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(54) Title: WET BASED FORMULATIONS FOR THE SELECTIVE REMOVAL OF NOBLE METALS

(57) **Abstract**: Compositions and processes for leaching noble metals from materials comprising said noble metals. Advantageously, the halide-based composition is environmentally friendly and effectively removes noble metals at room temperature without the need for high pressures and electrodes.

WET BASED FORMULATIONS FOR THE SELECTIVE REMOVAL OF NOBLE METALS

FIELD

[0001] The present invention relates generally to processes for recycling/reclaiming of noble metals, such as ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, and gold from source materials.

DESCRIPTION OF THE RELATED ART

[0002] There are a number of sources of noble metals such as gold, silver and platinum group metals which offer the opportunity for economical recovery. For example, gold is available from ores and numerous scrap sources, including industrial wastes, gold plated electronic circuit boards, and in alloys with copper, zinc, silver or tin in the karat gold used in jewelry. Silver is available from photographic and x-ray film emulsions, scrap sterling, and numerous industrial sources. Platinum group metals are available from industrial sources, such as catalysts. There are numerous instances in which it is desirable to recover these metals from an aggregate material.

[0003] Platinum is a silvery, white, ductile metal which is insoluble in mineral and organic acids, but soluble in aqua regia. Platinum does not corrode or tarnish, and forms strong complexes with halides (i.e., chloride, bromide, fluoride and iodide). Platinum is used as a catalyst (nitric acid, sulfuric acid, and high-octane gasoline production; automobile exhaust gas converters), in laboratory ware, spinnerets for rayon and glass fiber manufacture, jewelry, dentistry, electrical contacts, thermocouples, surgical wire, bushings, electroplating, electric furnace windings, chemical reaction vessels, anti-cancer drugs and permanent magnets. Palladium is similarly a silvery, white, ductile metal which does not tarnish in air. It is the least noble (e.g., most reactive) of the platinum group, is insoluble in organic acids, but soluble in aqua regia and fused alkalies. Palladium is used as a catalyst for chemical processes including reforming cracked petroleum fractions and hydrogenation, for metallizing ceramics, as "white gold" in jewelry, in protective coatings, and in hydrogen valves (in hydrogen separation equipment). . Both platinum and palladium are good electrical conductors and are used in alloys for electrical relays in switching systems and telecommunication equipment, resistance wires and aircraft spark plugs. Further, platinum group metal applications include industrial radiography, catalysts, pen points, electrical contacts, jewelry, coatings and headlight reflectors.

[0004] Methods for the recovery of noble metals have taken many forms in the prior art. The conventional leaching of gold ores, for example, with alkaline cyanide solutions, has been widely practiced on a commercial scale, but has known disadvantages including, for example, slow leaching rates, long contact times, and toxicity associated with the use of cyanide. Other methods have included the use of aqua regia or high temperature oxidative pressure leaching. However, and in addition to well known disadvantages, aqua regia has its limitations. For example, aqua regia is unable to dissolve some noble metals, e.g., silver.

[0005] Accordingly, there has remained a need for cost-effective methods and compositions for the recovery of noble metals from a variety of sources of such metals. Thus, while prior art approaches have been successful, these methods have typically suffered from one or more disadvantages. The present disclosure is directed to methods and processes that use halide-based compositions at room temperature to efficiently remove noble metals from the source comprising same.

SUMMARY

[0006] The present invention relates generally to compositions and processes for leaching noble metals from sources comprising same including, but not limited to, ores, jewelry, scraps comprising said noble metals, waste materials, alloys, catalyst materials, and various industrial sources. More specifically, the compositions for leaching noble metals from sources are acidic, halide-based compositions that efficiently remove noble metals from the source at room temperature.

[0007] In one aspect, a leaching composition is described, said composition comprising at least one oxidizing agent, at least one halide, at least one acid, and at least one solvent.

[0008] In another aspect, a method of removing noble metals from a source is described, said method comprising contacting said source under conditions with the leaching composition, wherein said noble metals are dissolved or otherwise solubilized in the leaching composition, and wherein the leaching composition comprises at least one oxidizing agent, at least one halide, at least one acid, and at least one solvent.

