



(12) **Patent Application Publication**
Whitehead et al.

(43) **Pub. Date:** **Oct. 14, 2010**

Publication Classification

(51) **Int. Cl.**
C25B 1/00 (2006.01)
C25C 1/22 (2006.01)
C25C 1/20 (2006.01)
C25C 1/18 (2006.01)
C25C 1/14 (2006.01)
C25C 1/00 (2006.01)
C25C 1/12 (2006.01)

(52) **U.S. Cl. 205/538; 205/334; 205/563; 205/565;
205/597; 205/610; 205/560; 205/464; 205/586**

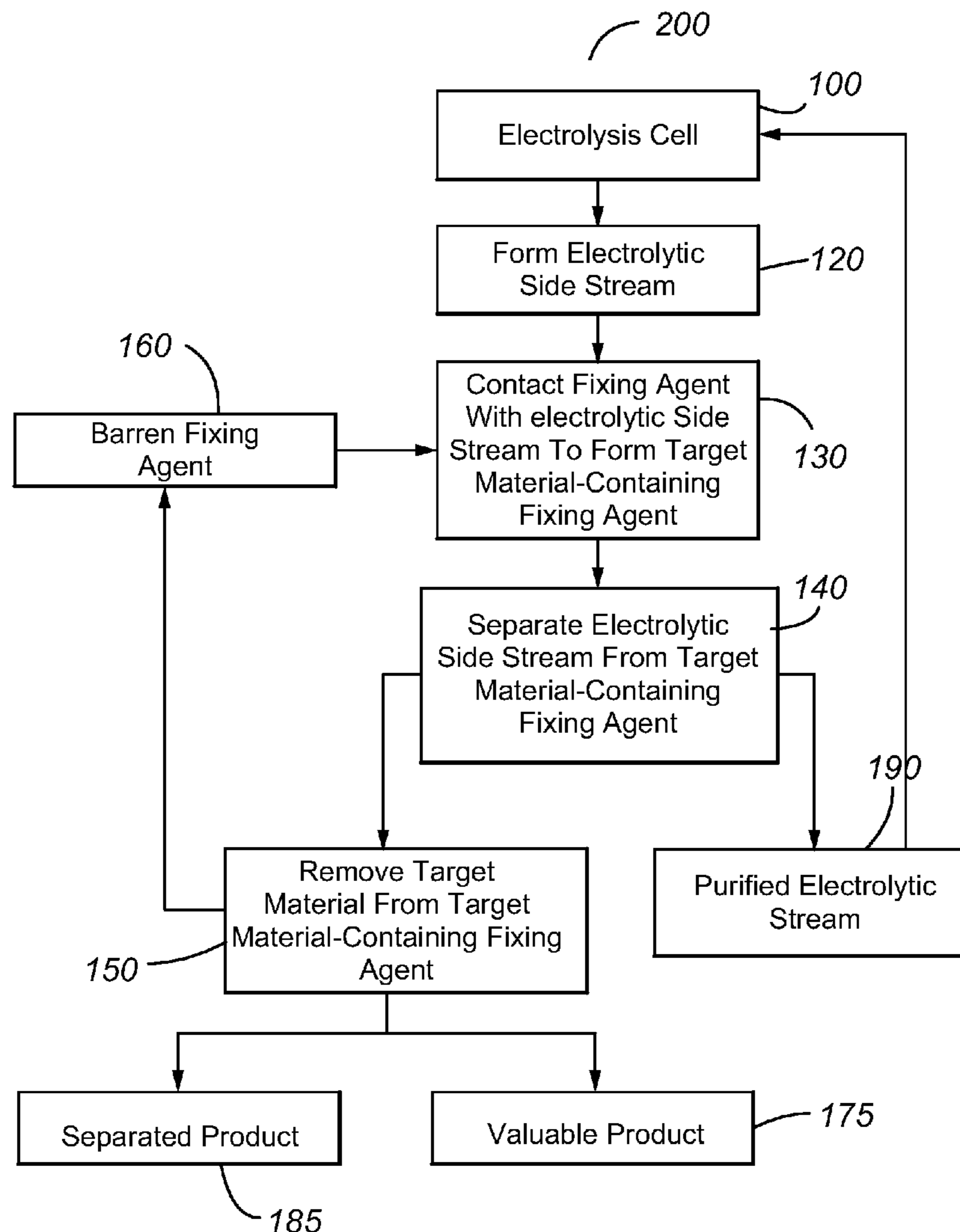
(57) **ABSTRACT**

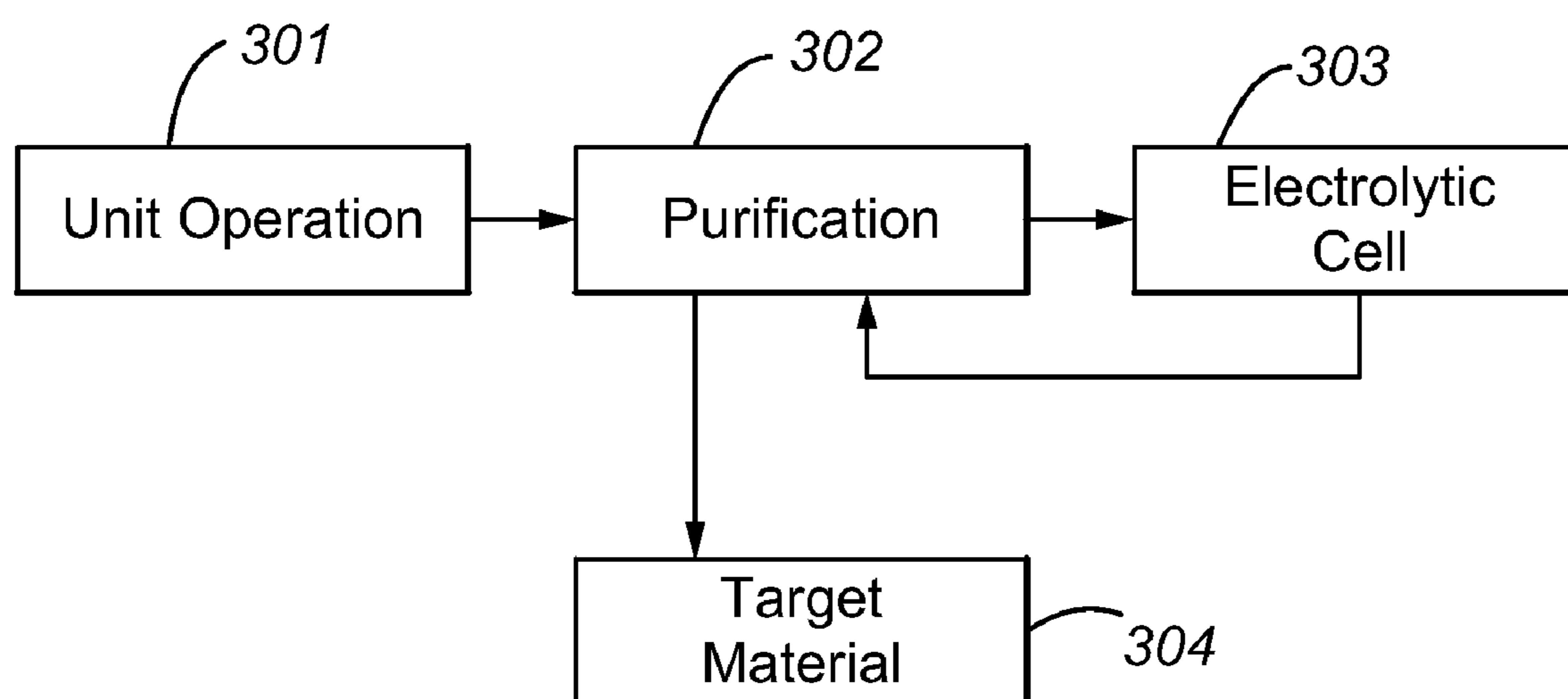
The invention relates generally to a process for removing one or more contaminants from an electrolytic solution and more particularly to a process for removing the one or more contaminants contained in an electrorefining solution using rare earth metals.

(22) Filed: **Apr. 9, 2010**

Related U.S. Application Data

(60) Provisional application No. 61/168,097, filed on Apr. 9, 2009.



