Title: OPTIMIZED ORE PROCESSING USING MOLTEN SALTS FOR LEACHING AND THERMAL ENERGY SOURCE

Abstract: A method for the electrolytic production of pure copper from copper-containing compounds dissolved in a high-temperature bath of molten salts which function as an electrolyte in an electrolytic cell. An electric current is passed between an anode immersed in the copper-iron rich molten salt bath and a cathode or cathode-lined kettle in which the molten salt bath is contained, thereby reducing the dissolved copper ions to form pure molten copper. The deposited molten copper collects at the bottom of the kettle and can be separated from the molten salt bath using conventional means.

[Continued on next page]

Published:
— with international search report (Art. 21(3))
FIELD OF THE INVENTION

Embodiments described herein generally relate to the electrolytic extraction of pure metals from metal-containing compounds. More particularly, the present invention relates to the electrolytic production of pure copper in two phases. In the first phase, copper ions are extracted from copper-containing compounds such as copper ore, concentrated copper, and slag using a high-temperature bath of molten chloride salts in the presence of oxygen. In the second phase, an electric current is passed between an anode immersed in the copper-ion rich molten salt bath and a cathode kettle in which the molten salt bath is contained, thereby reducing the dissolved copper ions to form pure molten copper. Because the density of molten copper is higher than that of the salts which make up the molten salt bath, the deposited molten copper collects at the bottom of the kettle and can be separated from the molten salt bath using conventional means.

This method has been tested for copper extraction and electrodeposition, but is believed to be equally applicable to the extraction of any metal whose formal reduction potential is more positive than the most noble metal ion in a molten chloride salt (e.g., in a molten salt comprised of NaCl/KCl/ZnCl₂, the most noble metal ion is Zn^{2+}, which has a reduction potential of -0.76 V versus NHE) and less than the reduction potential of oxygen, the most aggressive oxidant in air, whose reduction potential is 1.23 V versus NHE. Among the clearly desirable metals that can be extracted using the claimed method are gold, silver, copper, nickel, etc.
Description of Related Art

[0003] Conventional metal mining operations, such as for copper, silver, and gold, have the primary purpose of extracting pure metals from metallic ore. Naturally occurring copper is present in various ionic forms, such as copper sulfide (CuS), copper oxide (CuO), and copper chloride (CuCl). In conventional methods, the copper ore is usually treated with chemicals to dissolve ionic copper in an aqueous solution which is then treated with reducing agents to yield metallic copper.

[0004] The most effective conventional copper extraction methods take place in an aqueous solution and combine ion-exchange and solvent-extraction processes, which can be broken down into four principal stages:

[0005] Leaching (L): In this step, copper ions are removed from the ore using chemical agents called lixiviants, typically a solution of sulfuric acid. When the lixiviant is applied to the ore, it dissolves the copper ions to yield a pregnant leach solution (PLS).

[0006] Ion Exchange (IX): In this step, the copper containing PLS is passed through a resin in columns, and copper is adsorbed on the resin. The column is then regenerated with sulfuric acid solution, which yields a relatively impure copper sulfate solution (electrolyte), suitable for further treatment through the solvent extraction process.

[0007] Solvent Exchange (SX): In this step, an organic extractant that selectively binds copper but not other impurities is dissolved in an organic solvent (diluent) and is mixed with the copper-containing aqueous solution. The copper-loaded organic solution is separated from the impurities in the aqueous solution in a settler tank. The barren aqueous solution, called raffinate, is sent back to the leaching-ion exchange process for reuse. Sulfuric acid solution, comprising mostly spent electrolyte returned from the electro-winning process is then added to the loaded organic mixture, which strips the copper into a highly purified aqueous copper sulfate electrolytic solution ready for electrowinning.

[0008] Electrowinning (EW): In the final step, electrolysis of a pregnant copper sulfate electrolyte solution, produced in the solvent extraction step above, takes place and copper ions in solution are plated (electrolytically deposited) as copper metal onto a cathode.

[0009] A well-known conventional copper extraction process is typified by the Cominco Engineering Services Ltd. (CESL) process. In this process, a hypothetical refinery produces 154,000 tpy Cu from 550,000 tpy concentrate containing 29% Cu and 9 g/t Au. For this hypothetical scenario, preliminary operating costs for the gold/silver process are estimated to add about US$ 0.024/lb Cu to the existing CESL copper process, for a total of US$ 0.20/lb Cu. The net cash flow is improved by approximately US$ 74 Million per year, compared to the alternative of selling the concentrate to a
smelter and paying realization costs. This is equivalent to US$ 0.22/lb Cu increased cash flow, before amortization costs.

[0010] Metallic gold and silver can also be recovered from copper sulfide concentrates using cyanide to leach residue from existing copper processes. This process was developed as a hydrometallurgical alternative to smelting and refining, and consists of five main process steps (described above):

1. Pressure oxidation of concentrate at 'medium temperature,' i.e., above the melting point of sulfur, (T > 116° C) but below phase transition point (160° C) of sulfur;
2. Copper leaching of the solid oxidation product with raffinate at atmospheric conditions to produce a Pregnant Leach Solution (PLS);
3. Solvent extraction of PLS to produce a high purity electrolyte and regenerate raffinate;
4. Partial neutralization of raffinate to remove any excess sulfate; and
5. Electrowinning to recover copper in commercial product form (full cathodes).