[0009] Other aspects, features and advantages will be more fully apparent from the ensuing disclosure and appended claims.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS THEREOF

[0010] The present invention relates generally to compositions and processes for leaching noble metals from sources comprising same including, but not limited to, ores, jewelry, scraps comprising said noble metals, waste materials, alloys, catalyst materials, and various industrial sources. More specifically, the compositions for leaching noble metals from sources are acidic, halide-based compositions that efficiently remove noble metals from the source at low temperatures.

[0011] As used herein, "noble metals" refers to the group of metals including gold, silver, the platinum group metals, alloys comprising same, and combinations thereof. The "platinum group metals" include ruthenium, osmium, rhodium, iridium, palladium and platinum.

[0012] As used herein, "base metals" corresponds to iron, nickel, zinc, copper, aluminum, tungsten, molybdenum, tantalum, magnesium, cobalt, bismuth, cadmium, titanium, zirconium, antimony, manganese, beryllium, chromium, germanium, vanadium, gallium, hafnium, indium, niobium, rhenium, thallium, alloys comprising same, and combinations thereof.

[0013] "Substantially devoid" is defined herein as less than 2 wt. %, preferably less than 1 wt. %, more preferably less than 0.5 wt. %, and most preferably less than 0.1 wt. %. "Devoid" corresponds to 0 wt. %.

[0014] As used herein, "about" is intended to correspond to ± 5 % of the stated value.

[0015] As used herein, "halide" corresponds to fluoride, chloride, bromide or iodide-containing species such as salts or acids.

[0016] As used herein, the "source" is a noble metal-containing material including, but not limited to, ores, jewelry, scraps comprising said noble metals, waste materials comprising said noble metals including electronic waste, alloys, catalyst materials, various industrial sources, and combinations thereof.

[0017] As used herein, "to remove" noble metals from a source means that the noble metal is substantially dissolved or solubilized or the like in the leaching composition, while base metals are not substantially dissolved or solubilized or the like. "Substantially dissolved" is defined herein more than 95 wt. % of the material originally present is dissolved or solubilized or the like, preferably more than 98 wt. %, more preferably more than 99 wt. %, and most preferably more than 99.9 wt. %. "Not substantially dissolved" is defined herein less than 5 wt. % of the material originally present is dissolved or solubilized or the like, preferably less than 2 wt. %, more preferably less than 1 wt. %, and most preferably less than 0.1 wt. %.

[0018] As used herein, the term "leaches" or "leaching" corresponds to the complete or partial removal or extraction of the gold and/or other noble metals from the source into the leaching composition. The gold or other noble metal is dissolved or otherwise solubilized in the leaching composition, preferably dissolved.

[0019] As defined herein, "crushing" the source corresponds to any method that substantially exposes the gold and other noble metals of the source material to the leaching composition, e.g., crushing, cracking, pulverizing, shredding, or grinding.

[0020] As defined herein, "agitation means" include, but are not limited to, physical agitation such as mixing, recirculation, turbulence, and combinations thereof.

[0021] Compositions may be embodied in a wide variety of specific formulations, as hereinafter more fully described. In all such compositions, wherein specific constituents of the composition are discussed in reference to weight percentage ranges including a zero lower limit, it will be understood that such constituents may be present or absent in various specific embodiments of the composition, and that in instances where such constituents are present, they may be present at concentrations as low as 0.001 weight percent, based on the total weight of the composition in which such constituents are employed.

[0022] In a first aspect, a method of removing noble metals from a source is described, wherein said noble metals are dissolved or otherwise solubilized in a leaching composition. More specifically, the method of removing noble metals from a source comprises contacting said source with a leaching composition, wherein said noble metals are dissolved or otherwise solubilized in the leaching composition. Preferably, noble metals are selectively removed relative to base metals also present in the source.

[0023] Advantageously, once a volume of a source has been processed and the noble metals removed (from the leaching composition), new volumes of the source can be added to the leaching composition and the process of removing the noble metals can be repeated again and again until the leaching composition is saturated with noble metals. Alternatively, a "feed and bleed" process may be used wherein clean leaching composition is periodically introduced to the working leaching composition with simultaneous withdrawal of some of the working leaching composition. The leaching composition comprising the noble metals can be processed to obtain useful forms of said noble metals (e.g., electrochemically, by electrowinning, or using reducing agents).