***Fig. 1***

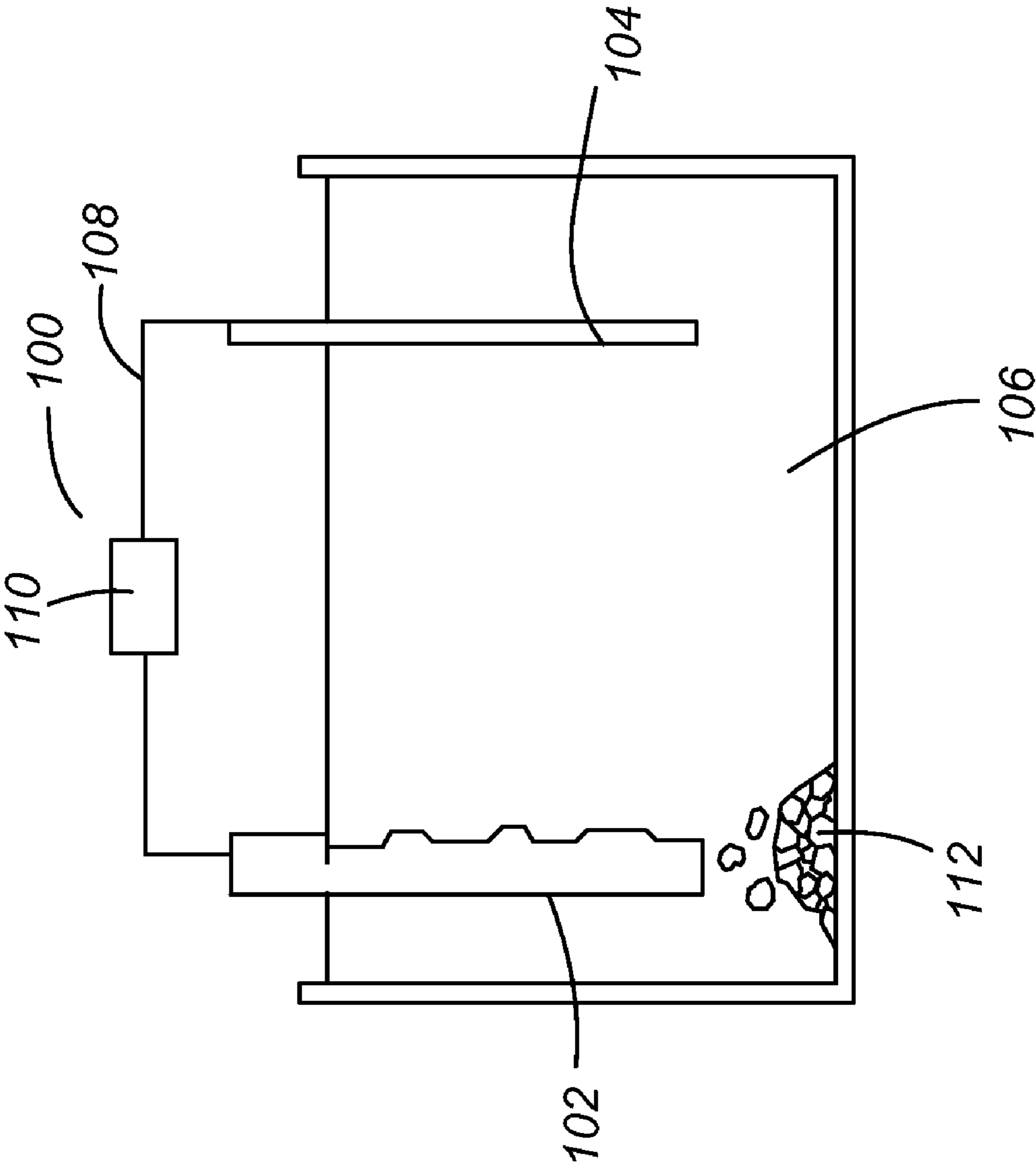


Fig. 2

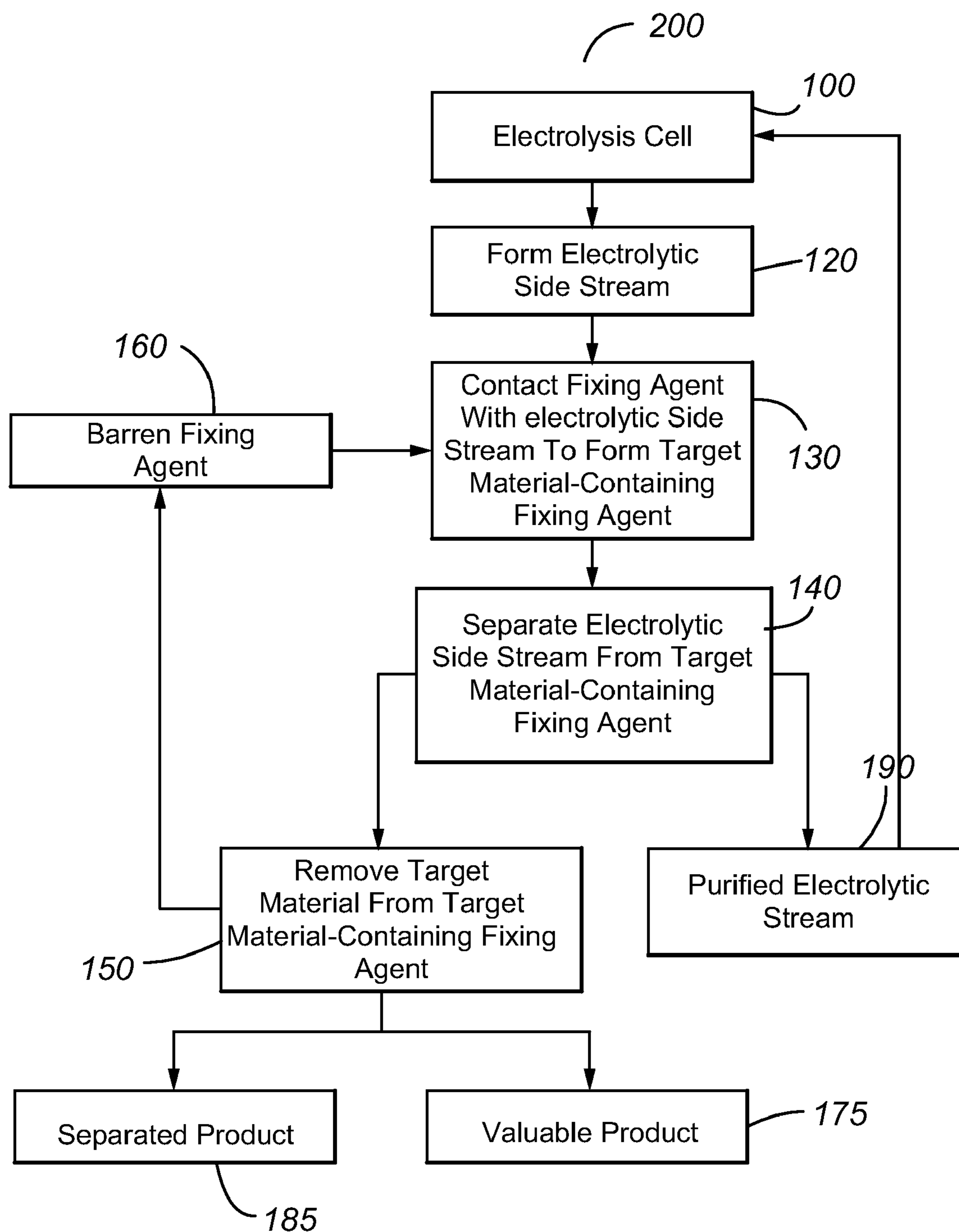


Fig. 3

USE OF A RARE EARTH FOR THE REMOVAL OF ANTIMONY AND BISMUTH

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of U.S. Provisional Application Ser. No. 61/168,097 filed Apr. 9, 2009, entitled "Use of High Surface Area Cerium Oxide Media for the Removal of Antimony and Bismuth from Water", which is incorporated herein by this reference in its entirety.

[0002] Cross reference is made to U.S. patent application Ser. Nos. 12/616,653, filed Nov. 11, 2009; 11/958,602, filed Dec. 18, 2007; 11/958,644, filed Dec. 18, 2007; and 11/958,968, filed Dec. 18, 2007, each of which is incorporated herein by this reference in its entirety.

FIELD OF INVENTION

[0003] The invention relates generally to a process for removing one or more contaminants from an electrolytic solution and more particularly to a process for removing the one or more contaminants in an electrorefining solution using rare earth metals.

BACKGROUND OF THE INVENTION

[0004] Electrometallurgy is a process for recovering a metal from an electrolytic solution using electricity. The electrometallurgy process comprises passing an electric current through the electrolytic solution to extract or purify the metal. The electrometallurgical process of extracting the metal from the electrolytic solution is typically called electrowinning, while the process of purifying the metal by passing the electric current through the electrolytic solution is called electrorefining.

[0005] Electrorefining comprises dissolving the metal at an anode and re-depositing the same metal at a cathode in an electrochemical cell. In electrorefining, the metal being refined is oxidized at the anode and enters the electrolytic solution as cation according to the following half-cell reaction:



The oxidation process produces electrons at the anode. The number (n) of electrons (e^{-}) produced is determined by the cationic species (M^{n+}) of the metal (M) produced electrochemically.

[0006] Typically, the anode contains species other than the metal being electrorefined, these species may have higher, lower, or similar oxidation potentials to the metal being electrorefined. Species having higher oxidation potentials than the metal being electrorefined are considered to be more noble. More noble species, such as noble metals, are not oxidized at the anode and do not enter the electrolytic solution during the anodic process. As such, a noble metal-containing sludge forms during the anodic process of dissolving of the metal. Species contained within the anode having oxidation potentials substantially similar to or oxidatively more active than the metal are typically oxidized and enter the electrolytic solution as contaminants during the anodic dissolving process. These contaminants are present within the electrolytic solution as dissolved species and accumulate within the electrolytic solution. More importantly, these contaminants may interfere with the cathodic deposition of the metal.

[0007] The cathodic re-deposition process of the metal is represented by the chemical half-reaction:



where, the dissolved (M^{n+}) cationic species of the metal is reduced to the elemental metal (M^0) by taking on n electrons (e^{-}) at the cathode. Compared to the anode, the cathode contains a substantially purer form of the metal. The cathodically re-deposited metal is substantially free of the more noble metals and/or the contaminants previously contained within the anode.

[0008] Copper is a metal that is commonly electrorefined. The noble metals commonly recovered in the electrorefining of copper are gold, silver and platinum group metals. The contaminants, other than the noble metals, typically are arsenic, antimony, bismuth, selenium, tellurium, lead, tin, iron, cobalt, zinc, and nickel.

[0009] The presence of arsenic, antimony and bismuth are troublesome materials in the electrorefining of copper. Arsenic, antimony and bismuth typically are contained in copper anodes used in copper electrorefining. Copper, arsenic, antimony and bismuth have similar standard reduction potentials. During the electrorefining process most of the arsenic and some of the antimony and bismuth contained in the copper anode are electrochemically dissolved in the electrolytic solution. As such, arsenic, antimony, and bismuth concentrations within the electrolytic solution increase. One or more of the arsenic, antimony and bismuth may be cathodically electrodeposited with the copper affecting the cathode quality, such as copper grain structure and copper purity level of the electrorefined copper. Therefore, it is important to control the concentration of arsenic, bismuth, antimony and other contaminants during the electrorefining of copper.

SUMMARY OF THE INVENTION

[0010] These and other needs are addressed by the various embodiments and configurations of the present invention. This disclosure relates generally to target material removal from an electrolytic solution and the stabilization of one or both of the target material and the electrolytic solution.

[0011] One embodiment of the present invention is a process comprising:

[0012] (a) receiving a rich feed solution having a target material and a valuable metal;

[0013] (b) electrodepositing the valuable metal onto an electrode to form an electrolyzed solution, wherein at least most of the valuable metal is electrodeposited onto the electrode; and

[0014] (c) contacting at least a portion of at least one of the rich feed solution and the electrolyzed solution with a rare earth-containing fixing agent to form a target material-loaded insoluble fixing agent, the target material-loaded insoluble fixing agent comprising at least most of the target material in the at least a portion of the at least one of the rich feed solution and the barren solution, wherein the target material, in the target material-loaded insoluble fixing agent, forms a composition with the fixing agent and the target material is at least one of antimony and bismuth.

[0015] In one configuration, the process further comprises separating the target material-laded insoluble fixing agent from at least one of the rich feed stream and the electrolyzed solution to form a purified stream. In another configuration, the process further comprises at least one of recovering the

target material and recycling the purified stream to electrolysis cell. The electrodepositing process is one of electrowinning or electrorefining.

[0016] Preferably, little, if any, of the valuable metal is removed from one or both of the rich feed stream and the electrolyzed solution in the contacting step (c). The valuable metal is a metal having an atomic number of 22-30, 40-48, and 72-79.

[0017] In one configuration, the process further comprises contacting the target material-loaded insoluble fixing agent with a stripping solution to dissolve, solublize, or otherwise displace most of the target material in the target material-loaded insoluble fixing agent to form a loaded stripping solution and barren insoluble fixing agent, wherein the stripping solution comprises at least one of a strong base, an oxalate, ethanedioate, a strongly absorbing exchange oxyanion, a reductant or reducing agent, and an oxidant or oxidizing agent. In another configuration, the process further comprises cycling the barren insoluble fixing agent to contacting step (c), wherein the barren insoluble fixing agent is contacted with one of the rich feed stream and the electrolyzed solution to form the target material-loaded insoluble fixing agent. In yet another configuration, the process further comprises removing at least most of the dissolved target material from the loaded stripping solution.

[0018] A preferred embodiment of the present invention is a process comprising:

[0019] (a) forming, from an electrolytic cell, an electrolytic side stream comprising a target material and a valuable metal, wherein the electrolytic side stream has a first target material concentration;

[0020] (b) contacting the electrolytic side stream with an insoluble fixing agent to form a target material-loaded insoluble fixing agent and a purified electrolytic stream, the insoluble fixing agent comprising at least one of yttrium, scandium, and a lanthanoid, the target material-loaded insoluble fixing agent comprising most of the target material in the electrolyte side stream, wherein the target material, in the target material-loaded insoluble fixing agent, forms a composition with the insoluble fixing agent; and

[0021] (c) cycling the purified electrolytic stream to the electrolytic cell, wherein the purified side stream has a second target material concentration substantially less than the first target material concentration.

[0022] In contacting step (b), substantially little, if any, of the valuable metal is removed from the electrolytic side stream. Preferably, the valuable metal is copper.

[0023] In a preferred embodiment, the target material is at least one of arsenic, antimony, bismuth, tin, lead, selenium, tellurium, platinum, iridium, ruthenium, and rhodium. In another preferred embodiment, the target material is an oxyanion. In a more preferred embodiment, the target material is an oxyanion of at least one of tellurium, selenium, bismuth, antimony and arsenic.

[0024] In one configuration, the insoluble fixing agent is a finely divided solid having a surface area from about 25 m²/g to about 500 m²/g. In another configuration, the process further comprises contacting the target material-loaded insoluble fixing agent with a stripping solution to dissolve, solublize, or otherwise displace most of the target material in the target material-loaded insoluble fixing agent to form a loaded stripping solution and barren insoluble fixing agent. Preferably, the stripping solution is one of a strong base, an

oxalate, ethanedioate, a strongly absorbing exchange oxyanion, a reductant or reducing agent, and oxidant or oxidizing agent.

[0025] In another configuration, the process further comprises cycling the barren insoluble fixing agent to contacting step (b), wherein the barren insoluble fixing agent is contacted with the electrolytic side stream to form the target material-loaded insoluble fixing agent.

[0026] In yet another configuration, the process further comprises removing at least most of the dissolved target material from the loaded stripping solution.