[0011] Copper, gold and silver recovery by simple cyanidation of the resulting residue is unsatisfactory as it consumes very large amounts of cyanide, due to formation of both thiocyanate and also copper cyanides, typically consuming > 30 kg NaCN/ton residue. Cyanide consumption can be reduced to lower levels by a combination of new processing improvements, which include pressure cyanidation for short retention times to minimize thiocyanate formation, partial suppression of copper cyanide formation, and finally by recovering cyanide as efficiently as possible from the (reduced) copper cyanide complexes. Total cyanide consumption with the improved cyanide processing can be reduced to approximately 2 kg NaCN/ton of concentrate. Using this method, gold and silver recovery of approximately 90% can be achieved. However, this extra processing adds extra complexity, time and labor. The cyanide consumption due to thiocyanate is between 0.5 - 1.3 kg NaCN/ton residue (slag). This accounts for about half of the known cyanide consumption. This low cyanide consumption is the most efficient of the known conventional methods of processing of copper/gold/silver concentrates in competition with conventional smelters.

[0012] In this process, the copper residue contains two components, residual copper and sulfur, which tend to consume very large amounts of cyanide if the residue is further processed. When the residue is leached under "standard" conditions, i.e. leaching with low concentration cyanide solution
in atmospheric conditions for 1 - 3 days. The residue still has a significant copper content, despite the fact that it has already been processed specifically for copper extraction. Since extraction is about 95 - 98% efficient for Cu, the residue typically contains 1.0 - 1.5% Cu. This small Cu content is partly (15 - 25%) soluble in standard cyanide leach conditions, leading to the formation of soluble copper cyanide compounds, as well as other cyanide compounds such as cyanate. Also present in the copper residue is elemental sulfur that typically constitutes 25 - 35% of the residue. A minor amount of elemental sulfur also reacts with cyanide solutions leading to the formation of thiocyanate compounds. Both of these phenomena lead to very high cyanide consumption when the copper residue is treated in a standard cyanide leach, e.g. 30 kg NaCN consumed per ton of copper residue, or more than 100X the consumption typically experienced in leaching gold ores. Such levels of cyanide consumption render the process far too expensive in view of the modest value of gold and silver to be extracted. Worse still, the gold and silver themselves cannot easily be extracted from the Cu process residue by cyanide leach solutions, and extractions of gold and silver from leach residue are generally incomplete.

[0013] In summary, with standard cyanide leaching of the copper residue, costs are high, gold and silver recoveries are poor, and the costs of the process tend to outweigh the value of the recovered metals. Efforts to overcome these difficulties have been devised to reduce cyanide consumption and boost metal recovery. This process is fairly complex, involving a number of steps and still uses cyanide and sulfuric acid, which are hazardous and toxic if they escape into the environment. On the other hand, in aerobic molten chloride salts, gold silver and copper are readily extracted. Gold has a reduction potential of 0.99 volt versus SHE. Where SHE is defined as the Standard Hydrogen Electrode whose potential is defined as 0 volts and is the reference potential for all reduction potentials and where SHE is associated with the reduction of proton to hydrogen in 1 normal acid solution. Silver has a reduction potential of 0.8 volt and copper 0.34 volt. The metal most resistant to extraction is gold with a potential of 0.99 volt versus SHE which is 0.23 volts low than the reduction potential of oxygen, whose potential is 1.23 volt versus SHE. Still oxygen having 0.24 volt higher reduction potential than gold allows oxygen to dissolve gold metal into chloride salt melt. Ordinarily gold has a standard reduction potential of 1.5 volt versus SHE (for Au^{3+} + 3 e^- \rightarrow Au metal). However in chloride salt the relevant gold reduction (and gold metal oxidation) process is AuCl_{4^-} + 3 e^- \rightarrow Au metal + 4 Cl^-. Clearly due to the shift of gold reduction potential below oxygen reduction, even gold can be extracted when gold ore is in in molten chloride salts. Silver and copper, which in pure form already had low formal reduction potentials than oxygen (Ag 0.8 volt, Cu 0.34 volt), experience a negative shift in molten chloride salt (Ag 0.2 volt, Cu < Ovolt), which makes them even easier to extract when in silver and copper ores are treated in aerobic molten chloride salts. The extracted metals can be selectively plated one by one by
controlling the potential of the plating process (0.9 for plating Au metal, 0.1 for Ag and finally < 0 volt for Cu). In summary gold, silver and copper metal can all be dissolved as chloride salts allowing metal extraction from their respective ores, and then these chloride salts can be simultaneously plated at high reduction potentials (< 0 volt) or selectively plated one at a time by controlling the reduction potential of the plating bath to the a specific reduction potential for each specific metal. Metal extraction and deposition from metal rich earths is accomplished using relatively benign aerobic molten chloride salt and graphite electrodes, and no other chemical or solvents which have been problematic in the past due to waste of water, energy, desired metal and hazardous to the environment. The metal deposition process from molten chloride salt is presently targeted to commodity and precious metal but the process is general. For example, using the proper molten chloride (like and aluminum based molten chloride) and silicon chlorides (like Si2Cl6) and substrates, then high valued semiconducting silicon can be deposited in polycrystalline and single crystalline forms in a simple reactor using very low energy and virtually no waste nor emission of toxic wastes.