[0024] In removal applications, the leaching composition is contacted in any suitable manner to the source, e.g., by spraying the leaching composition on the source, by dipping the source in a volume of the leaching composition, by contacting the source with another material, e.g., a pad, or fibrous sorbent applicator element, that has the leaching composition absorbed thereon, by contacting the source with a recirculating composition, or by any other suitable means, manner or technique, by which the leaching composition is brought into contact with the source. It should be appreciated that the source (i.e., noble metal containing material) can be added to the leaching composition as is, pulverized into a powder, shredded into pieces, crushed, or in any other form so long as the metals contained in the source are readily exposed for removal from the source. The leaching composition and the source can be agitated such that the source is substantially exposed to the leaching composition.

[0025] In use of the leaching compositions described herein for removing noble metals from a source comprising same, the leaching composition typically is contacted with the source for a time of from about 1 min to about 120 minutes, preferably about 3 min to 60 at temperature in a range of from about 20°C to about 100°C, preferably in a range from about 20°C to about 60°C, more preferably about 20°C to about 40°C, and most preferably about room temperature. Such contacting times and temperatures are illustrative, and any other suitable time and temperature conditions may be employed that are efficacious to remove the noble metals from the source comprising same.

[0026] In a second aspect, a leaching composition is described, said leaching composition comprising, consisting of, or consisting essentially of at least one oxidizing agent, at least one halide, at least one acid, and at least one solvent. In one embodiment, the leaching composition comprises, consists of, or consists essentially of at least one oxidizing agent, at least one chloride salt, at least one acid, and at least one solvent. In another embodiment, the leaching composition comprises, consists of, or consists essentially of at least one oxidizing agent, at least one chloride salt, at least one sulfur-containing acid, and at least one solvent. In still another embodiment, the leaching composition comprises, consists of, or consists essentially of at least one oxidizing agent, at least one alkaline chloride salt, at least one sulfur-containing acid, and at least one solvent. In yet another embodiment, the leaching composition comprises, consists of, or consists essentially of at least one nitrate salt oxidizing agent, at least one alkaline chloride salt, at least one sulfur-containing acid, and at least one solvent. The leaching composition is aqueous in nature and has a pH less than about 2, more preferably less than about 1.

[0027] In another embodiment, the leaching composition comprises, consists of, or consists essentially of at least one oxidizing agent, at least one halide salt, at least one acid, and at least one solvent, present in the following weight percentages, based on the total weight of the composition:

component	preferably	more preferably	most preferably
at least one oxidizing agent	about 1 wt% to about 40 wt%	about 1 wt% to about 30 wt%	about 4 wt% to about 20 wt%
at least one halide	about 1 wt% to about 40 wt%	about 2 wt% to about 30 wt%	about 3 wt% to about 15 wt%
at least one acid	about 1 wt % to about 50 wt %	about 2 wt % to about 40 wt %	about 7 wt % to about 30 wt %
at least one solvent	about 1 wt % to about 93 wt%	about 1 wt % to about 87 wt%	about 35 wt % to about 86 wt%

[0028] In still another embodiment, the leaching composition comprises, consists of, or consists essentially of at least one nitrate salt oxidizing agent, at least one alkaline chloride salt, at least one sulfur-containing acid, and at least one solvent, present in the following weight percentages, based on the total weight of the composition:

component	preferably	more preferably	most preferably
at least one nitrate salt oxidizing agent	about 1 wt% to about 40 wt%	about 1 wt% to about 30 wt%	about 4 wt% to about 20 wt%
at least one alkaline chloride	about 1 wt% to about 40 wt%	about 2 wt% to about 30 wt%	about 3 wt% to about 15 wt%
at least one sulfur-containing acid	about 1 wt % to about 50 wt %	about 2 wt % to about 40 wt %	about 7 wt % to about 30 wt %
at least one solvent	about 1 wt % to about 93 wt%	about 1 wt % to about 87 wt%	about 35 wt % to about 86 wt%

