encourage generation of copper (II).
7. The method of claim 5, further including applying a size reduction to the feed material prior to leaching.
8. The method of claim 7, wherein the grinding is by (a) agitating the feed material feed stream and the lixiviant in the at least one leaching vessel, (b) stirring the feed material feed stream and the lixiviant in the at least one leaching vessel, (c) rotating the at least one leaching vessel in order to tumble the feed material feed stream and the lixiviant in the at least one leaching vessel or (d) all of the above (a)-(c).

9. The method of claim 8, further including providing a grinding media, adapted for grinding the feed material, in the at least one leaching vessel.
10. The method of claim 9, further including selecting the grinding media from a non-limiting group of materials consisting of ceramics, stones (a non-limiting example is zircon), metals, plastics, thermoset (epoxy) resins, or heterogenous (multiphase), and combinations thereof.
11. The method of claim 5, further including completing the electrowinning using an electrowinning cell including (a) a cathode, (b) an anode, and (c) a diaphragm surrounding the cathode and defining a cathode compartment within the diaphragm.
12. The method of claim 11, further including injecting pregnant leaching solution from the leaching circuit into the cathode compartment defined within the diaphragm.
13. The method of claim 12, further including using a diaphragm made from a material selected from a group consisting of nylon, polypropylene or combinations thereof.
14. The method of claim 5, further including completing the electrowinning using an electrowinning cell including (a) a cathode, (b) an anode, and (c) a diaphragm surrounding the anode and defining an anode compartment within the diaphragm.
15. The method of claim 14, further including injecting pregnant leaching solution from the leaching circuit into a cathode compartment defined outside the diaphragm.
16. The method of claim 15, further including using a diaphragm made from a material selected from a group consisting of nylon, polypropylene or combinations thereof.
17. The method of claim 5 including recovering residual copper from electrolyte discharged following the electrowinning.
18. The method of claim 17, wherein the recovering of the residual ammonia includes (a) washing the electrolyte with ammonia in countercurrent fashion while preventing copper precipitation, (b) recovering the ammonia and captured copper from remaining liquid and (c) heating the remaining liquid to evaporate and recover residual ammonia.

19. The method of claim 5, further including treating vapor phase fluids generated during the method in an ammonia and water recovery circuit including a condenser, an absorber, an evaporator and a boiler.
20. The method of claim 19, including condensing ammonia vapor in the condenser.
21. The method of claim 20, including contacting fluids discharged from the condenser with cooling water in the absorber whereby ammonia is absorbed in the water and treated gas is discharged to atmosphere.
22. The method of claim 21, including heating outflow from the absorber in the evaporator to drive off remaining ammonia that is returned to the condenser and discharging underflow of ammonia-free water to the boiler.
23. The method of claim 22, including boiling the ammonia-free water received from the evaporator and using that steam to heat other streams used during the method.
24. The method of claim 5, further including leaching base metals other than copper from the feed material and recovering the other base metals from the lixiviant.
25. The method of claim 5, including completing the electrowinning using an anode made from a first material selected from a first group consisting of stainless steel, 316 stainless steel, 316L stainless steel, titanium, platinized titanium, titanium coated with mixed metal oxide, graphite and combinations thereof and using a cathode made from a second material selected from a second group of materials consisting of stainless steel, 316 stainless steel, 316L stainless steel, titanium, platinized titanium and combinations thereof.
26. The method of claim 5, including (a) maintaining the lixiviant at a pH of between about 5 and 13.5, (b) maintaining the current density during the electrowinning between about 50 and about 1500 A/m² to induce plating of the copper rather than the generation of copper(I) and (c) maintaining an Eh between about 0.0 and about -400 mv versus Ag/AgCL reference electrode to maintain Cu(II) as dominant Cu ion in the lixiviant.
27. The method of claim 5, including (a) maintaining the lixiviant at a pH of between about 10 and 13.5, (b) maintaining the current density during the electrowinning between about 50 and

about 1500 A/m² to induce plating of the copper rather than the generation of copper(I) and (c) maintaining an Eh between about 0.0 and about -400 mv versus Ag/AgCL reference electrode to maintain Cu(II) as dominant Cu ion in the lixiviant.