**Aluminum Production (Hall-Heroult Process) as a Model for Copper Production in Molten Salts**

[0014] Aluminum production is a well-known process and consists of mining bauxite ore, and extracting the naturally-occurring aluminum oxides [Al(OH)3, bohemite γ-AIO(OH), and diaspore α-AIO(OH) which can simply be designated Al2O3 or alumina] in the bauxite using the Bayer process. For the Bayer process, a large amount of heat (steam) is required that is typically produced with boilers or steam from co-generation plants. Approximately two tons of bauxite ore will produce one ton of alumina (Al2O3). The alumina can then be transported to an aluminum smelter to be extracted via the Hall-Heroult process. Approximately two tons of alumina will produce one ton of aluminum.

[0015] In the Hall-Heroult process, aluminum oxides (Al2O3) are dissolved in a molten fluoride salt (cryolite, Na3AlF6) bath contained in a carbon-cathode lined electrolytic cell that is maintained at approximately 1000° C. A low voltage direct current passes from carbon anodes immersed in the molten salt bath to the carbon-cathode cell lining, causing liquid aluminum metal to be deposited at the cathode, while the oxygen from the alumina combines with carbon from the anode to produce carbon dioxide. As the electrolytic reaction proceeds, aluminum, which is slightly denser than the electrolyte solution, is continuously deposited in a metal pool at the bottom of the cell where it can be collected using conventional means such as a siphon. In addition to CO2, the cell also produces hydrogen fluoride from the cryolite and flux which are either treated or vented into the atmosphere.

[0016] In an analogous process, metals and metal ions in copper rich earths and concentrates can be dissolved in oxygenated molten chloride salts forming metal chlorides at 500° C which can then be plated directly from the molten salt to a cathode with virtually 100% extraction and plating efficiency.
Generally, all metal is recovered at one high over potential (i.e., at a potential more cathodic than the reduction potential of the least noble metal), but a specific metal can be separated by selectively plating at a specific cathode potential if desired.

[0017] Electrochemically, the extraction and purification of copper by dissolving copper oxide-containing ore or slag or copper-sulfide concentrate in a molten chloride salt bath and plating the metal in carbon vessels is similar to the process used to make aluminum metal. However, it is believed these methods of aluminum-making have not heretofore been applied to the extraction of metallic copper and other desirable metals, for several reasons. Moreover, each intermediate step in the copper extraction process is less costly, more environmentally-friendly, and safer than the corresponding step in the Hall-Heroult Process.

[0018] For example, the electrolyte solution consists of inexpensive, recyclable chloride salts (< $1 per kilogram) rather than consumed fluoride salts in the Hall-Heroult Process. Additionally, aluminium oxide has such a high heat of formation (\(\text{Al}_2\text{O}_3 = -1675.7\, \text{kJ/mol}\)) that all the water introduced in the bauxite clay has to be removed during the bauxite preparation for the refining process, which adds cost. This cost is not incurred in the analogous copper metal plating because copper oxide has a relatively much lower heat of formation (\(\text{CuO} = -157.3\, \text{kJ/mol}\) and \(\text{Cu}_2\text{O} = -168.6\, \text{kJ/mol}\)), so copper metal does not readily combine with water to reform copper oxide. If the removal of water is desired then this can easily be done if excess heat (steam) is available, which could come from the using the molten salt to transfer heat from slag to the refining reactor or using a cogeneration power plant if the fuel cost is low. Finally, the reduction potential of copper is over 2 volts more positive than the reduction potential of aluminum, so the electrodeposition of carbon is thermodynamically favored relative to that of aluminum, meaning that less electricity and cost is required to extract copper. In fact, the yield of copper from ore has recently been found at the University of Arizona to be virtually 100% of theoretical yield.

**Objects of the Present Invention**

[0019] An object of the present invention is to provide an optimized method and apparatus suitable for large-scale, environmentally-friendly processing of copper ore, copper sulfide concentrates, or even slag using a molten salt bath to produce a highly purified copper cathode product via electrolytic deposition.

[0020] A further object of the present invention is to provide a method and apparatus for the extraction of metallic copper which is economical in operation and construction, and which does not require the use of highly toxic chemicals such as cyanide and sulfuric acid.
[0021] A further object of the present invention is to provide a method and apparatus for optimizing the extraction of copper and other desired metals by employing a reference electrode to monitor and control both the initial ionization of copper in the molten salt bath and the electrolytic deposition of desired metals at the cathode.

SUMMARY OF THE INVENTION

[0022] The present invention relates to the electrolytic production of pure copper in two phases. In the first phase, copper ions (Cu⁺ and Cu²⁺) are extracted from copper-containing compounds such as copper ore, concentrated copper, and even slag using a high-temperature (i.e., greater than 500 to as high as 1085° C) bath of molten chloride salts in the presence of oxygen and water from air. In the second phase, an electric current is passed between an anode immersed in the copper-ion rich molten salt bath and a cathode or cathode-lined kettle in which the molten salt bath is contained, thereby reducing the dissolved copper ions to form pure molten copper at temperatures \( \geq 1085° \) C. Because the density of molten copper is higher than that of the salts and earths that contained the copper which make up the molten salt bath, the deposited molten copper collects at the bottom of the kettle and can be separated from the molten salt bath using conventional means.