[0029] Oxidizing agents are included in the composition to oxidize the metals to be removed into an ionic form and accumulate highly soluble salts of dissolved metals. Oxidizing agents contemplated herein include, but are not limited to, ozone, nitric acid (HNO_3), bubbled air, cyclohexylaminosulfonic acid, , hydrogen peroxide (H_2O_2), oxone (potassium peroxymonosulfate, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), ammonium polyatomic salts (e.g., ammonium peroxomonosulfate, ammonium chlorite (NH_4ClO_2), ammonium chlorate (NH_4ClO_3), ammonium iodate (NH_4IO_3), ammonium perborate (NH_4BO_3), ammonium perchlorate (NH_4ClO_4), ammonium periodate (NH_4IO_3), ammonium persulfate ($(NH_4)_2S_2O_8$), ammonium hypochlorite (NH_4ClO)), sodium polyatomic salts (e.g., sodium persulfate ($Na_2S_2O_8$), sodium hypochlorite ($NaClO$)), potassium polyatomic salts (e.g., potassium iodate (KIO_3), potassium permanganate ($KMnO_4$), potassium persulfate, potassium persulfate ($K_2S_2O_8$), potassium hypochlorite ($KClO$)), tetramethylammonium polyatomic salts (e.g., tetramethylammonium chlorite ($(N(CH_3)_4)ClO_2$), tetramethylammonium chlorate ($(N(CH_3)_4)ClO_3$), tetramethylammonium iodate ($(N(CH_3)_4)IO_3$), tetramethylammonium perborate ($(N(CH_3)_4)BO_3$), tetramethylammonium perchlorate ($(N(CH_3)_4)ClO_4$), tetramethylammonium periodate ($(N(CH_3)_4)IO_4$), tetramethylammonium persulfate ($(N(CH_3)_4)S_2O_8$), tetramethylammonium nitrate), tetrabutylammonium polyatomic salts (e.g., tetrabutylammonium peroxomonosulfate, tetrabutylammonium nitrate), peroxomonosulfuric acid, urea hydrogen peroxide ($(CO(NH_2)_2)H_2O_2$), peracetic acid ($CH_3(CO)OOH$), sodium nitrate, potassium nitrate, ammonium nitrate, and combinations thereof. Most preferably, the oxidizing agent comprises a nitrate ion including, but not limited to, nitric acid, sodium nitrate, potassium nitrate, ammonium nitrate, tetraalkylammonium nitrate, and combinations thereof.

[0030] The at least one halide is preferably a chloride-containing compound including, but not limited to, hydrochloric acid, and alkaline chlorides (e.g., sodium chloride, potassium chloride, rubidium chloride, cesium chloride, magnesium chloride, calcium chloride, strontium chloride, ammonium chloride, quaternary ammonium chloride salts), and combinations thereof, with the proviso that the chloride-containing compound cannot include copper chloride, chlorine gas, or a second, different halide. For example, the at least one halide is devoid of compounds such as $CuCl_2$, Cl_2, and $BrCl_2^-$. Preferably, the at least one halide comprises an alkaline chloride, even more preferably an alkali metal chloride such as sodium chloride. The at least one halide can also include salts and/or acids comprising bromide and iodide including, but not limited to, sodium bromide, sodium iodide, potassium bromide, potassium iodide, rubidium bromide, rubidium iodide, cesium bromide, cesium iodide, magnesium bromide, magnesium iodide, calcium bromide, calcium iodide, strontium bromide, strontium iodide, ammonium bromide, ammonium iodide, quaternary ammonium bromide salts, and quaternary ammonium bromide salts. The at least one halide is preferably substantially devoid of fluoride ions.

[0031] The at least one acid is preferably a sulfur-containing species such as sulfuric acid, sulfate salts (e.g., sodium sulfate, potassium sulfate, rubidium sulfate, cesium sulfate, magnesium sulfate, calcium sulfate, strontium sulfate, barium sulfate), sulfonic acid, sulfonic acid derivatives, and combinations thereof. Sulfonic acid derivatives contemplated include methanesulfonic acid (MSA), ethanesulfonic acid, 2-hydroxyethanesulfonic acid, n-propanesulfonic acid, isopropanesulfonic acid, isobutenesulfonic acid, n-butanesulfonic acid, n-octanesulfonic acid), benzenesulfonic acid, benzenesulfonic acid derivatives, and combinations thereof. Preferably, the at least one acid comprises sulfuric acid, preferably concentrated sulfuric acid.