[0027] In still yet another configuration of the process, first and second fixing agents are used. In a first step, the electrolyte side stream comprises a target material-bearing stream, having a first concentration of target material. The electrolyte side stream is contacted with an insoluble first fixing agent, such as an adsorbent or absorbent, to produce a target material-bearing first fixing agent. The first contacting step removes most, if not all, of the target material from the electrolyte side stream. In a second contacting step, the target material-bearing first fixing agent is contacted with an alkaline stripping solution ("release agent") to produce an intermediate target material-rich solution having a second concentration of the target material. The second concentration of target material may exceed the first concentration of target material. The alkaline stripping solution can be or include, for example, a leaching agent. Commonly, the second concentration of target material is a concentration about equal to the solubility limit of the target material (at the process conditions of the second step). More commonly the second concentration of the target material is between about 0.1 and about 2,500 g/L, even more commonly between about 0.1 and about 1,000 g/L, and even more commonly between about 0.25 g/L and about 500 g/L. Finally, a soluble or dissolved second fixing agent is contacted with the intermediate target material-rich solution in an amount sufficient to precipitate most, if not all, of the target material as a target material-bearing solid. The target material-bearing solid may be separated from the intermediate target material-rich solution by any suitable solid/liquid separation technique to produce a separated solid for disposal and/or recovery of the target material and a stripping solution for recycle to the second contracting step.

[0028] The insoluble fixing agent, including the first fixing agent, is commonly a particulate solid. The insoluble fixing agent (including the first fixing agent) is preferably an insoluble rare earth metal compound, more preferably an insoluble rare earth oxide comprising an insoluble rare earth compound, such as hydrous or anhydrous rare earth oxides, fluorides, carbonates, fluorocarbonates, silicates, and the like. A particularly preferred insoluble fixing agent is CeO₂. The fixing agent is particularly effective in removing arsenic having an oxidation state of +3 or +5.

[0029] The soluble or dissolved second fixing agent typically has an oxidation state lower than the oxidation state of the insoluble (first) fixing agent. Preferably, the oxidation state of the second fixing agent is one of +3 or +4. The soluble fixing agent preferably is a soluble rare earth metal compound and more preferably includes salts comprising rare earth compounds, such as bromides, nitrates, phosphites, chlorides, chlorites, chlorates, nitrates, and the like. More preferably, the soluble fixing agent is a rare earth (III) chloride.

[0030] The intermediate solution can include a valuable product. The valuable product is commonly any metal of

interest, more commonly includes one or more of the transition metals and even more commonly includes a metal selected from the group of metals consisting of copper, nickel, cobalt, lead, precious metals, and mixtures thereof. All or a portion of the residual valuable product may be recovered from the intermediate solution.

[0031] Another preferred embodiment of the present invention is a process comprising:

[0032] (a) forming from an electrolytic cell an electrolytic side stream comprising a target material and a valuable metal, wherein the electrolytic side stream has a first target material concentration;

[0033] (b) contacting the electrolytic side stream with a fixing agent to form an insoluble composition;

[0034] (c) removing the insoluble composition from the electrolytic side stream to form a purified electrolyte stream; and

[0035] (d) cycling the purified electrolytic stream to the electrolytic cell, wherein the purified side stream has a second target material concentration substantially less than the first target material concentration.

[0036] In one configuration, the fixing agent is a non-rare earth salt additive. The non-rare earth salt additive is a non-rare earth metal having a +3 oxidation and is substantially free of a rare earth. The insoluble composition is a precipitate formed between the target material and the non-rare earth salt additive. Preferably, the non-rare earth salt additive comprises one of boron, aluminum, gallium, indium, thallium and a transition metal.

[0037] In another configuration, the rare earth-containing fixing agent is a rare earth salt additive. The rare earth salt additive is a rare earth having a +3 oxidation state and a non-rare metal having a +3 oxidation state. The insoluble composition is a precipitate formed between the target material and at least one of the rare earth and the non-rare earth. Preferably, the non-rare earth metal comprises one of boron, aluminum, gallium, indium, thallium and a transition metal.

[0038] In yet another configuration, the fixing agent is a rare earth, preferably a soluble rare earth. The insoluble composition is an insoluble target material-containing composition formed by the contacting of the target material and the soluble rare earth.

[0039] The electrolytic side stream contains a valuable metal. At least most, if not all, of the valuable metal within the electrolytic side stream is cycled to the electrolytic cell.

[0040] In a preferred embodiment, the electrolytic side stream contains copper. At least most, if not all, of the copper within the electrolytic side stream is cycled to the electrolytic cell by the purified electrolytic stream.

[0041] In yet another preferred embodiment of the present invention is a process comprising:

[0042] (a) forming from an electrolytic cell an electrolytic side stream comprising a target material and dissolved copper, wherein electrolytic side stream has a first target material concentration;

[0043] (b) contacting the electrolytic side stream with an insoluble rare earth-containing fixing agent to form a target material-loaded insoluble fixing agent and a purified electrolytic stream having at least most, if not all, of the copper contained with the electrolytic side stream, the rare earth-containing insoluble fixing agent comprising at least one of yttrium, scandium, and a lanthanoid, the target material-loaded insoluble fixing comprising most of the target material in the electrolyte side stream, wherein the target material, in

the target material-loaded insoluble fixing agent, forms a composition with the insoluble fixing agent; and

[0044] (c) cycling the purified electrolytic stream to the electrolytic cell, wherein the purified side stream has a second target material concentration substantially less than the first target material concentration.

[0045] Preferably, substantially little, if any, of the dissolved copper is removed from the electrolytic side stream in the contacting step (b). Moreover, the process preferably further comprises:

[0046] (d) contacting the target material-loaded insoluble fixing agent with a stripping solution to dissolve, solublize, or otherwise displace most of the target material in the target material-loaded insoluble fixing agent to form a loaded stripping solution and barren insoluble fixing agent, wherein the stripping solution comprises at least one of a strong base, an oxalate, ethanedioate, a strongly absorbing exchange oxyanion, a reductant or reducing agent, and oxidant or oxidizing agent.

[0047] In another configuration, the process further comprises:

[0048] (e) cycling the barren insoluble fixing agent to contacting step (b); and

[0049] (f) removing at least most of the dissolved target material from the loaded stripping solution.

[0050] Preferably, the barren insoluble fixing agent is contacted with the electrolytic side stream to form the target material-loaded insoluble fixing agent.

[0051] In some embodiments, the target material will be present in a reduced oxidation state and this condition might be undesirable. In such cases, an oxidant may be contacted with the electrolyte feed stream to increase the target material oxidation state. Using arsenic as an example, the presence of arsenite might favor the use of an oxidant before the fixing agent is applied.

[0052] In another embodiment, a process is provided that includes the steps of:

[0053] (a) contacting an electrolytic solution comprising a target material with a soluble fixing agent, the soluble fixing agent comprising a rare earth, to form an insoluble target material-containing composition comprising the target material and the rare earth; and

[0054] (b) removing the insoluble target material-containing composition from the electrolytic solution to form a purified electrolytic solution.

[0055] The insoluble target material-containing composition is typically in the form of precipitate that can be removed as a solid. Preferably, the insoluble target material-containing composition has at least about 0.01 wt. %, even more preferably at least about 0.1 wt. %, and even more preferably ranges from about 5 to about 50 wt. % of the target material. The target material is commonly in the form of an oxygen-containing anion with an oxyanion being illustrative. Preferably, the target material is one or more of arsenic, antimony, bismuth, selenium, tellurium, tin, platinum, ruthenium, rhodium, and iridium. The soluble fixing agent, or precipitant, can be supported by a suitable carrier or can be unsupported.

[0056] In yet another embodiment, a method includes the steps of:

[0057] (a) providing an electrolytic stream containing a target material;

[0058] (b) contacting the electrolytic stream with one or both of the following:

[0059] (i) a rare earth salt additive, the rare earth salt additive comprising a rare earth in the +3 oxidation state and a non-rare metal in the +3 oxidation state; and

[0060] (ii) a non-rare earth salt additive, the non-rare salt additive comprising a non-rare earth metal in the +3 oxidation state and being substantially free of a rare earth; and forming a precipitate between the target material and at least one of the rare earth and non-rare earth salt additives.

[0061] The non-rare earth metal can be any non-rare earth metal in the +3 oxidation state, with transition metals, boron, aluminum, gallium, indium, and thallium being preferred, and the transition metals and aluminum being particularly preferred. Preferred transition metals include the elements having atomic numbers 22-29, 40-45, 47, 72-77, and 79.

[0062] The rare earth salt additive is, in one formation, a bimetallic, lanthanide-based salt solution. The non-rare earth salt additive, in a preferred formulation, contains aluminum in the +3 oxidation state. In a preferred formulation, the rare earth salt additive includes cerium in the +3 oxidation state and the non-rare earth salt additive includes aluminum in the +3 oxidation state.

[0063] In still yet another embodiment, a method is provided that includes the steps:

[0064] (a) providing an electrolytic stream comprising a dissolved target material and dissolved valuable product, the target material being in the form of an oxyanion and the valuable product being at least one of a transition metal;

[0065] (b) contacting the electrolytic stream with a rare earth fixing agent to precipitate at least most of the dissolved target material as a target material-containing precipitate while leaving at least most of the valuable product dissolved in a treated electrolytic stream; and

[0066] (c) separating at least most of the target material-containing precipitate from the treated electrolytic stream.

[0067] The present invention can include a number of advantages depending on the particular configuration. The process of the present invention can remove variable amounts of target materials as needed to comply with application and process requirements. For example, the target material removal process can remove high concentrations of target materials to produce a treated electrolytic stream having no more than about 500 ppm, in some cases no more than about 100 ppm, in other cases no more than about 50 ppm. In still other cases, the target material removal process can produce a treated electrolytic stream having no more than about 20 ppb, and in still other cases no more than about 1 ppb target material. The insoluble rare earth/target material product can be qualified as non-hazardous waste. The target material removal process can be relatively insensitive to pH. The disclosed process can effectively fix target materials, particularly arsenic, antimony and/or bismuth, from electrolytic streams over a wide range of pH levels, as well as at extremely high and low pH values. In contrast to many conventional target material removal technologies, the capability of the present invention to treat electrolytic streams over a wide range of pH values can eliminate the need to alter and/or maintain the pH of the solution within a narrow range when removing the target material. Moreover, where the electrolytic stream is a copper elector fining stream, the stream can be flexibly treated without significant concern for the pH of electrolytic stream. Further still, significant cost advantages

can be achieved by eliminating the need to adjust and maintain pH while fixing the target materials contained within the electrolytic stream. The target material removal process can also be relatively insensitive to target material concentration. The process can remove relatively low and/or high levels of target materials, particularly arsenic, antimony and bismuth from electrolytic streams. The process can be a robust and/or versatile process.

[0068] These and other advantages will be apparent from the disclosure of the invention(s) contained herein.

[0069] As used herein, the term “a” or an entity refers to one or more of that entity. As such, the terms “a” (or “an”), one or more and at least one can be used interchangeably herein. It is also to be noted that the terms “comprising”, “including”, and “having” can be used interchangeably.

[0070] As used herein, “absorption” refers to the penetration of one substance into the inner structure of another, as distinguished from adsorption.

[0071] As used herein, “adsorption” refers to the adherence of atoms, ions, molecules, polyatomic ions, or other substances of a gas or liquid to the surface of another substance, called the adsorbent. The attractive force for adsorption can be, for example, ionic forces such as covalent, or electrostatic forces, such as van der Waals and/or London’s forces.

[0072] As used herein, at least one, one or more, and “and/or” are open-ended expressions that are both conjunctive and disjunctive in operation. For example, each of the expressions at least one of A, B and C”, at least one of A, B, or C”, one or more of A, B, and C”, one or more of A, B, or C” and “A, B, and/or C” means A alone, B alone, C alone, A and B together, A and C together, B and C together, or A, B and C together.

[0073] As used herein, a “composition” refers to one or more chemical units composed of one or more atoms, such as a molecule, polyatomic ion, chemical compound, coordination complex, coordination compound, and the like. As will be appreciated, a composition can be held together by various types of bonds and/or forces, such as covalent bonds, metallic bonds, coordination bonds, ionic bonds, hydrogen bonds, electrostatic forces (e.g., van der Waal’s forces and London’s forces), and the like.

[0074] As used herein, “insoluble” refers to materials that are intended to be and/or remain as solids in water and are able to be retained in a device, such as a column, or be readily recovered from a batch reaction using physical means, such as filtration. Insoluble materials should be capable of prolonged exposure to water, over weeks or months, with little (<5%) loss of mass.