[0023] According to the present invention, there is provided an apparatus for the extraction of metallic copper from copper-containing compounds, comprising: a high-temperature, corrosion resistant vessel (preferably of graphite or other carbon material) in communication with a cathode in an electrical circuit; a molten salt bath comprising one or more chloride salts which functions as an electrolyte solution in the electrical circuit; an anode (preferably of graphite or other carbon material) immersed in the molten salt bath; a direct current (DC) electrical supply; and a conventional means of separating the pure molten copper electrodeposited at the cathode from the molten salt bath. The cathode or cathode-lined vessel is filled with the metal ion rich molten salt bath.

[0024] The molten salts or ionic liquids used in the present disclosure have a very low vapor pressure, such as between about two pounds per square inch gauge (2 psig) at an operating temperature of 500 degrees Celsius to about 1/2 atmosphere (i.e. 7 psig) or less at 800 degrees Celsius to 1 atmosphere or less at temperatures as high as 1400 degrees Celsius. The salts also have low temperatures of melting (i.e. will transition from a solid to a liquid phase, as low as 200 degrees Celsius and as high as 450 degrees Celsius). The salts are aerated (i.e. exposed to air in an open container) to dissolve the oxygen and water from air into the molten salts or ionic liquid to form a mixture which extracts all metal and metal ions in the ore or slag into the salt as ionic metal chlorides. The metal and metal oxides are unstable and dissolve in the aerated molten halide salt by the process in which metals
and metal ions are transformed to metal halides, which in turn can then be electrodeposited on a cathode in the same pot as metals.

[0025] Not only is the refining of copper in molten salts much safer and more environmentally benign than aluminum-making using molten fluoride salts, but the claimed apparatus and process achieves significant advantages over conventional means of refining copper and other metals using water and toxic solvents including sulfuric acid and cyanides. In one or more embodiments, such as for small scale operations, the extraction and electrodeposition steps occur sequentially in the same vessel (e.g. crucible, pot, kettle, container, etc.). Additionally, the present disclosure covers large scale mining operations where the metal extraction and electrodeposition are conducted in close proximity to each other, but in separate vessels, or collocated at the same facility.

[0026] It is also possible to recycle heat using the chlorides as the molten chloride salts being used to extract and plate copper were originally developed at the University of Arizona as heat transfer fluids for concentrating solar power for electrical power generation. Molten salts and ionic liquids can be very useful heat carriers for recovering thermal energy from slags. This last development is due to the fact that at the high temperature (up to 1300 degrees Celsius) these kinds of liquid salts can operate as heat transfer fluids, whereas no other known conventional heat carrier can work at such temperatures, e.g. slag is about 1650 degrees Celsius and thus conventional methods of metal extraction using acids, bases or cyanides on slag do not work, and non-molten salts would not work with slag.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] Fig. 1. is a schematic depicting one embodiment of the system and process of the present disclosure.

[0028] Fig. 2. is a flowchart of the process steps of the present invention.

[0029] Fig. 3 illustrates a schematic of the process steps described herein using molten salts as the low vapor pressure liquid, and using a heat exchanger to store and provide thermal heat.

[0030] Fig. 4. is a schematic diagram of a pilot plant for extracting metal ion into molten salt and electrodeposition of metal from the metal ions dissolved in molten salt.

DESCRIPTION OF THE INVENTION

[0031] The foregoing objects of the present invention are accomplished and the problems and shortcomings associated with the prior art, techniques and approaches are overcome by the present invention as described below in the following non-limiting embodiments.
The invention includes an electrolytic cell for the production of copper from copper-containing compounds dissolved in a molten salt electrolyte. Preferably, the molten electrolyte is maintained at a temperature of between 500°C and 1200°C. The copper-containing compounds can be added to the cell as a batch or on a continuous basis. The electrolytic cell employs anodes and cathodes, the cathode being in communication with the vessel containing the molten salt electrolyte. In the process of the invention, electric current is passed from the anode through the molten electrolyte to the cathode, reducing the ionic copper dissolved in the electrolyte and depositing metallic copper at the cathode.

The electrolytic cell of the present invention employs electrolytes comprised of molten halide salts, preferably chloride salts of alkali metals and/or alkaline earth metals. In other preferable embodiments, the molten salt electrolyte may comprise NaCl-KCl-ZnCb or NaCl-KCl-AlCl₃ in several eutectic compositions, including without limitation 2-aluminum and 3-magnesium chlorides mixed with Na and K chlorides, and 4-stable ionic liquids with various cations and chloride anions. In one embodiment, the electrolyte is composed of a 50:50 (mole-to-mole) mixture of NaCl and KCl salts, or 50:50 (mole-to-mole) mixture of MgCl₂ and KCl salts, or other suitable mixtures of molten salts known and used by those of ordinary skill in the art.

One-Pot System and Process

One or more embodiments of the present disclosure comprise a container, in a one-pot metal extraction and electrodeposition apparatus. The apparatus, or system, comprises: 1) a high temperature resistant, corrosion resistant outer crucible, wherein the outer crucible comprises non-porous glassy carbon material, or non-porous ceramic-filled graphite or quartz or a nonporous ceramic material; 2) a high temperature resistant, corrosion resistant inner crucible centered within a bottom of the outer crucible, wherein the inner crucible is cathodic (i.e. functions as a cathode in an electric circuit), and the inner crucible comprises porous graphite or non-porous glassy carbon material or a non-porous ceramic-filled graphite; 3) a molten salt within the inner crucible produced by combining a low melting aerated chloride salt and metal ore or slag; 4) an anode rod positioned vertically within the inner crucible; 5) a power supply operatively connected to the inner crucible cathode and the anode rod; and, 6) a means to stir for continuously mixing the molten salt and slag/ore within the inner crucible.