[0032] The at least one solvent includes, but is not limited to, water, methanol, ethanol, isopropanol, butanol, pentanol, hexanol, 2-ethyl-1-hexanol, heptanol, octanol, ethylene glycol, propylene glycol, butylene glycol, tetrahydrofurfuryl alcohol (THFA), butylene carbonate, ethylene carbonate, propylene carbonate, dipropylene glycol, diethylene glycol monomethyl ether, triethylene glycol monomethyl ether, diethylene glycol monoethyl ether, triethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, ethylene glycol monohexyl ether, diethylene glycol monohexyl ether, ethylene glycol phenyl ether, propylene glycol methyl ether, dipropylene glycol methyl ether (DPGME), tripropylene glycol methyl ether (TPGME),dipropylene glycol dimethyl ether, dipropylene glycol ethyl ether, propylene glycol n-propyl ether, dipropylene glycol n-propyl ether (DPGPE), tripropylene glycol n-propyl ether, propylene glycol n-butyl ether, dipropylene glycol n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol phenyl ether, 2,3-dihydrodecafluoropentane, ethyl perfluorobutylether, methyl perfluorobutylether, alkyl carbonates, alkylene carbonates, 4-methyl-2-pentanol, tetramethylene glycol dimethyl ether, and combinations thereof. Preferably, the at least one solvent comprises water.

[0033] In another embodiment, the leaching composition further comprises a corrosion inhibitor, specifically a base metal corrosion inhibitor, so as to ensure that the leaching composition selectively removes noble metals from the source relative to base metals. Accordingly, the leaching composition can comprise, consist of, or consist essentially of at least one oxidizing agent, at least one halide, at least one acid, at least one solvent, and at least one corrosion inhibitor. In one embodiment, the leaching composition comprises, consists of, or consists essentially of at least one oxidizing agent, at least one chloride salt, at least one acid, at least one solvent, and at least one corrosion inhibitor. In another embodiment, the leaching composition comprises, consists of, or consists essentially of at least one oxidizing agent, at least one chloride salt, at least one sulfur-containing acid, at least one solvent, and at least one corrosion inhibitor. Corrosion inhibitors for passivating the base metals include, but are not limited to, ascorbic acid, adenosine, adenine, L(+)-ascorbic acid, isoascorbic acid, ascorbic acid derivatives, citric acid, ethylenediamine, gallic acid, oxalic acid, tannic acid, ethylenediaminetetraacetic acid (EDTA), uric acid, 1,2,4-triazole (TAZ), triazole derivatives (e.g., benzotriazole (BTA), tolyltriazole, 5-phenyl-benzotriazole, 5-nitro-benzotriazole, 3-amino-5-mercapto-1,2,4-triazole, 1-amino-1,2,4-triazole, hydroxybenzotriazole, 2-(5-amino-pentyl)-benzotriazole, 1-amino-1,2,3-triazole, 1-amino-5-methyl-1,2,3-triazole, 3-amino-1,2,4-triazole, 3-

mercapto-1,2,4-triazole, 3-isopropyl-1,2,4-triazole, 5-phenylthiol-benzotriazole, halo-benzotriazoles (halo = F, Cl, Br or I), naphthotriazole), 2-mercaptobenzimidazole (MBI), 2-mercaptobenzothiazole, 4-methyl-2-phenylimidazole, 2-mercaptothiazoline, 5-aminotetrazole (ATA), 5-amino-1,3,4-thiadiazole-2-thiol, 2,4-diamino-6-methyl-1,3,5-triazine, thiazole, triazine, methyltetrazole, 1,3-dimethyl-2-imidazolidinone, 1,5-pentamethylenetetrazole, 1-phenyl-5-mercaptotetrazole, diaminomethyltriazine, imidazoline thione, mercaptobenzimidazole, 4-methyl-4H-1,2,4-triazole-3-thiol, 5-amino-1,3,4-thiadiazole-2-thiol, benzothiazole, and combinations thereof. Most preferably, the passivating agent comprises BTA, TAZ, triazole derivatives, or combinations thereof.

[0034] The leaching composition of the second aspect can further comprise noble metal chelators, surfactants, defoamers, and combinations thereof, as readily determined by the person skilled in the art.