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FIG. 1

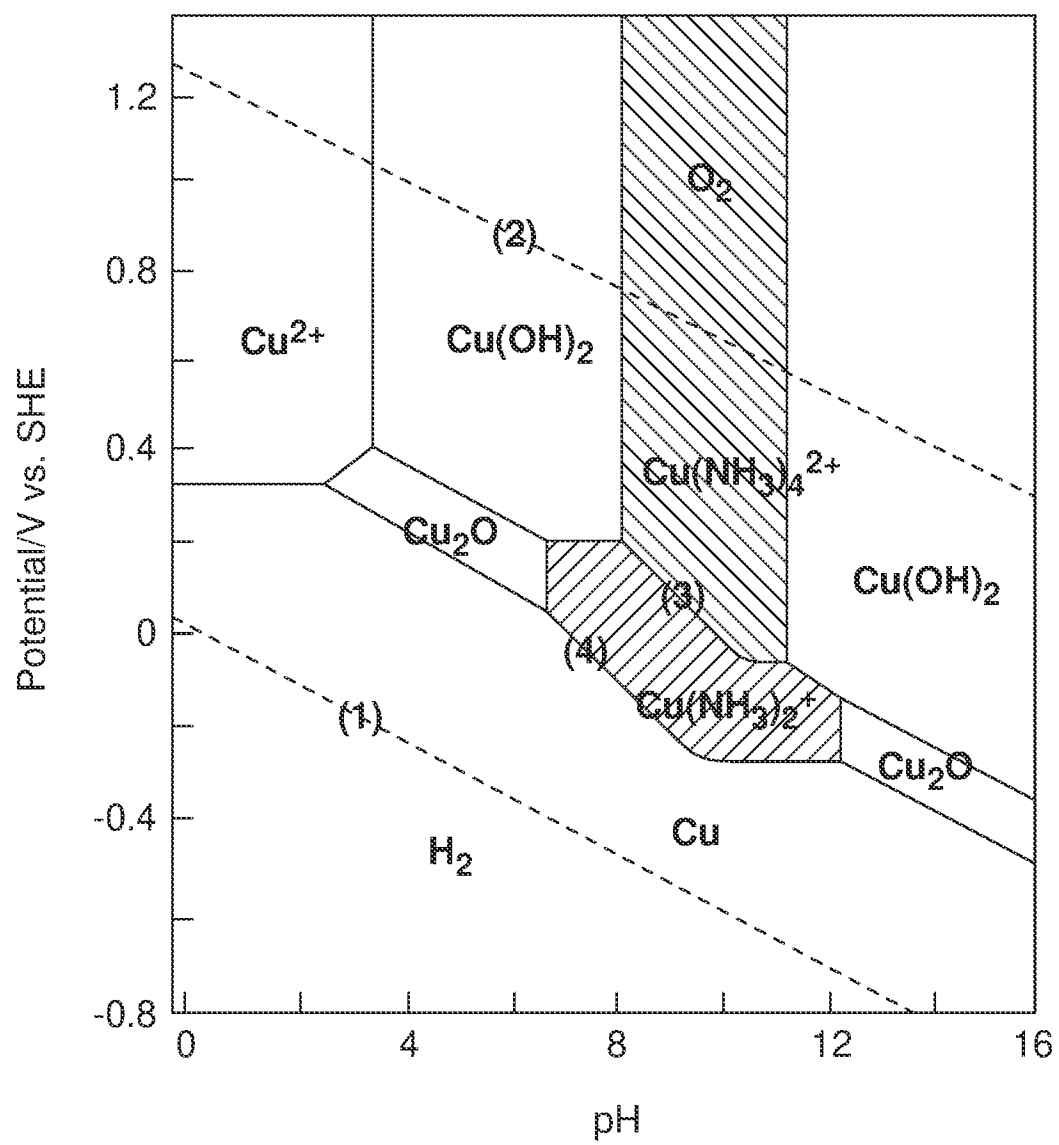