This one-pot method has been tested for copper extraction and electrodeposition but should work for any metal whose formal reduction potential is more positive than the reduction potential of the most noble metal ion in a molten chloride salt (for example, in NaCl KCl ZnCb, it is the reduction potential of zinc, which is -0.76 V versus NHE) and less than the reduction potential of oxygen, the
most aggressive oxidant in air, whose reduction potential is 1.2 V versus NHE. Clearly desirable metals can be processed including gold, silver, nickel, etc.

**Multi-Crucible System and Process**

[0036] Various embodiments of the present disclosure also comprise environmentally friendly processes for extracting and depositing metals from ore and/or slag, while using a plurality of crucibles, vessels, reactors, containers, etc. The multi-crucible system and process is suitable for full scale manufacturing operations that extract and deposit large quantities of metal from ore and/or slag.

[0037] The various embodiments of the multi-crucible system comprise the following components: a mixing crucible able to heat and dissolve metal in slag and/or ore that is aerobically mixed with a low vapor-pressure molten salts or ionic liquid; a mechanism to remove the undissolved slag or ore from the mixture (e.g. by filtration or decanting); an electro-chemical reactor able to conduct electrodeposition to remove the pure metal from the liquid solution by depositing it on a cathode electrode.

[0038] The electro-chemical reactor comprises: a high temperature resistant crucible storing the liquid solution; a cathode electrode and an anode electrode (e.g. graphite) connected to a direct current power supply on an upper end, and immersed in the liquid solution on a bottom end; and, one or more valves to drain the electrified liquid solution from the reactor crucible and into a movable re-cycle tank.

[0039] The movable re-cycle tank is able to first receive dense metal (e.g. copper) and then be replaced by an empty tank for receiving the metal-depleted electrified liquid solution comprising molten salts or ionic liquid, which can then be used to transport the electrified liquid salt solution back to the mixing crucible and/or a heat exchanger unit. In an embodiment, the re-cycle tank is heat and liquid sealed to prevent significant loss of heat and the used liquid solution.

**Heat Recycling**

[0040] In an embodiment of the invention, it is also possible to recycle heat using the chlorides as the molten chloride salts being used to extract and plate copper were originally developed at the University of Arizona as heat transfer fluids for concentrating solar power for electrical power generation. During the copper making process which occurs in molten chloride salt, copper-depleted, deoxygenated and dehydrated molten chloride salt or fresh deoxygenated and dehydrated molten chloride salt can be stored in a tank and passed through pipes where heaps of hot ground copper earth, concentrates or slag are stored in order to extract heat from the heaps. The salt needs to be deoxygenated and dehydrated only if metal tanks and pipes are used. For example if graphite, or clay filled graphite, pipes and containers are used, the salt need not be deoxygenated and dehydrated.

[0041] One scenario illustrating the use of the heat exchanger is the fact that can be extracted from a slag heap piled into a closed bucket with a heat collecting tube containing molten salt and passing
through the hot slag heap. Collecting heat into the collecting tube is just like the heat collecting tube used to collect heat from sun shining on a pipe containing molten salt in a plant for concentrating solar power. The slag can stay in the bucket until most of the usable heat is sent into the molten salt to make electricity. That is, the freshly heated molten salt can go to a heat exchanger, in a steam generator, to make steam to, in turn, make electricity for electroplating copper or for providing electrical power in the plant or even nearby residential housing. Instead of sending the heated molten salt to the steam generator, the heated molten salt can fill a graphite kettle which is used to process slag or ore.

[0042] The molten salt in the slag or ore is used to dissolve metals in the molten salt, and after metal ions are dissolved, the metal ions are electroplated at temperatures over the melting point of metal (e.g., 1,984° F or 1,085° C for copper), causing the liquid metal sinks to the bottom of the kettle, which can then be poured out of the kettle by means of a drain. When most of the desired heat is transferred from the slag to the salt for whatever reason, then the slag can be dropped into the graphite kettle by opening the bottom of the bucket so slag passes through the pipe into the graphite kettle for processing into copper metal and then new hot slag is put into the bucket and the whole process is started again.

[0043] Any heat not used to make electricity for making copper ions to copper metal can be used to make electricity for factories and houses in nearby areas. Two hundred and fifty (250) megawatts is enough electricity for 70,000 households. So the huge amounts of waste heat in copper heaps can be used to make commercial amounts of electricity. Any of the heat in the molten salt which is not extracted from the heat exchanger can be stored as hot salt in tanks and the stored energy can be extracted for heating the smelter process(s) or sent to a steam generator for making electricity on demand.

DETAILED DESCRIPTION OF THE DRAWINGS

[0044] The present invention is further illustrated with reference to the accompanying drawings, throughout which reference numbers indicate corresponding parts in the various figures. These reference numbers are shown in parentheses in the following detailed description.

[0045] Referring to FIG. 1, there is shown a schematic drawing of one embodiment of the system and process of the present disclosure. Metal ore and/or slag 110 (e.g. comprising copper, gold, silver, or any combinations thereof) is added to and stirred in crucible 120 which contains high temperature, molten salt (MS) or ionic liquid (IL) recycled from tank 150. The crucible 120 is exposed to air, meaning that the top of the crucible remains uncovered, or that air is stirred into the liquid solution. In an embodiment, the molten salt comprises sodium chloride and potassium chloride and zinc chloride eutectic (i.e. NaCl-KCl-ZnCl2), in a mixture of a 0.5 to 0.5 to 1 molar ratio, respectively. This NaCl-
KCl-ZnCl$_2$ molten salt melts at about 200° C and has very low vapor pressure (7 psig) and is chemically stable to over 1000° C in air.