[0075] As used herein, “oxyanion” or oxoanion is a chemical compound with the generic formula $A_xO_y^{z-}$ (where A represents a chemical element other than oxygen and O represents an oxygen atom). In target material-containing oxyanions, “A” represents metal, metalloid, and/or Se (which is a non-metal), atoms. Examples for metal-based oxyanions include chromate, tungstate, molybdate, aluminates, zirconate, bismuthate, etc. Examples of metalloid-based oxyanions include arsenate, arsenite, antimonate, germanate, bismuthate, silicate, etc.

[0076] As used herein, “particle” refers to a solid or microencapsulated liquid having a size that ranges from less than one micron to greater than 100 microns, with no limitation in shape.

[0077] As used herein, “precipitation” refers not only to the removal of target material-containing ions in the form of

insoluble species but also to the immobilization of contaminant-containing ions on or in insoluble particles. For example, “precipitation” includes processes, such as adsorption and absorption.

[0078] As used herein, “rare earth” refers to one or more of yttrium, scandium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium erbium, thulium, ytterbium, and lutetium. As will be appreciated, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium erbium, thulium, ytterbium, and lutetium are known as lanthanoids.

[0079] As used herein, “soluble” refers to materials that readily dissolve in water. For purposes of this invention, it is anticipated that the dissolution of a soluble compound would necessarily occur on a time scale of minutes rather than days. For the compound to be considered to be soluble, it is necessary that it has a significantly high solubility product such that upwards of 5 g/L of the compound will be stable in solution.

[0080] As used herein, “sorb” refers to adsorption and/or absorption.

[0081] The preceding is a simplified summary of the invention to provide an understanding of some aspects of the invention. This summary is neither an extensive nor exhaustive overview of the invention and its various embodiments. It is intended neither to identify key or critical elements of the invention nor to delineate the scope of the invention but to present selected concepts of the invention in a simplified form as an introduction to the more detailed description presented below. As will be appreciated, other embodiments of the invention are possible utilizing, alone or in combination, one or more of the features set forth above or described in detail below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0082] The accompanying drawings are incorporated into and form a part of the specification to illustrate several examples of the present invention(s). These drawings, together with the description, explain the principles of the inventions(s). The drawings simply illustrate preferred and alternative examples of how the invention(s) can be made and used and are not to be construed as limiting the invention(s) to only the illustrated and described examples.

[0083] Further features and advantages will become apparent from the following, more detailed, description of the various embodiments of the invention(s), as illustrated by the drawings referenced below.

[0084] FIG. 1 depicts a process according to an embodiment of the present invention;

[0085] FIG. 2 depicts an electrolysis cell according to an embodiment of the present invention; and

[0086] FIG. 3 depicts another process according to another embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0087] One aspect of the present invention uses one or both of insoluble and soluble fixing agents to remove selected target materials from an electrolytic solution. Preferably, the electrolytic solution comprises an aqueous solution. The fixing agent, whether soluble or insoluble, preferably includes a rare earth. Specific examples of such materials for removing target materials include lanthanum (III) compounds, soluble lanthanum metal salts, lanthanum oxide, cerium dioxide, and

soluble cerium salts, which have been described in U.S. patent application Ser. No. 12/616,653 with a filing date of Nov. 11, 2009, the contents of which is incorporated herein in its entirety by this reference.

[0088] The electrolytic solution can be a rich electrolytic solution formed in unit operation **301** (FIG. 1) and/or an electrolyzed-electrolytic solution formed in an electrolysis cell **303**. The rich electrolytic solution is substantially pregnant with a valuable metal to be electrodeposited on an electrode of the electrolysis cell **303**. The electrolyzed-electrolytic solution can be one of an electrolytic solution substantially depleted of the valuable metal (which was electrodeposited on an electrode, such as in an electrowinning process) or substantially laden with contaminants generated within the electrolysis cell (such as in an electrorefining process).

[0089] The unit operation comprises forming an electrolytic solution rich in the valuable metal to be electrodeposited on an electrode in the electrolysis cell **303**. While not wanting to be limited by example, the unit operation **301** may comprise one or more of resin-in leach, carbon-in leach, resin-in pulp, carbon-in pulp, stripping, leaching, ion-exchange, hydrometallurgy and combinations thereof. The electrolytic solution can be formed in leaching process, such as, an acid leach, bio-leach, pressure oxidation leach, or other leaching process known to one of ordinary skill in the art. Furthermore, the leaching process can include a resin or carbon source to concentrate and/or capture the valuable metal during the leaching process, including pulp leaching processes. The electrolytic solution can be formed in an ion-exchange process, wherein the valuable metal is captured and/or concentrated on an ion-exchange resin, followed by elution to form a concentrated solution containing the valuable metal. The electrolytic solution can be formed by a stripping and/or extraction process, such as, with a complexing and/or phase transfer agent to selectively extract and concentrate the valuable metal in solution.

[0090] A target material contained with the electrolytic solution is removed contacting the electrolytic solution with a rare earth-containing fixing agent to form a target material-loaded insoluble fixing agent (process **302**). The target material contained with the electrolytic solution can be from one or both of the unit operation **301** or the electrolysis cell **303**. Preferably, at least most, if not all, of the target material is removed from the electrolytic solution by the contacting of the electrolytic solution with the rare earth-containing fixing agent. The target material-loaded insoluble fixing agent is separated from at least one of the rich feed stream and the electrolyzed stream to form a purified stream. The purified stream forms at least some of the electrolytic solution comprising the electrolytic cell **303**.

[0091] In one embodiment, the process **302** can further include separating the target material from the target material-loaded insoluble fixing agent to form a target material product **304**.

[0092] The particular target materials removed depend on whether the fixing agent is insoluble or soluble in the aqueous solution, particularly under standard conditions (e.g., Standard Temperature and Pressure “STP”). While not wishing to be bound by any theory, it is believed, using arsenic and cerium as an example, that insoluble cerium fixing agents effectively remove arsenic, when arsenic is part of a complex multi-atomic unit having an oxidation state preferably of +3 or higher and even more preferably a oxidation state from +3

to +5, while soluble cerium fixing agents remove effectively arsenic, when arsenic is part of a complex multi-atomic unit and has an oxidation state of +5.

[0093] “Target materials”, as used herein, preferably includes not only arsenic but also elements having an atomic number selected from the group of consisting of atomic numbers 5, 9, 13, 14, 22 to 25, 31, 32, 33, 34, 35, 40 to 42, 44, 45, 49 to 53, 72 to 75, 77, 78, 80, 81, 82, 83, 85, 92, 94, 95, and 96 and more preferably from the group consisting of atomic numbers 13, 14, 33, 34, 40 to 42, 44, 45, 50, 51, 52, 77, 78, 80, 81, 82, 83, 92, 94, 95, and 96. These atomic numbers include the elements of arsenic, aluminum, astatine, bromine, boron, fluorine, iodine, silicon, titanium, vanadium, chromium, manganese, gallium, thallium, germanium, selenium, mercury, zirconium, niobium, molybdenum, ruthenium, rhodium, indium, tin, antimony, tellurium, hafnium, tantalum, tungsten, rhenium, iridium, platinum, lead, uranium, plutonium, americium, curium, and bismuth. Examples of target materials amenable to removal and stabilization by the insoluble fixing agent include, without limitation, target materials in the form of complex anions, such as metal, metalloid, and selenium oxyanions.

[0094] In a preferred embodiment, the target material removed comprises one of tellurium, selenium, lead, bismuth, antimony, tin, arsenic, platinum, iridium, ruthenium, and rhodium. In a more preferred embodiment, the target material removed comprises one of tellurium, selenium, lead, tin, antimony, bismuth and arsenic.

[0095] In one configuration, the fixing agent reacts with the target material contained in electrolytic solution to form a purified electrolytic solution. Preferably, the target material comprises an oxyanion. In some instances, the fixing agent can comprise a mixture of fixing agents, the mixture comprising soluble or insoluble fixing agents. The fixing agent reacts with the target material to form an insoluble species with the fixing agent. The insoluble species is immobilized, for example, by precipitation, thereby yielding a treated and substantially purified electrolytic solution.

[0096] The electrolytic solution further comprises an aqueous solution of the dissolved cations of the valuable metal undergoing electrorefining. More over, the electrolytic solution comprises a mineral acid conjugate base, such as, but not limited to sulfate (SO_4^{2-} , hydrogen sulfate (HSO_4^{1-}), nitrate (NO_3^{1-} , chloride (Cl^{1-} , and bromide (Br^{1-}). In some embodiments, the electrolytic can comprise a sulfamate solution, such as, in some configurations for electrorefining of nickel.

[0097] FIG. 2 depicts an electrolysis cell 100 for electrorefining of a valuable-metal. The electrolysis cell 100 comprises an anode 102, a cathode 104, an electrolytic solution 106, an external current path 108 and a power source 110. In the electrorefining process, the anode 102 comprises a contaminant-containing valuable-metal. The cathode 104 preferably comprises one of a substantially contaminant-free valuable-metal or a metal substantially non-reactive with the valuable-metal upon which the valuable-metal is electrodeposited. The external current path 108 comprises an electrically conductive path, such as, a wire typically used within an electrical circuit. The power source 110 is any electric power source, such as, an electrical generator, an electrical power sub-station, or a battery.

[0098] The electrolytic solution 106 comprises an electrolyte solution, preferably an aqueous electrolyte solution. An electrolyte solution means a solution comprising a solvent (such as, water) and ionically dissociated components, where

the ionically dissociated components comprise cations and anions that conduct electricity and can be separated from the solution by an electrically charged electrode. The electrolytic solution 106 comprises the valuable-metal in a dissolved state as cation, such as M^{n+} , where n is an integer greater than zero. The electrolyte solution 106, preferably, further comprises a mineral acid or the conjugate base of a mineral acid. Preferred mineral acids comprise, without limitation, hydrochloric, hydrobromic, sulfuric, and nitric acids. Preferably, the mineral acid comprises sulfuric acid (H_2SO_4) and/or the conjugate bases of sulfuric acid (HSO_4^{1-} and/or SO_4^{2-}).

[0099] In the electrorefining process, the anode 102 has a positive charge (that is, the anode accepts electrons in an oxidative process) and the cathode 104 has a negative charge (that is, the cathode releases electrons in a reductive process). The electrochemical process at the anode 102 comprises dissolving the valuable-metal at the anode 102. That is, electrons are withdrawn and/or taken away from the anode 102 by the power source 110 and the oxidized species of the valuable-metal and contaminants are generated. The electrochemical reactions of the anode 102 can be expressed by the following chemical reactions:



where M represents the valuable-metal, K represents the one or more contaminants contained within the anode 102, and n and m are integers greater than zero.

[0100] The oxidized species M^{n+} and K^{m+} are dissolved in the electrolytic solution 106 as soluble components of the electrolytic solution 106. The oxidized species K^{m+} comprises contaminants substantially having electrochemical oxidation potentials (that is, for electrochemical potentials for the given electrolysis cell 100) about equal or more reactive (that is, less noble) than the valuable-metal.

[0101] In some configurations, the oxidized contaminant K is in the form of an oxyanion. The oxyanion comprises $\text{K}_x\text{O}_y^{z-}$ (where K represents a chemical element other than oxygen and O represents an oxygen atom).

[0102] Contaminants more noble, that is having an electrochemical oxidation potential greater than the valuable-metal, form little, if any, dissolved cationic species. The more noble contaminants form a solid, substantially insoluble slime 112 within the electrolysis cell 110. The slime 112 comprises one or more precious metal contaminants.