FIG. 2

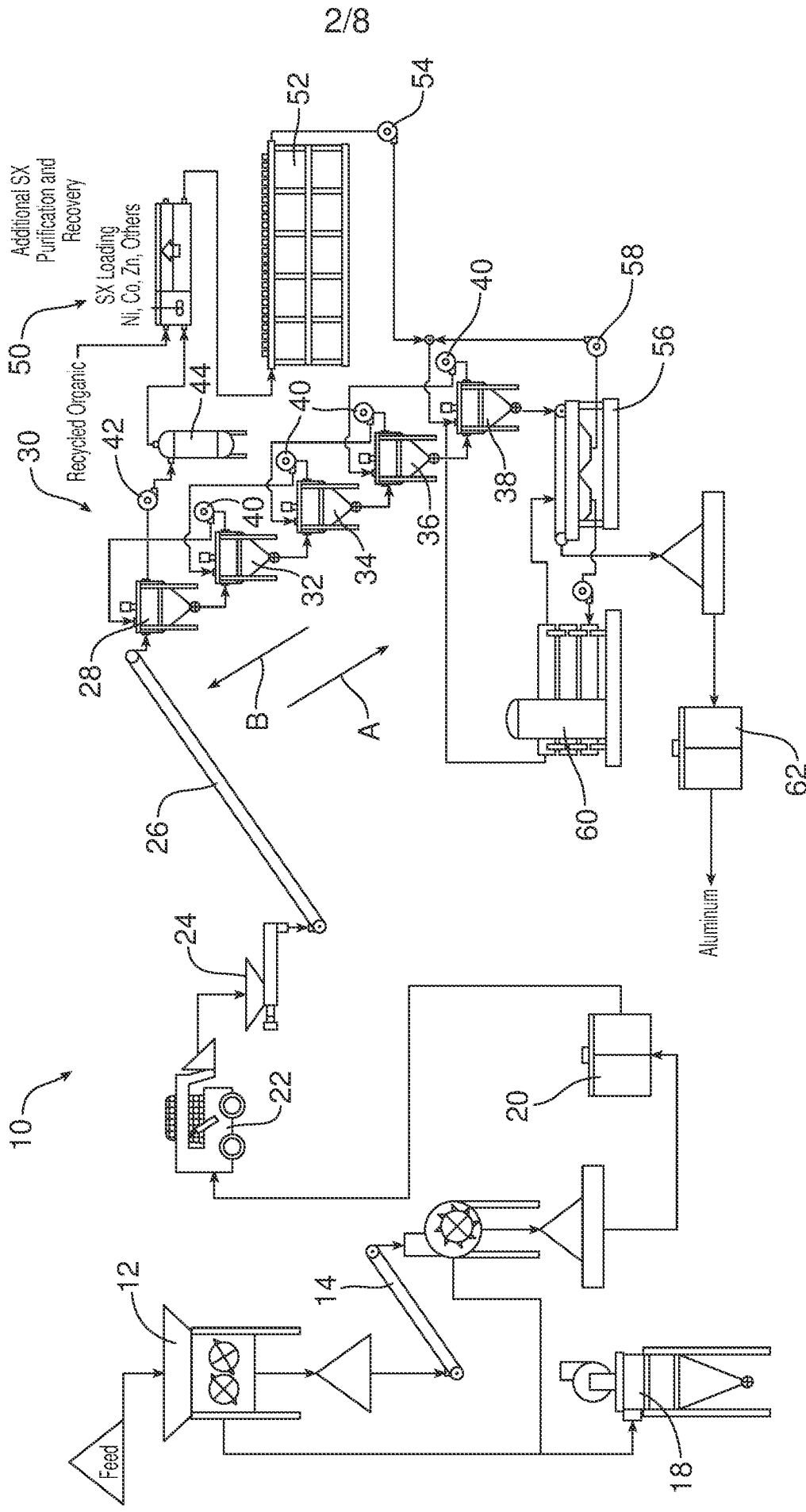
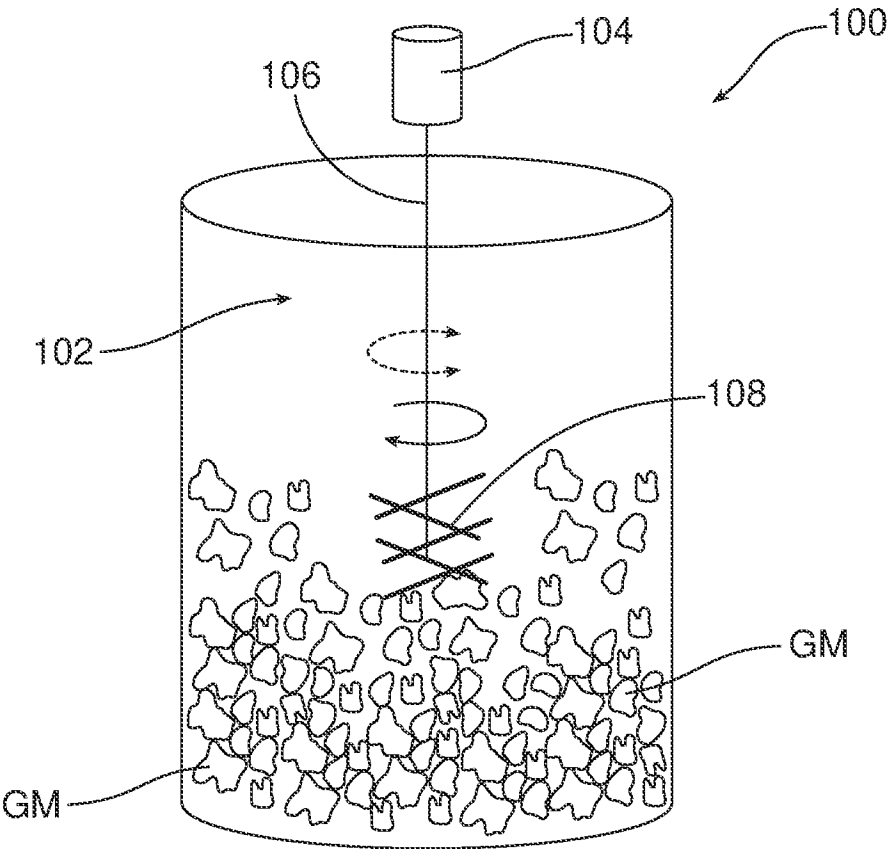