[0035] In a particularly preferred embodiment, the leaching composition comprises, consists of, or consists essentially of sodium chloride, sulfuric acid, nitric acid, and water, with the proviso that the leaching composition is substantially devoid of hydrogen peroxide, copper (II) chloride, chlorine gas, $BrCl_2^-$, fluoride-containing compounds, hydroxide-containing compounds, ferrous ions, a sulfur compound comprising a sulfur atom with an oxidation state in the range of -2 to +5, and cyanides.

[0036] It should be appreciated that when the leaching composition comprises a nitrate such as nitric acid, during the leaching of the noble metals from the source, NO_x gases can be emitted. Accordingly, preferably the leaching process is carried out in a system comprising a condenser, wherein the NO_x gases can be collected and converted back into nitric acid, as readily known to the person skilled in the art. As understood by the person skilled in the art, "NO_x" corresponds to mononitrogen oxides such as NO and NO_2.

[0037] Advantageously, the leaching composition is easily recyclable and can be employed in a closed-loop process generating minimal waste. For example, once the leaching composition has been exposed to the source and noble metals have been removed from the source, the resulting leaching composition including the noble metals can be recycled by reclaiming the noble metals. The recycled leaching solution can be reused, with or without the addition of fresh leaching composition chemistry. When necessary to dispose of, the leaching composition is essentially non-toxic once the noble metals are reclaimed and the excess acidity neutralized.

[0038] The leaching compositions described herein are easily formulated by simple addition of the respective ingredients and mixing to homogeneous condition. Furthermore, the leaching composition may be readily formulated as single-package formulations or multi-part formulations that are mixed at or before the point of use, e.g., the individual parts of the multi-part formulation may be mixed at the tool or in a storage tank upstream of the tool. The concentrations of the respective ingredients may be widely varied in specific multiples of the composition, i.e., more dilute or more concentrated, and it will be appreciated that the compositions described herein can variously and alternatively comprise, consist or consist essentially of any combination of ingredients consistent with the disclosure herein.

[0039] Advantageously, the leaching composition described herein is capable of substantially removing noble metals from a source at room temperature without the use of high temperatures (e.g., temperatures greater than about 100°C), high pressures (e.g., pressures greater than atmospheric pressure) or electrodes to maintain the voltage of the composition in a specific range. Moreover, the leaching composition is more environmentally friendly than the prior art cyanide compositions and more inexpensive than tri-iodide compositions. For example, the vessel that is used to process the source to remove the noble metals can comprise any material without any concern of corrosion or degradation.

[0040] The noble metals can be reclaimed from the leaching composition using a number of methods including, but not limited to, electrochemical techniques such as electrowinning, and chemical reduction processes. For example, a reducing agent can be added to the leaching composition containing noble metals to cause their precipitation. Depending on the noble metal content, various reducing agents can be applied to cause selective or non-selective precipitation of noble metals. Precipitation can be done in a manner to avoid the contamination of the leaching composition, so that the leaching composition can be regenerated and reused in the next leaching cycle after the noble metals have been removed. Preferably, the reducing agent is a so-called environmentally friendly chemical. Moreover, preferably the reduction occurs rapidly with minimal heating requirements. For example, precipitation with SO_2 is known to be selective for gold, non-contaminating to the leaching composition and inexpensive. Gold is precipitated as a fine powder that is separated from the leaching solution by filtration. To facilitate filtration, a flocculating agent can be added to the solution at the same time as the reducing agent, if the reducing agent is in liquid or gaseous form. If the reducing agent is in the form of powder, a flocculating agent can be added after complete dissolution of the reducing agent to prevent collection of particles of the reducing agent. For separation of gold powder, commercially available MAGNAFLOK-351 (Ciba Specialty Chemicals) that is typically used for concentrating finely ground gold ores, can be used. The use of a non-ionic flocculating agent is preferred to avoid the possible undesirable recovery of iodine from the composition.