[0103] Under an electric potential applied by the power source 110, electrons flow from the anode 102 to the cathode 104 through the external current path 108 and power source 110 and the cationic species (M^{n+} and K^{m+}) flow from the anode 102 to the cathode 104 through the electrolytic solution 106 to complete the electrical circuit. More over, anions comprising the electrolytic solution 106 within the electrolysis cell 100 flow from the cathode 104 to the anode 102. One or both of the cationic species are deposited at the cathode 106. When the oxidized contaminant K is in the form of an oxyanion, the oxyanion flows to the anode 102 under the applied electric potential. The electrochemical reactions of the cathode 104 can be expressed by the following chemical reactions:



[0104] At the cathode **104** one or both of the valuable-metal cation M^{n+} and the one or more contaminant cations K^{m+} , respectively, accept n and m electrons and are electrodeposited at the cathode **104** as reduced species, preferably, M^0 and K^0 . At least most of the valuable-metal M is deposited at the cathode **104** and little, if any, of the one or more contaminants K are deposited at the cathode **104**. The ability and/or extent that the valuable metal cation M^{n+} and the one or more contaminant cations K^{m+} are respectively deposited at the cathode are influenced by the reductive potentials for the valuable-metal and the one or more contaminants in the electrolytic solution **106** and the conditions under which the electrolysis cell **100** is operated. The valuable-metal can be any metal. Preferably, the valuable-metal is a transition metal. In a more preferred embodiment, the valuable metal is one of copper, nickel or cobalt.

[0105] In copper electrorefining, the anode **102** comprises copper. Preferably, the copper anode has a copper purity level of at least about 95%. More preferably, the copper purity level of the anode **102** is at least about 99%, more preferably at least about 99.9%.

[0106] The copper anode further comprises one or more contaminants. The one or more contaminants comprise arsenic, antimony, bismuth, nickel, cobalt, tin, zinc, iron, tellurium, selenium, lead, silver, gold, and platinum group metals. The platinum group metals are platinum, osmium, iridium, ruthenium, rhodium and palladium. The slime **112** comprises the one or more contaminants more noble than copper such as silver, gold, platinum, osmium, iridium, ruthenium, rhodium, palladium, nickel, lead (typically as insoluble lead sulfate) and mixtures thereof being non-limiting examples. The one or more contaminants having an oxidation potential about equal to and/or less noble than copper comprise arsenic, antimony, bismuth, nickel, iron, cobalt, tin, zinc, tellurium, selenium, and lead.

[0107] The electrolytic solution **106**, preferably, comprises an aqueous copper solution. More preferably, the electrolytic solution **106** comprises copper sulfate, more specifically, copper (II) sulfate. The electrolytic solution **106** has a copper sulfate concentration from about 20 to about 300 grams copper sulfate per liter. Preferably, the copper sulfate concentration of the electrolytic solution is from about 100 to about 200 grams copper sulfate per liter. More preferably, the electrolytic solution **106** copper sulfate concentration is from about 30 grams/liter to about 60 grams/liter. The electrolytic solution **106** further comprises sulfuric acid. Preferably, the sulfuric acid of the electrolytic solution **106** has a concentration from about 100 to about 500 grams H_2SO_4 per liter, more preferably from about 150 to about 250 grams H_2SO_4 per liter.

[0108] Furthermore, the electrolytic solution **106** comprises one or more contaminants. The one or more contaminants comprise arsenic, tin, zinc, antimony, bismuth, nickel, iron, cobalt, tellurium, selenium and lead. The lead and nickel can be present in the electrorefining cell in one or both of the electrolytic solution **106** as a cationic species (that is, Pb^{2+} and Ni^{2+}) and the slime **112** (as insoluble lead sulfate and as nickel metal). In electrolytic solutions comprising sulfate, the cationic Pb^{2+} is typically low due to the formation of a substantially insoluble $PbSO_4$ precipitate. The iron and cobalt are substantially present within the electrolytic solution **106** as cationic species, that is, respectively, as one or more of Fe^{2+} , Fe^{3+} , Co^{2+} , and Co^{3+} . Preferably, the cobalt and nickel comprising the electrolytic solution have a +2 oxidation state. The

arsenic, antimony, bismuth, tellurium and selenium are, preferably, present in the electrolytic solution **106** as ionic species. That is, arsenic is preferably present in the electrolytic solution **106** as one or both of arsenite, AsO_2^{1-} , and arsenate, AsO_4^{3-} , oxyanions. Preferably, at least most of the arsenic is present as arsenate. More preferably, at least about 95% of the arsenic comprising the electrolytic solution **106** comprises arsenate. Furthermore, the antimony comprising the electrolytic solution **106** can comprise one or more of $Sb(OH)_4^{1-}$, SbO_2^{1-} , $Sb(OH)_6^{1-}$ and SbO_3^{1-} , oxyanions. Preferably, the antimony comprises antimony having one of a +5 or +3 oxidation state. The electrolytic solution **106** can comprise one or more of the following ionic species of bismuth $Bi(H_2O)_6^{3+}$, $Bi(H_2O)_5(OH)^{2+}$, $Bi(H_2O)_4(OH)_2^{1+}$, $Bi(H_2O)_3(OH)_3$, $Bi(H_2O)_2(OH)_4^{1-}$, BiO_3^{1-} , BiO_2^{1-} , BiO_3^{3-} , and BiO^{1+} . Preferably, the bismuth comprises bismuth having one of a +5 or +3 oxidation state. The electrolytic solution can comprise one or more of the following tellurium and selenium species: TeO_3^{2-} , TeO_4^{2-} , TeO_6^{6-} , SeO_4^{2-} and SeO_3^{2-} . In some embodiments, the electrolytic solution **106** comprises silver having a +1 oxidation state.

[0109] The one or more contaminants dissolved in the electrolytic solution **106** increase in concentration as copper dissolved in the electrolyte **106** is electrodeposited on the cathode **104** and as further copper and contaminants are dissolved at the anode **102**. As the concentration of the contaminants increase, the electrodeposition of the contaminants at the cathode **104** can substantially increase. Furthermore, as the level of the contaminants increases in the electrolytic solution **106**, the contaminants can destabilize the electrolytic solution **106**. For example, high levels of arsenic within the electrolytic solution can form precipitates and/or complex ionic species with other contaminants within the electrolytic solution **106** (such as, but not limited to antimony, bismuth, selenium and tellurium). The contaminants having a reduction potential, at its concentration in the electrolytic solution **106**, about equal to or less noble than copper can be electrodeposited with the copper at the cathode **104**. The electrodeposition of at least some of the contaminants the cathode **104** can affect electrodeposited copper quality and purity. For example, the contaminants can affect grain structure of the electrodeposited copper.

[0110] The concentration of the contaminants can vary in the electrolyte solution **106**. While not wanting to be limited by example, the nickel concentration can be as large as about 150 g/L or greater. Preferably, the nickel concentration in the electrolyte solution **106** is from about 0 g/L to about 40 g/L. More preferably, the electrolyte solution **106** nickel concentration is from about 0 g/L to about 20 g/L. The arsenic concentration in the electrolyte solution **106** can be as large as about 60 g/L or greater. Preferably, the arsenic concentration in the electrolyte solution **106** is from about 0.1 g/L to about 25 g/L. More preferably, the electrolyte **106** arsenic concentration is from about 1 g/L to about 25 g/L. The iron concentration in the electrolyte solution **106** can be as large as about 25 g/L or greater. Preferably, the iron concentration in the electrolyte solution **106** is from about 0.1 g/L to about 15 g/L. More preferably, the electrolyte iron concentration is from about 3 g/L to about 5 g/L. The electrolyte solution antimony concentration can be as large as 2 g/L or greater. Preferably, the antimony concentration in the electrolyte solution **106** is from about 0.1 g/L to about 1.5 g/L. More preferably, the electrolyte antimony concentration is from about 0.8 g/L to about 1.0 g/L. The electrolyte solution bismuth concentration

can be as large as about 1.5 g/L or greater. Preferably, the bismuth concentration in the electrolyte solution **106** is from about 0.05 g/L to about 0.7 g/L. More preferably, the electrolyte solution bismuth concentration is from about 0.1 g/L to about 0.5 g/L. Furthermore, the electrolytic solution **106** can comprise one or more of: cobalt having a solution concentration from about 0 g/L to about 3 g/L; tin having a solution concentration from about 0 g/L to about 1 g/L; zinc having a solution concentration from about 0 g/L to about 1 g/L; tellurium having a solution concentration from about 0 mg/L to about 10 mg/L; and selenium having a solution concentration from about 0 mg/L to about 10 mg/L.

[0111] In the electrorefining of copper, at least most of the electrodeposited cathode **104** comprises copper. The electrodeposited cathode **104** comprises at least about 99% copper. Preferably, at least about 99.9% of the electrodeposited cathode **104** comprises copper. More preferably, the electrodeposited cathode **104** comprises at least about 99.99% copper. Even more preferably, at least about 99.999% of the electrodeposited cathode **104** comprises copper.

[0112] FIG. 3 depicts a process **200** for treating the electrolytic solution **106** having a target material and a valuable metal. The target material may comprise materials for disposal and/or recoverable materials of value.

[0113] In step **120**, a side stream **125** of the electrolytic solution **106** is removed from the electrolysis cell **100**. The side stream **125** may be a substantially continuously generated side stream, such as, a bleed stream, or may be an intermediately removed stream in the form of a batch volume side stream. It can be appreciated that the side stream **125** contains the target material contained within the electrolytic solution **106**. The side stream **125** comprises a volume percent of electrolytic solution **106** total volume, the volume percent of the side stream **125** is presented by the following formula:

$$\text{Volume \% side stream} = 100 * \frac{\text{volume of side stream}}{\text{total volume of electrolyte solution in process}} \quad (7)$$

[0114] Preferably, the volume percent of the side stream **125** is no greater than about 25% of the total volume of the electrolyte solution **106**. More preferably, the volume percent of the side stream **125** is no greater than about 3%. Even more preferably, the volume percent of the side stream **125** is no greater than about 1% of the total of the electrolyte solution **106**. In some configurations, the volume percent of the side stream **125** is from about 0.001% to about 0.1% of the total of the electrolyte solution **106**. It can be appreciated, that the side stream **125** volume can vary depending on one or more of the level of contaminants contained within the anode, the level of contaminants dissolved in the electrolytic solution **106**, and desired level of contaminants to which can be suitably maintained within the electrolytic solutions **106**.

[0115] In step **130**, the side stream **125** is contacted with a fixing agent. The fixing agent may be a soluble or insoluble fixing agent. While not wanting to be bound by any theory, it is believed that soluble and insoluble rare earth fixing agents commonly do not remove metal and metalloid dissociated cations from solution. This can permit metal and metalloid oxyanions to be removed selectively from a solution containing both metal and metalloid oxyanions and dissociated cations.

[0116] In a preferred embodiment, the side stream **125** is contacted with the insoluble fixing agent to form a target material-loaded insoluble fixing agent and a purified side stream **195**. The side stream **125** has an initial concentration

of the target material within the side stream **125**. The fixing agent may comprise an adsorbent or absorbent. The contacting of the fixing agent with the side stream **125** having the target material within the side stream **125** removes most, if not all, of the target material from the side stream **125** to form the purified side stream **195**. The purified side stream **195** has a purified concentration of the target material contained within the purified side stream **195**. The initial concentration is at least greater than the purified concentration. Preferably, most, more preferably about 75% or more, and even more preferably about 95% or more of the target material in the side stream **125** is loaded onto the insoluble fixing agent.

[0117] Preferably, the purified side stream **195** has an arsenic concentration less than about 15 g/l dissolved arsenic, more preferably less than about 10 g/L dissolved arsenic. Even more preferably, the dissolved arsenic concentration in the purified side stream is less than about 1 g/L. The dissolved antimony concentration in the purified side stream **195** is preferably less than about 300 mg/L, more preferably less than about 200 mg/L. Even more preferably, the purified side stream **195** has a dissolved antimony concentration less than about 100 mg/L. The dissolved bismuth concentration in the purified side stream **195** is preferably less than about 300 mg/L, more preferably less than about 200 mg/L. Even more preferably, the purified side stream **195** has a dissolved bismuth concentration less than about 100 mg/L. Preferably, the purified side stream **195** has a tellurium concentration less than about 1 mg/l dissolved tellurium, more preferably less than about 0.5 mg/L dissolved tellurium. Even more preferably, the dissolved tellurium concentration in the purified side stream is less than about 0.1 mg/L. Preferably, the purified side stream **195** has a selenium concentration less than about 1 mg/l dissolved selenium, more preferably less than about 0.5 mg/L dissolved selenium. Even more preferably, the dissolved selenium concentration in the purified side stream is less than about 0.1 mg/L.