FIG. 3



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FIG. 4

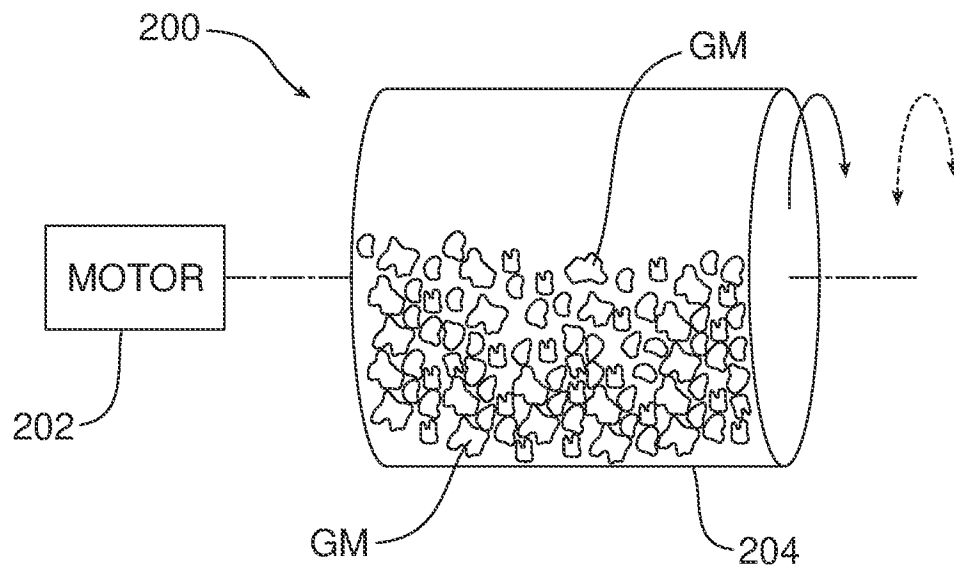


FIG. 5