[0046] The ore or slag is added to crucible 120 via standard machinery known in the art, such as via a crane or conveyer belt. The re-used molten salts or ionic liquids may be pumped or poured into the crucible 120 from the re-cycle tank 150.

[0047] Heat is applied to the crucible 120 while the metal from ore or slag is dissolved into the molten salt or into the liquid, and the mixture is stirred to dissolve the metal ore or slag. This will produce a liquid solution containing a metal chloride (e.g. CuCl$_2$). The appropriate temperature range for the applied heat is about five hundred to eleven hundred degrees Celsius, although other temperatures are envisioned within the scope of the present disclosure and are a function of the type of molten salt or ionic liquid used and the metal being extracted. The source of the heat 130 may be melted slag from ore smelters (e.g. up to 1650 degrees Celsius) and/or standard heat generating electro-mechanical devices known by one of skill in the art.

[0048] In one embodiment (as shown in FIG. 1), the liquid solution is passed through a filter 140 by gravity or a vacuum pump 170. Excess slag residue is discarded by inverting the crucible by using, e.g., a crane or other mechanical method. The remaining solution enters a crucible 106 which is subjected to heat via source 132. Crucible 106 comprises a pair of electrodes 108 (anode) and 109 (cathode). Crucible 106 further comprises a pressure release mechanism 105 as a safety mechanism for when the pressure becomes too high within the crucible. Crucible 106 further comprises a valve 107 to first drain the molten metal into a recycling tank 150 and then to drain the used metal depleted molten salt or ionic liquid into the tank 150. The used, heated molten salt in the recycling tank is then transported back to and added into the stirring crucible 120, via for example the use of a crane. One of skill in the art would readily know of mechanisms to transfer used molten salt or ionic liquid from tank 150 to crucible 120 (e.g. automated rail movement, vehicle operated by driver, etc.). Thus the hot molten salt is re-cycled to reduce operating cost for materials and for heating.

[0049] During the metal plating step a variety of types of electrodes 108, 109 can be used, (e.g. graphite, glassy carbon, or any stable refractory metal). Metal forms on graphite cathode 109. As metal forms on the cathode 109, the graphite anode 108 will oxidize to carbon dioxide due to the presence of trace water in the molten salt in contact with air.

[0050] Referring to FIG. 2, there is shown a summary of the general steps of the metal leaching process using low vapor pressure, aerated molten salts or ionic liquids of the various embodiments disclosed herein, and FIG. 3 is one exemplary embodiment of FIG. 2. The vessel further comprises a bottom and walls extending upward from said bottom. The opening formed by the top of the vessel
walls is exposed to air, and the vessel is optionally configured with a mechanical stirrer. In operation, the mixture of molten electrolyte and metal-ion rich material is stirred to aerate the mixture of molten electrolyte salt and metal-ion rich material, thereby causing metal ions to dissolve in the electrolyte.

[0051] In step 210, the metal ore or slag is mixed with the low vapor-pressure molten salt or ionic liquid to form a mixture. The mixture is aerated, via for example having the crucible not be covered. The crucible is temperature controlled to enable all metal and metal oxides to be extracted from the ore or slag, and to form metal ions which are dissolved in the liquid solution in the mixture.

[0052] In step 220, the liquid solution with the metal ions is separated from the metal depleted solid ore or slag by filtration or decanting (pouring off from a level just above the metal depleted solid), or other industrial separation process. The metal depleted solid can be dumped at this point, for example by inverting the vessel, which can then be reused to transfer heat to a new liquid solution of metal rich ore or slag and molten salts or ionic liquid.

[0053] In step 230, the metal-rich hot liquid solution is put into an electrochemical reactor for electrodeposition. At this step the very hot liquid (about or above 1000° C) can be passed in a metal tube from the pot (heat exchanger to a water bath) and the cooled (500° C) liquid back to a graphite pot which acts as a cathode to make metal. The exchanged heat can be used to make steam from water to drive a turbine generator to make electricity.

[0054] In step 240, metal ions from the liquid solution are electrodeposited as pure metal at a carbon cathode while carbon dioxide forms at a carbon anode using an electrical current.

[0055] The metal is denser than the salt and can be poured out from the bottom of the reaction vessel (like a graphite crucible) while metal-depleted low vapor-pressure liquid remaining on top in the electrochemical reactor may then be recycled to the initial step for again extracting metal from ore or slag.

[0056] Referring now to FIG. 3, there is shown a schematic chart of an exemplary embodiment of a method and system for extracting metal ion into molten salt (e.g. leaching metals from slags using molten salts). The heat from the hot melted slag 305 passes through a heat exchanger 315. The heat exchanger 315 provides heat to the molten salt and this last hot salt is stored in an isolated tank 320. The melted slag 305 that passes through the heat exchanger 315 goes to a granulator 330; where in the granulator 330 are produced small particles of slag. The particles of slag are mixed with the molten salt; then slag and molten salt are stirred in a tank 340. Separation of molten salt and the slag residues is carried out by decanting or filtration 350. The aerobic molten salt produced during the stirring process dissolves metal ions and the ions are reduced and electrodeposited as metals layers on graphite electrodes 360, wherein the metals are recovered from the graphite. After electrodeposition of the
metals, the molten salt is released of metal ions and it is deposited in a tank 370, and now it is ready to be recycled. The recycled molten salt goes to the initial heat exchanger 315 to be heated again and used as a heat transfer fluid.