[0118] In a preferred embodiment, the insoluble fixing agent comprises one of yttrium, scandium and a lanthanoid. The insoluble fixing agent is preferably a particulate solid. The insoluble fixing agent is preferably is an insoluble rare earth compound comprising an insoluble rare earth oxide, such as hydrous or anhydrous rare earth oxides, or a rare earth fluoride, carbonate, fluorocarbonate, silicate, and the like. The insoluble fixing agent is particularly effective in removing arsenic have an oxidation state of +3 or +5. In a more preferred embodiment, the insoluble fixing agent comprises cerium. In a more preferred embodiment, the insoluble fixing agent comprises cerium oxide. A particularly preferred insoluble fixing agent is CeO_2 . The insoluble fixing agent is preferably a finely divided solid having an average surface area of between about 25 m^2/g and about 500 m^2/g , more preferably between about 70 m^2/g and about 400 m^2/g , and even more preferably between about 90 m^2/g and about 300 m^2/g .

[0119] The insoluble fixing agent may be derived from precipitation of a rare earth metal salt or from thermal decomposition of, for example, a rare earth metal carbonate or oxalate at a temperature preferably between about 100 to about 700 and even more preferably between about 180 and 350° C. in a furnace in the presence of an oxidant, such as air. Formation of the insoluble fixing agent is further discussed in copending U.S. application Ser. No. 11/932,837, filed Oct. 31, 2007, which is incorporated herein by this reference.

[0120] Although the preferred insoluble fixing agent comprises a rare earth compound, other fixing agents may be employed. Any fixing agent, whether solid, liquid, gaseous, or gel, that is effective at fixing the target material in solution through precipitation, ion exchange, or some other mechanism may be used. Examples of other fixing agents include at least those set forth above.

[0121] In one configuration, the insoluble fixing agent is an aggregated particulate having a mean surface area of at least about $1 \text{ m}^2/\text{g}$. Depending on the application, higher surface areas may be desired. For example, the aggregated particulates can have a surface area of at least about $5 \text{ m}^2/\text{g}$; in other cases, more than about $10 \text{ m}^2/\text{g}$; and, in still other cases, more than about $25 \text{ m}^2/\text{g}$. Where higher surface areas are desired, the particulates can have a surface area of more than about $70 \text{ m}^2/\text{g}$; in other cases, more than about $85 \text{ m}^2/\text{g}$; in still other cases, more than about $115 \text{ m}^2/\text{g}$; and, in still other cases, more than about $160 \text{ m}^2/\text{g}$. The aggregated particulates can include a polymer binder, such as thermosetting polymers, thermoplastic polymers, elastomeric polymers, cellulosic polymers, and glasses, to at least one of bind, affix, and/or attract the insoluble fixing agent constituents into particulates having one or more of desired size, structure, density, porosity, and fluid properties.

[0122] The insoluble fixing agent can include one or more flow aids, with or without a binder. Flow aids can improve the fluid dynamics of a fluid over and/or through the insoluble fixing agent to prevent separation of slurry components, prevent the settling of fines, and, in some cases, hold the fixing agent and other components in place.

[0123] The insoluble fixing agent can be blended with or include other components, such as ion-exchange materials (e.g., synthetic ion exchange resins), porous carbon such as activated carbon, metal oxides (e.g., alumina, silica, silica-alumina, gamma-alumina, activated alumina, acidified alumina, and titania), metal oxides containing labile metal anions (such as aluminum oxychloride), non-oxide refractories (e.g., titanium nitride, silicon nitride, and silicon carbide), diatomaceous earth, mullite, porous polymeric materials, crystalline aluminosilicates such as zeolites (synthetic or naturally occurring), amorphous silica-alumina, minerals and clays (e.g., bentonite, smectite, kaolin, dolomite, montmorillonite, and their derivatives), ion exchange resins, porous ceramics metal silicate materials and minerals (e.g., one of the phosphate and oxide classes), ferric salts, and fibrous materials (including synthetic (for example, without limitation, polyolefins, polyesters, polyamides, polyacrylates, and combinations thereof) and natural (such as, without limitation, plant-based fibers, animal-based fibers, inorganic-based fibers, cellulosic, cotton, paper, glass and combinations thereof).

[0124] The target material-loaded insoluble fixing agent comprises most of the target material in the side stream **125**. The insoluble fixing agent and the target material form a substantially insoluble target material-loaded fixing agent. Preferably, most, and even more preferably about 75% or more, of the target material is loaded on the insoluble fixing agent. The affinity of the insoluble fixing agent for specific target materials is believed to be a function of pH and/or target material concentration. The insoluble fixing agent is commonly used as a particulate in a fixed or fluidized bed and, in certain configurations, may be desirable for use in a stirred tank reactor. In one configuration, the insoluble fixing agent

includes a flocculent and/or dispersing agent, as discussed herein, to maintain a substantially uniform particle distribution in the bed.

[0125] In some embodiments, the target material will be present in a reduced oxidation state and this condition might be undesirable. In such cases, an oxidant may be contacted with the side stream **125** to increase the oxidation state of target material. That is, the contacting step **130** may be preceded by an oxidation step to oxidize the target material for better target material removal efficiency and/or affinity of the target material for the insoluble fixing agent. Using arsenic as an example, the presence of arsenite might favor the use of an oxidant before the fixing agent is applied.

[0126] The process **200** operational conditions should be controlled. When arsenic is the target material, for example, the insoluble fixing agent, under proper process conditions, selectively removes at least most of the arsenic while leaving at least most of the valuable product as dissolved (cationic) species in the side stream **125**. Although the insoluble fixing agent can effectively fix arsenic from solutions over a wide range of pH levels, the pH of the side stream **125** preferably is no more than about pH 6 and even more preferably is no more than about pH 2 to adsorb both arsenic (V) and arsenic (III). Arsenic (III) sorbs onto the insoluble fixing agent over a broad pH range while arsenic (V) is preferably sorbed by the insoluble fixing agent at lower pH levels.

[0127] In step **140**, the purified side stream **195** is separated from the target material-loaded insoluble fixing agent. The separation process may be any method known to one of skill in art for separating a liquid stream from a solid, such as, but not limited to, centrifugation, cyclonic (including hydrocycloning), decantation (including counter-current decantation), filtration (including screening), sedimentation (including gravity separating techniques) and combinations and/or variations thereof.

[0128] In one configuration, the insoluble fixing agent can be supported and/or configured for the side stream **125** to flow through the insoluble fixing agent. The target material-loaded insoluble fixing agent is formed on the support and/or configured for the purified side stream **195** to flow through the insoluble fixing agent.

[0129] When a pre-selected degree of target material loading on the fixing agent occurs, the target material-loaded fixing agent is contacted, in step **150**, with a stripping solution, or release agent, to unload, or dissolve, preferably most and even more preferably about 95% or more of the target material from the target material-loaded fixing agent and form a barren fixing agent **160** (which is recycled to step **130**) and one or both of a separated product **185** and a valuable product **175**.

[0130] Any acidic, neutral, or basic stripping solution or release agent may be employed. The desorption process of the target material-loaded fixing agent is believed to be a result of a one or more of: 1) a stronger affinity by the rare earth comprising the fixing agent for the release agent than the sorbed target material or its composition and 2) an upward or downward adjustment of the oxidation state of the rare earth comprising the surface of the fixing agent and/or of the sorbed target material and/or the sorbed target material-containing oxyanion.

[0131] In one application, the stripping solution is alkaline and comprises a strong base. Preferably, the stripping solution comprises at least one of an alkali metal hydroxide and group I salt of ammonia, an amide, and an amine (such as a

primary, secondary, tertiary, or quaternary amine) and mixtures thereof. More preferably, the stripping solution comprises an alkali metal hydroxide. While not wishing to be bound by any theory, it is believed that, at high concentrations, hydroxide ions compete with, and displace, oxyanions from the surface of the insoluble fixing agent. In one formulation, the stripping solution includes a caustic compound in an amount preferably ranging from about 1 to about 15 wt. %, even more preferably from about 1 to about 10 wt. %, and even more preferably from about 2.5 to about 7.5 wt. %, with about 5 wt. % being even more preferred.

[0132] The preferred pH of the stripping solution is preferably greater (e.g., more basic) than the pH at which the target material was loaded onto the fixing agent. The stripping solution pH is preferably at least about pH 10, even more preferably at least about pH 12, and even more preferably at least about pH 14.

[0133] In another application, the (first) stripping solution comprises an oxalate or ethanedioate, which, relative to target material-containing oxyanions, is preferentially sorbed, over a broad pH range, by the insoluble fixing agent. In one process variation to desorb oxalate ions, the insoluble fixing agent is contacted with a second stripping solution having a preferred pH of at least about pH 9 and even more preferably of at least about pH 11 to desorb oxalate and/or ethanedioate ions in favor of hydroxide ions. A strong base is preferred for the second stripping solution. Alternatively, the sorbed oxalate and/or ethanedioate anions can be heated to a preferred temperature of at least about 500 degrees Celsius to thermally decompose the sorbed oxalate and/or ethanedioate ions and remove them from the insoluble fixing agent.

[0134] In another application, the (first) stripping solution includes a strongly adsorbing exchange oxyanion, such as phosphate, carbonate, silicate, vanadium oxide, or fluoride, to displace the sorbed target material-containing oxyanion. The first stripping solution has a relatively high concentration of the exchange oxyanion. Desorption of the exchange oxyanion is at done at a different (higher) pH and/or exchange oxyanion concentration than the first stripping solution. For example, desorption can be by a second stripping solution which includes a strong base and has a lower concentration of the exchange oxyanion than the oxyanion concentration in the first stripping solution. Alternatively, the exchange oxyanion can be thermally decomposed to regenerate the insoluble fixing agent. Alternatively, the exchange oxyanion can be desorbed by oxidation or reduction of the insoluble fixing agent or exchange oxyanion.

[0135] In another application, the stripping solution includes a reductant or reducing agent, such as ferrous ion, lithium aluminum hydride, nascent hydrogen, sodium amalgam, sodium borohydride, stannous ion, sulfite compounds, hydrazine (Wolff-Kishner reduction), zinc-mercury amalgam, diisobutylaluminum hydride, lindlar catalyst, oxalic acid, formic acid, and a carboxylic acid (e.g., a sugar acid, such as ascorbic acid), to reduce the rare earth, sorbed target material, and/or sorbed target material-containing oxyanion. While not wishing to be bound by any theory nor by way of example, surface reduction of the insoluble fixing agent will reduce cerium (IV) to cerium (III), which may interact less strongly with target materials and oxyanions. Following or concurrently with surface reduction of the insoluble fixing agent, the pH is increased to desorb the sorbed target material or its oxyanion.

[0136] In another application, the stripping solution includes an oxidant or oxidizing agent, e.g., peroxygen compounds (e.g., peroxide, permanganate, persulfate, etc.), ozone, chlorine, hypochlorite, Fenton's reagent, molecular oxygen, phosphate, sulfur dioxide, and the like, that oxidizes the sorbed target material and/or its oxyanion to a higher oxidation state, e.g., arsenic (III) to arsenic (V), followed by a pH adjustment and a desorption process. Desorption of arsenic (V) from insoluble rare earth compounds, for example, typically occurs at a pH of at least about pH 12 and even more typically at least about pH 14.

[0137] Regardless of the precise stripping mechanism, a first concentration of the target material in the side stream **125** is typically less than a second concentration of the target material in one or both of the separated-product **185** and the valuable product **175**. Commonly, the first concentration of the target material is no more than about 75% of the second concentration and even more commonly no more than about 50% of the second concentration. By way of example, a first concentration of the arsenic is between about 0.1 mg/L to about 5 g/L, and the second concentration of arsenic is between about 0.25 g/L and about 7.5 g/L.

[0138] Optionally (not shown), the target material is removed from one or both of the separated product **185** and the valuable product **175** by a suitable technique to form a target material and a barren stripping solution (which may be recycled to step **150**). Removal may be effected by any suitable technique including precipitation (such as using a sulfide (for transition metals), an alkaline earth metal carbonate (for fluoride), and a rare earth or iron salt (for arsenic)), adsorption, absorption, electrolysis, cementation, amalgamation, and the like. In one configuration, the target material is precipitated using a soluble rare earth fixing agent as noted above.