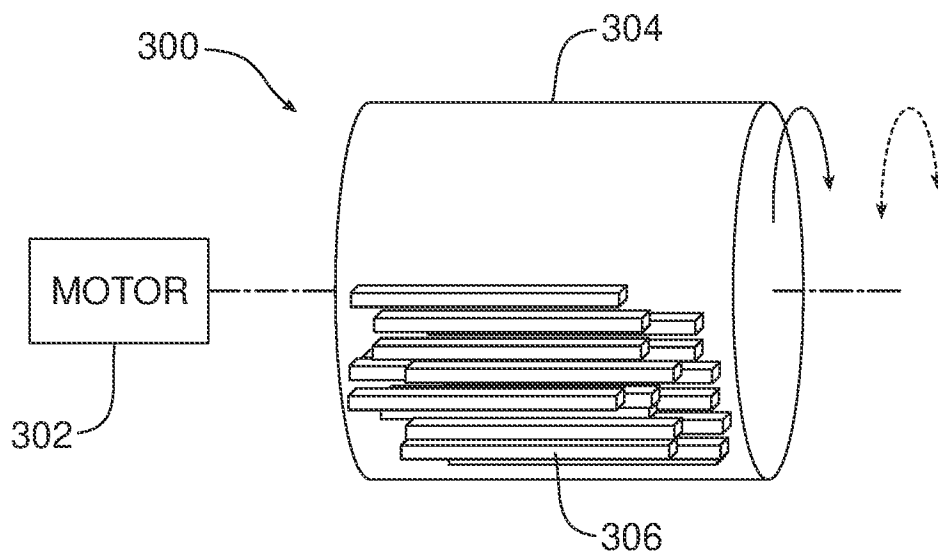


FIG. 6

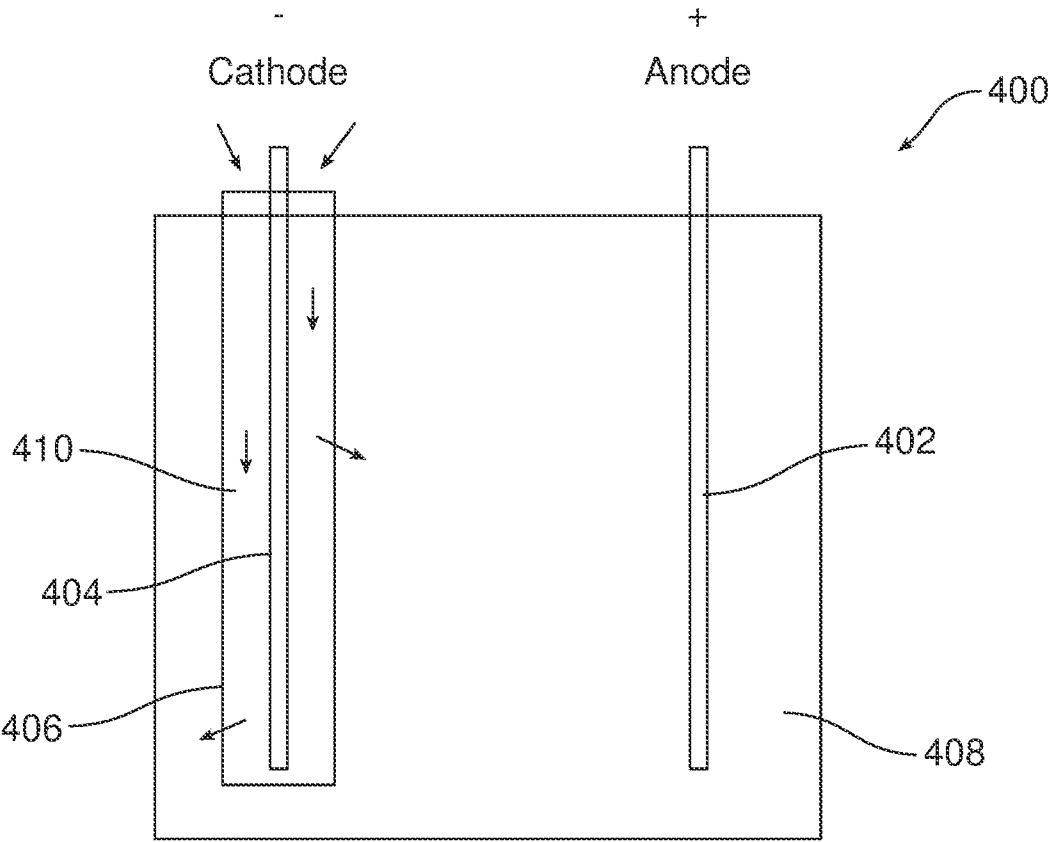
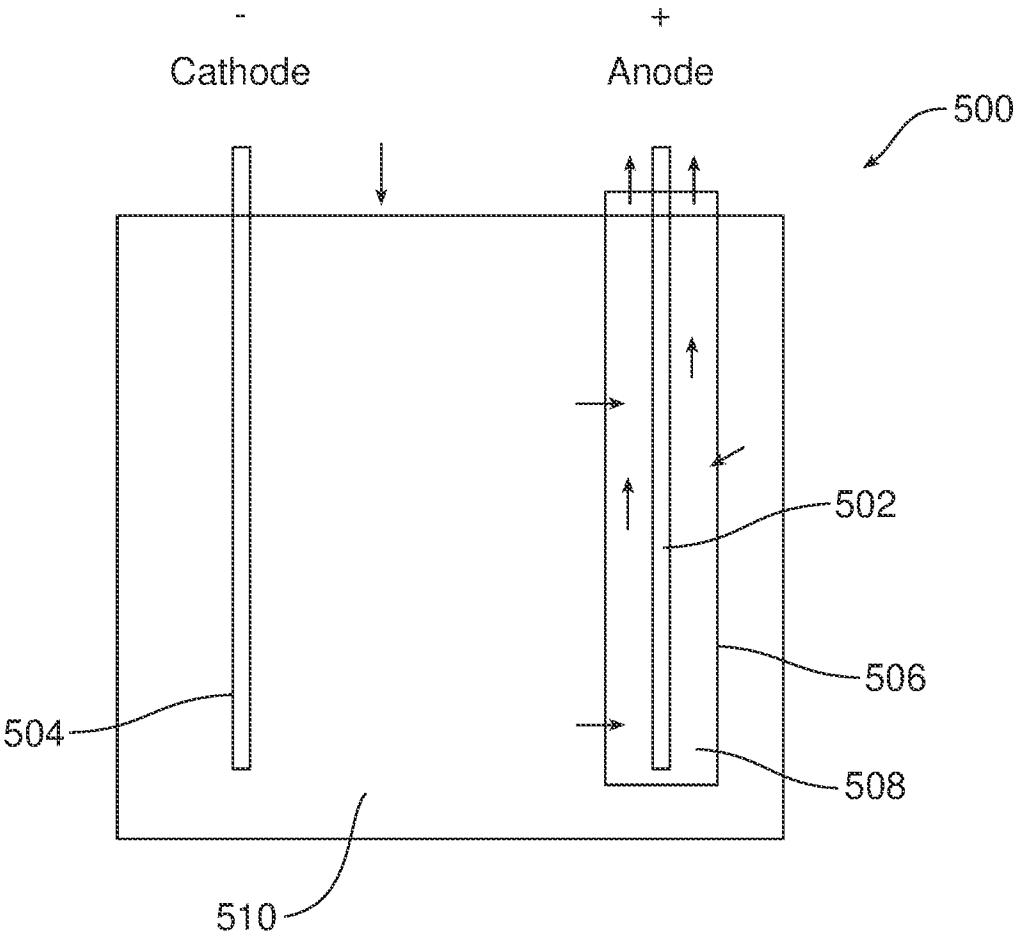