[0057] FIG. 4 shows a schematic diagram of an exemplary production plant system 400 for extracting metal ions from ore or slag using molten salt based upon the process and system of FIGS. 2 and 3. The plant can be scaled to various sizes by one of skill in the art.

[0058] In tank 405 the melted slag is separated from the ore smelter, and it passes through a heat exchanger 410 where the molten slag provides thermal energy to the recycled molten salt dropping from shaft 475 past the heat exchanger 410 to tank 420. The molten slag decreases its temperature due to the heat exchanger and goes to a granulation process where small particles are obtained at tank 415. All of the molten salt that is recycled is deposited in a heat insulation tank 420 where it can be mixed with fresh salts for recovering of the salt wasted in the process. From the heat insulation tank 420 is taken molten salt and it is mixed at tank 425 with the slag that comes from the granulator system 415. The mixture is maintained under stirring via device 430 for some time until it reaches the thermodynamic equilibrium. In this part of the process the metal ions are extracted into the molten salt.

[0059] For separation of the molten salt that contains metal ions from the residual slag, the stirring is stopped and after waiting some time the precipitation of the residual slag is carried out; the residual slag goes to the bottom of the tank at 435. In the bottom of the tank at 435 is a gate that is opened for decanting or filtration of the molten salt. In the separation process the residual slag is taken out using a circular arm and the molten salt passes over the slag or through a filter 440. The stirring process keeps a constant temperature by using molten salt that comes from the heat insulation tank.

[0060] After separating the molten salt from slag, the molten salt goes to a container 455 with two graphite electrodes at 450 where the metal ions are separated from the molten salt by electrodeposition of metal on a graphite electrode. As metal forms at the graphite cathode, on the anode the graphite will oxidize to carbon dioxide, due to anodic current and the presence of trace water in the molten salt in contact with air. The water ultimately comes from the air. The container where the electrodeposition is carried out is maintained at elevated temperature (greater than 400 degrees Celsius) using heat exchanged from the molten salt that came from the heat insulation tank 420 at pipe opening 460. When almost all of the metal ions are separated from the molten salt by electrodeposition, a gate is open and the metal depleted molten salt is poured into a second heat insulation tank 470 or piped in via pipes 465. From this second insulation tank 470, the molten salt is recycled to the heat exchanger via piping to opening 475 and/or by using a mobile container in order to be heated again at the heat exchanger 410.
[0061] It is recognized that the system illustrated in FIG. 4 is one exemplary embodiment, and that one of skill in the art could readily modify the schematic to arrive at an equivalent system of a large scale facility for extracting metal from melted slag.

[0062] The terms "plurality" may be used throughout the specification to describe two or more components, devices, elements, units, parameters, or the like. Unless explicitly stated, the method embodiments described herein are not constrained to a particular order or sequence. Additionally, some of the described method embodiments or elements thereof can occur or be performed at the same point in time.

[0063] Although various features of the present disclosure may be described in the context of a single embodiment, the features may also be provided separately or in any suitable combination. Conversely, although the various embodiments may be described herein in the context of separate embodiments for clarity, they may also be implemented in a single embodiment. It is to be understood that the phraseology and terminology employed herein is not to be construed as limiting and are for descriptive purpose only. It is to be understood that the details set forth herein do not construe a limitation to an application of the various embodiments.
THE INVENTION CLAIMED IS

1. A method of producing pure metallic copper in an electrolytic cell containing a molten salt electrolyte, the method comprising the steps of:
   - providing a vessel for containing the molten salt electrolyte at a temperature of between 500° C and 1200° C, said vessel comprising a bottom and walls extending upwardly from said bottom, wherein said vessel further comprises an outlet configured as a drain;
   - providing at least one copper-containing compound;
   - dissolving said at least one copper-containing compound in said molten salt electrolyte;
   - providing at least one anode in liquid communication with said molten salt electrolyte;
   - providing at least one cathode in communication with said vessel bottom;
   - passing an electrical current through said anode and said cathode, thereby depositing molten copper at said cathode and producing gas at said anode;
   - removing copper deposited at said cathode through the outlet in said vessel.

2. The method of claim 1, wherein said vessel further comprises a mechanical stirrer configured to aerate said molten salt electrolyte and any copper copper-containing compounds dissolved therein.

3. The method of claim 1, wherein said vessel is composed of fused quartz.

4. The method of claim 1, wherein said anode and said cathode are composed of graphite carbon.

5. The method of claim 1, wherein said electrolyte comprises at least one compound selected from the group consisting of the halide salts of alkali metals, alkaline earth metals, and magnesium.

6. The method of claim 1, further comprising the step of monitoring the electric potential of the molten salt electrolyte using a reference electrode.