[0139] Preferably, the second concentration of the target material is about equal to the solubility limit (concentrations) of the target material (at the given process conditions). More preferably, the second concentration of the target material is between about 0.1 and about 2,500 g/L, even more commonly between about 0.1 and about 1,000 g/L, and even more commonly between about 0.25 g/L and about 500 g/L. Finally, a soluble or dissolved second fixing agent is contacted with one or both of the separated-product **185** and valuable product **175** in an amount sufficient to precipitate most, if not all, of the target material as a target material-bearing solid. The target material-bearing solid may be separated from the intermediate solution by any suitable solid/liquid separation technique to produce a stripping solution for recycle and a separated solid for disposal or recover a valuable solid (not shown).

[0140] The valuable product **175** and valuable solid may be any metal of interest. Non-limiting examples of metals of interest include, without limitation, one or more of the transition metals. Preferably, the metals of interest include a metal selected from the group of metals consisting of copper, nickel, cobalt, lead, precious metals, and mixtures thereof. All or a portion of the valuable product from the side stream **125** may be recovered.

[0141] The soluble second fixing agent typically has an oxidation state lower than the oxidation state of the first fixing agent. Preferably, the oxidation state of the second fixing agent is one of +3 or +4. The soluble fixing agent preferably is a soluble rare earth metal compound and more preferably includes salts comprising rare earth compounds, such as bro-

mides, nitrates, phosphites, chlorides, chlorites, chlorates, nitrates, and the like. More preferably, the soluble fixing agent is a rare earth (III) chloride.

[0142] Although not shown, the concentration of the target material in the side stream **125** may be increased by any suitable technique, such as through water removal. Water may be removed, for example, by evaporation, distillation, and/or filtration techniques (such as, membrane filtration). Other techniques include precipitation and re-dissolution, absorption or adsorption followed by stripping, ion exchange followed by stripping, and the like of the target material.

[0143] In step **190**, the separated purified side stream **195** is recycled to the electrolysis cell **100**. The purified side stream **195** has, relative to the side stream **125**, a reduced concentration of the target material. In one application, the purified stream **195** preferably has no more than about 1,000 ppm, even more preferably no more than about 500 ppm, even more preferably no more than about 50 ppm, and yet even more preferably no more than about 1 ppm of the target material. In some configurations, the purified stream **195** has no more than about 50 ppb, even more preferably no more than about 5 ppb of the target material.

[0144] In another embodiment where the fixing agent comprises a soluble fixing agent, the soluble fixing is contacted with the side stream **125** to form an insoluble target material-containing composition and a purified side stream **195**. The target material comprises the one or more contaminants contained within the side stream **125**. Preferably, the soluble fixing agent comprises a rare earth. More preferably, the soluble fixing agent comprises a rare earth-containing composition having one or more rare earths.

[0145] The insoluble target material-containing composition comprises the rare earth-containing composition having one or more rare earths. The insoluble target material-containing composition is typically in the form of precipitate that can be removed as a solid. Preferably, the insoluble target material-containing composition has at least about 0.01 wt. %, even more preferably at least about 0.1 wt. %, and even more preferably ranges from about 5 to about 50 wt. % of the target material.

[0146] The soluble fixing agent, or precipitant, can be supported by a suitable carrier or can be unsupported. The ability to form the insoluble target material-containing composition in the form of a solid comprising a relatively high concentration of the target material can greatly reduce the volume of the insoluble target material-containing composition requiring disposal, thereby reducing disposal costs.

[0147] Preferably, most and even more preferably about 75% or more of the target material or a composition incorporating the target material combines, with the soluble fixing agent to form the insoluble target material-containing composition. The soluble fixing agent is preferably one or more of scandium, yttrium, and a lanthanoid and is in a form that is soluble in water and/or the side stream **125**. When the soluble fixing agent comprises cerium, the cerium preferably has an oxidation state of +4 or less. The soluble fixing agent may be, without limitation, a salt comprising a bromide, nitrate, phosphite, chloride, chlorite, chlorate, and like of scandium, yttrium, or lanthanoid, with a chloride of cerium (III), cerium (IV) or a mixture thereof being preferred. While not wishing to be bound by any theory, it is believed that soluble forms of cerium (IV) can form noncrystalline cerium dioxide, which then sorbs target materials or a composition incorporating the target material. The soluble fixing agent is added, commonly

as a separate aqueous solution, to the side stream **125**. Preferably, soluble fixing agent is added to the side stream **125** in an amount to produce an average molar ratio of the fixing agent to the target material in solution of less than about 8:1 and preferably ranging from about 0.5:1 to about 5:1.

[0148] In one configuration, the pH of the side stream is adjusted to maintain at least some, if not at least most, of the soluble fixing dissolved in the side stream **125**. That is, the pH of the side stream **125** is adjusted to form little, if any, rare earth sulfate, carbonate, and/or hydroxide precipitate.

[0149] In another configuration, a chelating agent may be added to the soluble fixing agent aqueous solution and/or the side stream **125** to increase the solubility of the fixing agent in one or both of the fixing agent aqueous solution and/or side stream **125**. A typical chelating agent is a chemical compound containing at least two nonmetal entities capable of binding to a metal atom and/or ion. While not wishing to be bound by any theory, chelating agents function by making several chemical bonds with metal ions. Exemplary chelating agents include ethylene diamine tetra acetic acid (EDTA), dimercaprol (BAL), dimercaptosuccinic acid (DMSA), 2,3-dimercapto-1-propanesulfonic acid (DMPS), and alpha lipoic acid (ALA), aminophenoxyethane-tetraacetic acid (BAPTA), deferasirox, deferiprone, deferoxamine, diethylene triamine pentaacetic acid (DTPA), dimercapto-propane sulfonate (DMPS), ethylenediamine tetraacetic acid (calcium disodium versante) (CaNa₂-EDTA), ethylene glycol tetraacetic acid (EGTA), D-penicillamine, methanesulfonic acid, methane-phosphonic acid, and mixtures thereof.

[0150] The soluble fixing agent may further include one or both of an organic or inorganic additive. Preferably, the additive is one or more of a flocculent, coagulant, and thickener, to induce flocculation, settling, and/or formation of the precipitated solids. Examples of such additives include lime, alum, ferric chloride, ferric sulfate, ferrous sulfate, aluminum sulfate, sodium aluminate, polyaluminum chloride, aluminum trichloride, polyelectrolytes, polyacrylamides, polyacrylate, and the like.

[0151] In step **140**, the insoluble target material-containing composition is separated from a purified side of stream **195**. The insoluble target material-containing composition may be further processed to form one or more of a separated product **185**, valuable product **175**, valuable solid and/or separated solid.

[0152] In yet another embodiment, the contacting of the fixing agent with the side stream **125** comprises forming a precipitate between a target material and at least one of rare earth and non-rare earth salt additives and a purified side stream **195**. The target material comprises the one or more contaminants contained within the side stream **125**.

[0153] The rare earth salt additive comprises a rare earth in the +3 oxidation state. In one formulation, the rare earth salt additive comprises a bimetallic, lanthanide-based salt solution. In a preferred formulation, the non-rare earth salt additive comprises aluminum in the +3 oxidation state. In another preferred formulation, the rare earth salt additive comprises cerium in the +3 oxidation state.

[0154] The non-rare earth salt additive comprises a non-rare earth metal in the +3 oxidation state and is substantially free of a rare earth. The non-rare earth metal can be any non-rare earth metal in the +3 oxidation state, with transition metals, boron, aluminum, gallium, indium, and thallium being preferred, and the transition metals and aluminum being particularly preferred. The non-rare earth salt additive

particularly provides a significant reduction in the amount of rare earth needed to remove arsenic from the side stream 106. Preferred transition metals include the elements having atomic numbers 22-29, 40-45, 47, 72-77, and 79. The preferred transition metals comprise the transition metals titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, technetium, ruthenium, rhodium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, and gold.

[0155] Preferably, the rare earth and the non-rare earth salt additives are combined to form a mixed salt additive. For example, the soluble fixing agent(s) are combined with one or more non-rare earths having a +3 oxidation state, particularly a transition metal or metal from Group 13 of the Periodic Table of the Elements, with aluminum or iron in the +3 oxidation state being preferred. Preferably, the soluble fixing agent is a rare earth metal in the +3 oxidation state, and the soluble fixing agent and non-rare-earth metal are each in the form of water dissociable salts. For example, a double salt mixture is formed by mixing cerium (III) chloride with aluminum (III) chloride. In another example, the double salt mixture is formed by mixing lanthanum (III) chloride with aluminum (III) chloride. In another example, the double salt mixture is formed by mixing lanthanum (III) chloride with iron (III) chloride. In a preferred formulation, at least one mole of the non-rare-earth is present for each mole of the rare earth soluble fixing agent. In a more preferred formulation, at least 3 moles of the non-rare-earth are present for each mole of the rare earth soluble fixing agent. In an even more preferred formulation, at least one mole of the non-rare-earth having an oxidation state of +3 is present for each mole of the rare earth soluble fixing agent having an oxidation state of +3. In a yet even more preferred formulation, at least 3 moles of the non-rare-earth having an oxidation state of +3 are present for each mole of the rare earth soluble fixing agent having an oxidation state of +3. A solution comprising the mixed salt additive can have any pH; that is, the mixed salt solution can have an acidic, neutral, or basic pH. The mixed salt additive, which is typically a bimetallic lanthanide-based salt solution, is contacted with the side stream 125 at standard or higher temperature. The mixed salt solution can be contacted with the side stream 125 over a wide temperature range, preferably from about the freezing point of the side stream 125 to about the boiling point of the side stream 125.

[0156] The side stream 125 has a pH value. The pH value of the side stream 125, before and after mixed salt addition, can range from a pH of about pH 0 or less to a pH of about pH 14 or greater. In some configurations, the pH of the side stream 125 has a pH of less than about pH 8, prior to and after the contacting of the side stream 125 with the mixed salt solution. More preferably, the pH of the side stream after contacting the mixed salt solution is less than about pH 2.

[0157] In one configuration, the contacting of the rare earth and non-rare earth salt additives with the side stream 125 forms the precipitate. In another configuration, the contacting of the non-rare earth salt additive with the side stream 125 forms the precipitate. In a preferred configuration, the rare earth salt additive comprises cerium in the +3 oxidation state and the non-rare earth salt additive includes aluminum in the +3 oxidation state. The non-rare earth salt additive can provide significant reductions in the amount of rare earths required to remove the selected one or more contaminants from the side stream 106.

[0158] In step 140, the purified side stream 195 is separated from the precipitate. The precipitate may be further processed to form one or more of a separated product 185, valuable product 175, valuable solid and/or separated solid.

[0159] In still yet another embodiment, the contacting of the side stream 125 with the fixing agent further comprises providing a side stream having one or more dissolved contaminants and one or more dissolved valuable products and providing a fixing agent comprising a rare earth. Preferably, at least one of the one or more contaminants is in the form of any oxyanion. Preferably, at least one of the one or more dissolved valuable products is a transition metal. The contacting of the side stream 125 and the fixing agent precipitates at least most of the dissolved target material as a target-material containing precipitate and leaves at least most of the valuable product dissolved in a purified side stream 195. In step 140, the purified side stream 195 is separated from the target-material containing precipitate. The target-material containing precipitate may be further processed to form one or more of a separated product 185, valuable product 175, valuable solid and/or separated solid.

[0160] Residual soluble fixing may be removed by precipitation or other suitable separation methods known to one of skill within the art. The residual soluble fixing agent may be removed by forming an insoluble rare earth composition within the purified side stream 195. The insoluble rare earth composition may be formed by adjusting the pH and/or by adding a precipitating forming composition to the purified side stream 195. The precipitating forming composition contains one or more entities form a precipitate when contacted with the rare earth contained within the purified side stream 195. While not wanting to be bound by example, any solubilized and/or dissolved rare earth composition may be removed from the purified side stream 195 by contacting with one an oxalate and/or carbonate, carbonates being preferred for purified side streams having a pH greater than about pH 7.

[0161] In another embodiment of the present invention, the insoluble rare earth fixing agent can be added to the electrolytic solution contained within the electrolytic cell to remove one or more of the target contaminants. That is, the insoluble rare earth-containing fixing agent can be contacted with the electrolytic solution contained within the electrolytic cell to form a target material-loaded insoluble fixing agent. The target material-loaded insoluble fixing agent can be separated from the electrolytic solution by any solid liquid separation process. The separated target material-loaded insoluble fixing agent can be contacted with a stripping agent as described.