FIG. 7



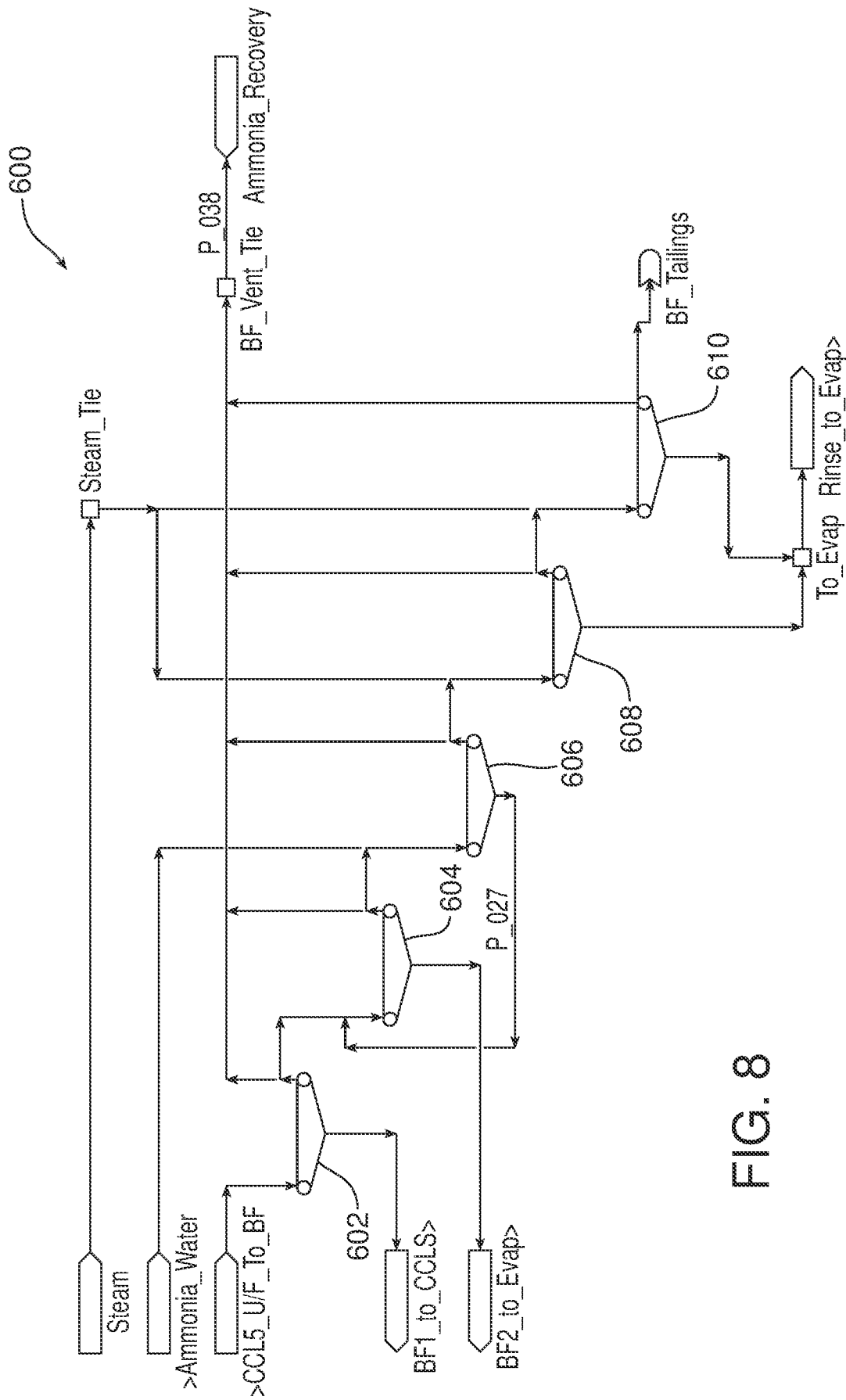