7. A method of producing pure metals from slag obtained from the copper mining process using an electrolytic cell containing a molten salt electrolyte, the method comprising the steps of:
   - providing an extraction vessel for containing a mixture of molten salt electrolyte and slag at a temperature of between 1000° C and 1200° C, wherein said extraction vessel comprises a bottom and walls extending upwardly from said bottom and is configured with a
mechanical stirrer to aerate the mixture of slag and molten salt electrolyte contained in the extraction vessel, thereby causing metal ions in the slag to be dissolved as metal ions in the electrolyte;

wetting said slag in said molten salt electrolyte in said extraction vessel;
removing metal ion-depleted slag from said extraction vessel;
transferring metal ion-rich electrolyte from said extraction vessel to said electrodeposition vessel;

providing an electrodeposition vessel in liquid communication with said extraction vessel, said electrodeposition vessel comprising:

a bottom and walls extending upwardly from said bottom, and further comprising an outlet configured as a drain;
at least one anode;
at least one cathode in communication with said vessel bottom in said electrodeposition vessel;

passing electrical current through said anode and said cathode in said electrodeposition vessel, thereby depositing molten metal at said cathode and producing gas at said anode;

removing metal deposited at said cathode through the outlet in said vessel.

8. The method of claim 7, wherein said vessel further comprises a mechanical stirrer configured to aerate said molten salt electrolyte and any copper copper-containing compounds dissolved therein.

9. The method of claim 7, wherein said vessel is composed of fused quartz.

10. The method of claim 7, wherein said anode and said cathode are composed of graphite carbon.

11. The method of claim 7, wherein said electrolyte comprises at least one compound selected from the group consisting of the halide salts of alkali metals, alkaline earth metals, and magnesium.

12. The method of claim 7, further comprising the step of monitoring the electric potential of the molten salt electrolyte using a reference electrode.

13. An electrolytic cell for the production of pure copper metal, the electrolytic cell comprising:

a molten salt electrolyte having at least one copper-containing compound dissolved in therein;
a vessel for containing the molten salt electrolyte at a temperature of between 500° C and 1200° C, said vessel comprising a bottom and walls extending upwardly from said bottom, wherein said vessel further comprises an outlet configured as a drain; at least one anode in liquid communication with said molten salt electrolyte; at least one cathode in communication with said vessel bottom; a source of electrical current in communication with said anode and said cathode.

14. The electrolytic cell of claim 13, further comprising a reference electrode for monitoring the electric potential of the molten salt electrolyte.

15. The electrolytic cell of claim 13, wherein said vessel further comprises a mechanical stirrer configured to aerate said molten salt electrolyte and any copper copper-containing compounds dissolved therein.

16. The method of claim 7, wherein said vessel is composed of fused quartz.

17. The method of claim 7, wherein said anode and said cathode are composed of graphite carbon.

18. The method of claim 7, wherein said electrolyte comprises at least one compound selected from the group consisting of the halide salts of alkali metals, alkaline earth metals, and magnesium.
A metal ore or slag is mixed with low vapor pressure liquid (e.g. molten salts or ionic liquid), at high temperature and until the metals are dissolved in the liquid solution.

210

The liquid solution is separated from the ore or slag by filtration.

220

The liquid solution is put into an electrochemical reactor for electrodeposition.

230

Metal ions from the liquid solution are electrodeposited on electrodes by applying a current.

240

FIG. 2
## INTERNATIONAL SEARCH REPORT

### A. CLASSIFICATION OF SUBJECT MATTER

PCT/US16/40145

**IPC(8):** C22B 3/02, 9/16, 4/02; H05B 7/06 (2016.01)

CPC: C22B 4/08, 9/18; C25C 1/12

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)

- IPC(8): C22B 3/02, 9/16, 4/02, 15/00; H05B 7/06 (2016.01)
- CPC: C22B 3/00, 4/08, 9/18, 15/00; C25C 1/12; USPC: 75/347; 205/367, 582

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

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

- PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, RU, AT, CH, TH, BR, PH, SE, NO, DK, FI, BE, NL, LU, MX, INPADOC Data); EBSO; PatentsGoogle; Google Scholar; sciencedirect.com; electrolytic cell, molten salt electrolyte, copper, fused quartz, producing gas at anode, stirrer, reference electrode

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 3,777,001 A (VELOSO, AE) 4 December 1973; abstract; figure; column 2, lines 15-20, 30-55, 65-71; column 3, lines 1-75; column 4, lines 1-20</td>
<td>1, 4-5, 13 --- 2-3, 6-12, 14-18</td>
</tr>
<tr>
<td>Y</td>
<td>(ELSENTRIECY, HH et al.) Clean and efficient extraction of copper ions and deposition as metal. Resource-Efficient Technologies. 17 July 2015. vol. 1; page 29, paragraphs 1-4; page 31, paragraphs 5-4; figure 6</td>
<td>2, 6-12, 14-18</td>
</tr>
<tr>
<td>Y</td>
<td>US 5,118,396 A (CLAUS, KG et al.) 2 June 1992; column 2, lines 40-50; column 4, lines 60-65</td>
<td>3, 9, 16</td>
</tr>
<tr>
<td>A</td>
<td>US 4,888,102 A (KESSIE, RW) 19 December 1989; entire document</td>
<td>1-18</td>
</tr>
<tr>
<td>A</td>
<td>WO 2014/153570 A9 (TRANSTAR GROUP, LTD) 25 September 2014; entire document</td>
<td>1-18</td>
</tr>
</tbody>
</table>

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
  - "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
  - "Y" 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
  - "A" document member of the same patent family

Date of the actual completion of the international search: 22 August 2016 (22.08.2016)

Date of mailing of the international search report: 07 SEP 2016

Name and mailing address of the ISA/Authorized officer

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-8300

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774