[0162] In another embodiment, an electrolytic stream is contacted with the rare earth fixing agent to remove one or more of the target contaminants. The electrolytic stream can be rich or lean in the valuable metal. That is, the electrolytic stream can comprise an electrolytic stream before, after or during the electrodepositing of the valuable metal contained within the electrolytic stream.

[0163] A number of variations and modifications of the invention can be used. It would be possible to provide for some features of the invention without providing others.

[0164] The present invention, in various embodiments, configurations, or aspects, includes components, methods, processes, systems and/or apparatus substantially as depicted and described herein, including various embodiments, configurations, aspects, subcombinations, and subsets thereof. Those of skill in the art will understand how to make and use the present invention after understanding the present disclo-

sure. The present invention, in various embodiments, configurations, and aspects, includes providing devices and processes in the absence of items not depicted and/or described herein or in various embodiments, configurations, or aspects hereof, including in the absence of such items as may have been used in previous devices or processes, e.g., for improving performance, achieving ease and/or reducing cost of implementation.

[0165] The foregoing discussion of the invention has been presented for purposes of illustration and description. The foregoing is not intended to limit the invention to the form or forms disclosed herein. In the foregoing Detailed Description for example, various features of the invention are grouped together in one or more embodiments, configurations, or aspects for the purpose of streamlining the disclosure. The features of the embodiments, configurations, or aspects of the invention may be combined in alternate embodiments, configurations, or aspects other than those discussed above. This method of disclosure is not to be interpreted as reflecting an intention that the claimed invention requires more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed embodiment, configuration, or aspect. Thus, the following claims are hereby incorporated into this Detailed Description, with each claim standing on its own as a separate preferred embodiment of the invention.

[0166] Moreover, though the description of the invention has included description of one or more embodiments, configurations, or aspects and certain variations and modifications, other variations, combinations, and modifications are within the scope of the invention, e.g., as may be within the skill and knowledge of those in the art, after understanding the present disclosure. It is intended to obtain rights which include alternative embodiments, configurations, or aspects to the extent permitted, including alternate, interchangeable and/or equivalent structures, functions, ranges or steps to those claimed, whether or not such alternate, interchangeable and/or equivalent structures, functions, ranges or steps are disclosed herein, and without intending to publicly dedicate any patentable subject matter.

What is claimed is:

1. A process, comprising:

- (a) forming, by an electrolytic cell, an electrolytic stream comprising a target material and a valuable metal, wherein the electrolytic stream has a first target material concentration;
- (b) contacting the electrolytic stream with an insoluble fixing agent to form a target material-loaded insoluble fixing agent and a purified electrolytic stream, the insoluble fixing agent comprising at least one of yttrium, scandium, and a lanthanoid, the target material-loaded insoluble fixing comprising most of the target material in the electrolyte stream, wherein the target material, in the target material-loaded insoluble fixing agent, forms a composition with the insoluble fixing agent; and
- (c) cycling the purified electrolytic stream to the electrolytic cell, wherein the purified stream has a second target material concentration substantially less than the first target material concentration.

2. The process of claim 1, wherein the electrolytic stream is a side stream.

3. The process of claim 1, wherein step (b) further comprises contacting at least a portion of the stream with the insoluble fixing agent.

4. The process of claim 1, wherein, in the contacting step (b), substantially little, if any, of the valuable metal is removed from the electrolytic stream.

5. The process of claim 1, wherein the target material comprises at least one of arsenic, antimony, bismuth, tin, lead, selenium, tellurium, platinum, iridium, ruthenium, and rhodium.

6. The process of claim 1, wherein the target material comprises an oxyanion.

7. The process of claim 6, wherein the oxyanion comprises at least one of tellurium, selenium, bismuth, antimony and arsenic.

8. The process of claim 1, wherein the valuable metal comprises copper.

9. The process of claim 1, wherein the insoluble fixing agent comprises cerium.

10. The process of claim 9, wherein the cerium comprises cerium oxide.

11. The process of claim 1, wherein the insoluble fixing agent comprises a finely divided solid having a surface area from about 25 m²/g to about 500 m²/g.

12. The process of claim 1, further comprising:

- (d) contacting the target material-loaded insoluble fixing agent with a stripping solution to dissolve, solublize, or otherwise displace most of the target material in the target material-loaded insoluble fixing agent to form a loaded stripping solution and barren insoluble fixing agent.

13. The process of claim 12, wherein the stripping solution comprises at least one of a strong base, an oxalate, ethanedioate, a strongly absorbing exchange oxyanion, a reductant or reducing agent, and oxidant or oxidizing agent.

14. The process of claim 12, further comprising:

- (e) cycling the barren insoluble fixing agent to contacting step (b), wherein the barren insoluble fixing agent is contacted with the electrolytic stream to form target material-loaded insoluble fixing agent.

15. The process of claim 12, further comprising:

- (f) removing at least most of the dissolved target material from the loaded stripping solution.

16. A process, comprising:

- (a) forming, by an electrolytic cell, an electrolytic stream comprising a target material and a valuable metal, wherein the electrolytic stream has a first target material concentration;
- (b) contacting the electrolytic stream with a fixing agent to form an insoluble composition;
- (c) removing the insoluble composition from the electrolytic stream to form a purified electrolyte stream; and
- (d) cycling the purified electrolytic stream to the electrolytic cell, wherein the purified stream has a second target material concentration substantially less than the first target material concentration.

17. The process of claim 16, wherein the electrolytic stream is a side stream.

18. The process of claim 16, wherein step (b) further comprises contacting at least a portion of the stream with the fixing agent.

19. The process of claim 16, wherein the fixing agent comprises a non-rare earth salt additive, the non-rare earth salt additive comprises a non-rare earth metal having a +3

oxidation and being substantially free of a rare earth and wherein the insoluble composition comprises a precipitate formed between the target material and the non-rare earth salt additive.

20. The process of claim **19**, wherein the non-rare earth salt additive comprises one of boron, aluminum, gallium, indium, thallium and a transition metal.

21. The process of claim **16**, wherein the rare earth-containing fixing agent comprises a rare earth salt additive, the rare earth salt additive comprises a rare earth having a +3 oxidation state and a non-rare metal having a +3 oxidation state and wherein the insoluble composition comprises a precipitate formed between the target material and at least one of the rare earth and the non-rare earth.

22. The process of claim **21**, wherein the non-rare earth is one of boron, aluminum, gallium, indium, thallium and a transition metal.

23. The process of claim **16**, wherein the fixing agent comprises a rare earth, the rare earth is a soluble rare earth, and wherein the insoluble composition comprises an insoluble target material-containing composition comprising the target material and the rare earth.

24. The process of claim **16**, wherein the electrolytic stream contains a valuable metal and wherein at least most, if not all, of the valuable metal within the electrolytic stream is cycled to the electrolytic cell by the purified electrolytic stream.

25. The process of claim **16**, wherein the electrolytic stream contains copper, wherein at least most, if not all, of the copper within the electrolytic stream is cycled to the electrolytic cell by the purified electrolytic stream and wherein the target material comprises one or more of arsenic, antimony, bismuth, tin, lead, selenium, tellurium, platinum, iridium, ruthenium, and rhodium.

26. A process, comprising:

- (a) forming, by an electrolytic cell, an electrolytic stream comprising a target material and dissolved copper, wherein the electrolytic stream has a first target material concentration;
- (b) contacting the electrolytic stream with an insoluble rare earth-containing fixing agent to form a target material-loaded insoluble fixing agent and a purified electrolytic stream having at least most, if not all, of the copper contained with the electrolytic stream, the rare earth-containing insoluble fixing agent comprising at least one of yttrium, scandium, and a lanthanoid, the target material-loaded insoluble fixing comprising most of the target material in the electrolyte stream, wherein the target material, in the target material-loaded insoluble fixing agent, forms a composition with the insoluble fixing agent; and
- (c) cycling the purified electrolytic stream to the electrolytic cell, wherein the purified stream has a second target material concentration substantially less than the first target material concentration.

27. The process of claim **26**, wherein the electrolytic stream is a side stream.

28. The process of claim **26**, wherein step (b) further comprises contacting at least a portion of the electrolytic stream with the insoluble rare earth-containing fixing agent.

29. The process of claim **26**, wherein substantially little, if any, of the dissolved copper is removed from the electrolytic stream in the contacting step (b), and wherein the target

material comprises at least one of arsenic, antimony, bismuth, tin, lead, selenium, tellurium, platinum, iridium, ruthenium, and rhodium.

30. The process of claim **26**, wherein the target material comprises an oxyanion of at least one of tellurium, selenium, bismuth, antimony and arsenic.

31. The process of claim **26**, wherein the rare earth-containing fixing agent comprises cerium oxide.

32. The process of claim **26**, wherein the insoluble fixing agent comprises a finely divided solid having a surface area from about 25 m²/g to about 500 m²/g.

33. The process of claim **26**, further comprising:

- (d) contacting the target material-loaded insoluble fixing agent with a stripping solution to dissolve, solublize, or otherwise displace most of the target material in the target material-loaded insoluble fixing agent to form a loaded stripping solution and barren insoluble fixing agent, wherein the stripping solution comprises at least one of a strong base, an oxalate, ethanedioate, a strongly absorbing exchange oxyanion, a reductant or reducing agent, and oxidant or oxidizing agent;
- (e) cycling the barren insoluble fixing agent to contacting step (b), wherein the barren insoluble fixing agent is contacted with the electrolytic stream to form target material-loaded insoluble fixing agent; and
- (f) removing at least most of the dissolved target material from the loaded stripping solution.

34. A process, comprising:

- (a) receiving a rich feed solution having a target material and a valuable metal;
- (b) electrodepositing the valuable metal onto an electrode to form an electrolyzed solution, wherein at least most of the valuable metal is electrodeposited onto the electrode; and
- (c) contacting at least a portion of at least one of the rich feed solution and the electrolyzed solution with a rare earth-containing fixing agent to form a target material-loaded insoluble fixing agent, the target material-loaded insoluble fixing agent comprising at least most of the target material in the at least a portion of the at least one of the rich feed solution and the barren solution, wherein the target material, in the target material-loaded insoluble fixing agent, forms a composition with the fixing agent and the target material is at least one of antimony and bismuth.

35. The process of claim **34**, further comprising:

- (d) separating the target material-laded insoluble fixing agent from at least one of the rich feed stream and the electrolyzed solution to form a purified stream and a solid target material-laded insoluble fixing agent.

36. The process of claim **35**, further comprising at least one of:

- (e) recover target material; and
- (f) recycle purified stream to electrolysis cell.

37. The process of claim **34**, wherein substantially little, if any, of the valuable metal is removed from one or both of the rich feed stream and the electrolyzed solution in the contacting step (c).

38. The process of claim **34**, wherein the target material comprises an oxyanion.

39. The process of claim **34**, wherein the electrodepositing is one an electrowinning or electrorefining of the valuable metal.

40. The process of claim **38**, wherein the valuable metal comprises a metal having an atomic number of 22-30, 40-48, and 72-79.

41. The process of claim **34**, wherein the insoluble fixing agent comprises cerium.

42. The process of claim **41**, wherein the cerium comprises cerium oxide.

43. The process of claim **34**, wherein the insoluble fixing agent comprises a finely divided solid having a surface area from about 25 m²/g to about 500 m²/g.

44. The process of claim **34**, further comprising:

(g) contacting the target material-loaded insoluble fixing agent with a stripping solution to dissolve, solublize, or otherwise displace most of the target material in the target material-loaded insoluble fixing agent to form a

loaded stripping solution and barren insoluble fixing agent, wherein the stripping solution comprises at least one of a strong base, an oxalate, ethanedioate, a strongly absorbing exchange oxyanion, a reductant or reducing agent, and an oxidant or oxidizing agent; and

(h) cycling the barren insoluble fixing agent to contacting step (c), wherein the barren insoluble fixing agent is contacted with one of the rich feed stream and the electrolyzed solution to form the target material-loaded insoluble fixing agent.

45. The process of claim **44**, further comprising:

(f) removing at least most of the dissolved target material from the loaded stripping solution.

* * * * *