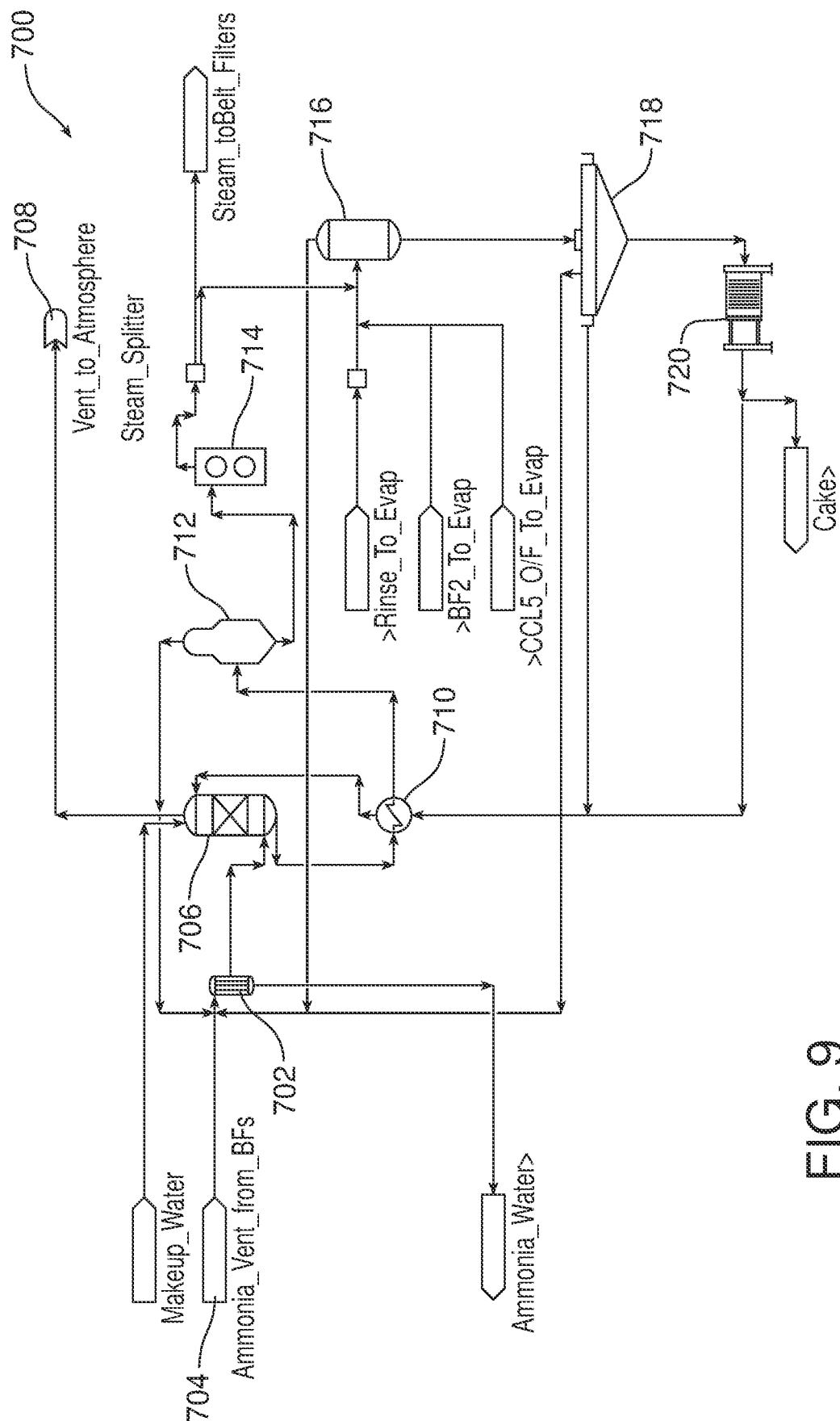


FIG. 8



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US23/30494

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. C25C 1/12; C22B 1/00; C22B 3/26; C22B 3/44 (2023.01)

ADD.

CPC - INV. C25C 1/12; C22B 1/00; C22B 3/26; C22B 3/44; C22B 7/005; C22B 7/008; C22B 11/042; C22B 15/0063

ADD. Y02P 10/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

*See Search History document

Electronic database consulted during the international search (name of database and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	WO 2021/159089 A1 (UNIV OF KENTUCKY RESEARCH FOUNDATION) 12 August 2021; entire document, in particular paragraphs [0011]-[0012], [0040]-[0043]; claims 1, 3	1, 5/1, 7/5/1, 24/5/1 --- 2-4, 5/1-4, 6, 7/5/2-4, 8-23, 24/5/2-4, 25/5/1, 26/5/1, 27/5/1
X --- Y	FORWARD, ET AL. "Chemistry of the Ammonia Pressure Process for Leaching Ni, Cu, and Co from Sherritt Gordon Sulphide Concentrates" JOURNAL OF METALS. March 1955; pages 458-462, figures 1, 9	1-3 --- 4, 5/1-3, 5/4, 17-23
Y	US 3,692,647 A (CHAMBERS) 19 September 1972; figure 1; column 3, lines 56-59; column 5, lines 57-75; column 10, lines 67-75; column 11, lines 1-11, 45-47; claims 1, 18	2-4, 5/2-4, 6, 7/5/2-4, 8-16, 24/5/2-4, 25/5/2-4, 26/5/2-4, 27/5/2-4
Y	US 6,895,740 B2 (ERICKSON) 24 May 2005; column 3, lines 37-39, 45-47	22-23
Y	GARRIDO, ET AL. "Copper Recovery From Ammonia Solutions Through Electro-Electrodialysis (EED)" 28 January 2021; pages 3, 7; DOI: 10.3389/fchem.2020.622611	25/5/1-4, 26/5/1-4, 27/5/1-4

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

29 October 2023 (29.10.2023)

Date of mailing of the international search report

NOV 30 2023

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