[0041] Alternatively, the reducing agents can include, but are not limited to, sodium borohydride, ascorbic acid, diethyl malonate, sodium metabisulfite, polyphenon 60 (P60, green tea extract), glucose, and sodium citrate. For example, as introduced in International Patent Application No. PCT/US11/48449 filed on August 19, 2011 and entitled “Sustainable Process for Reclaiming Precious Metals and Base Metals from e-Waste,” which is hereby incorporated by reference herein in its entirety, ascorbic acid introduced to a composition comprising Au^{3+} ions at pH 1 produces highly pure gold metal. Sodium metabisulfite (SMB) can be added to a composition comprising Au^{3+} ions at pH 1 or pH 7 and produce highly pure gold metal. Alternatively, the noble metal ions can be converted to noble metals via electrowinning or electrochemical techniques. Any suitable means can be used to remove the precipitated noble metals. Settling and decanting, filtering the solution through a filter press or centrifuging are convenient procedures for such removal.

[0042] After separation of the solid gold by filtering, centrifugation or any other appropriate method, the leaching composition may still include leached silver and palladium ions. A selective reducing agent may be added for precipitation of silver, such as hydroxylamine. The use of a flocculating agent is suggested to facilitate filtration. After separation of precipitated silver, palladium can be precipitated, for example, with the use of a stabilized alkali metal borohydride and a flocculating agent.

[0043] It should be appreciated that the source material subsequent to leaching can be rinsed (e.g., with water) to further recover the residual leaching composition on the surface of the source material, which can contain very significant amounts of dissolved noble metals.

[0044] Electrowinning is a common way of gold recovery from solutions, but if the rinse water comprising dissolved gold is recovered, conventional electrowinning becomes ineffective as gold is present in rinse water in small concentrations. The removal of gold from rinse water solutions can become effective if high surface area (HSA) electrodes are used for electrowinning. HSA electrowinning may economically remove gold having a concentration greater than 10 ppm down to ppb level. Iodide can also be oxidized and recovered using the same process if an undivided electrowinning cell is used.

[0045] The features and advantages of the invention are more fully illustrated by the following non-limiting examples, wherein all parts and percentages are by weight, unless otherwise expressly stated.

Example 1

[0046] 40 g of a leaching composition comprising 30 wt% water, 29 wt% sulfuric acid (96%), 18 wt% nitric acid (70%) and 23 wt% saturated sodium chloride was prepared. The leaching composition was divided into four test tubes containing 10g each of the leaching composition. Gold fingers, pure Pd, pure Pt and pure Ag were added to each of the test tubes and processed as indicated and the pre- and post-weight of the noble metals determined, as summarized in Table 1.

	Au	Ag	Pd	Pt
processed at 60ºC for 60 minutes in 10 g leaching composition				
pre-weight (g)	0.084	0.098	0.039	0.046
post-weight (g)	0	0.099	0.01	0.048
additional Au/Pd metals added to same solution and processed for 120 min at 60°C				
pre-weight (g)	0.183		0.112	
post-weight (g)	0		0	
additional Au/Pd metals added to same solution and processed for 3 days at room temperature				
pre-weight (g)	0.102		0.052	

post-weight (g)	0.057		0	0.041
total dissolved metal (g)	0.312	0	0.203	0.005

[0047] It can be seen that the leaching composition effectively and efficiently dissolved gold and palladium and could be loaded with additional metal as more source is added to said composition.

[0048] Although the invention has been variously disclosed herein with reference to illustrative embodiments and features, it will be appreciated that the embodiments and features described hereinabove are not intended to limit the invention, and that other variations, modifications and other embodiments will suggest themselves to those of ordinary skill in the art, based on the disclosure herein. The invention therefore is to be broadly construed, as encompassing all such variations, modifications and alternative embodiments within the spirit and scope of the claims hereafter set forth.

THE CLAIMS

What is claimed is:

1. A leaching composition comprising, at least one oxidizing agent, at least one halide, at least one acid, and at least one solvent.

2. The leaching composition of claim 1, wherein the composition includes a pH of less than about 2.

3. The leaching composition of claims 1 or 2, wherein the at least one oxidizing agent comprises at least one species selected from the group consisting of ozone, nitric acid (HNO_3), bubbled air, cyclohexylaminosulfonic acid, , hydrogen peroxide (H_2O_2), oxone, ammonium peroxomonosulfate, ammonium chlorite (NH_4ClO_2), ammonium chlorate (NH_4ClO_3), ammonium iodate (NH_4IO_3), ammonium perborate (NH_4BO_3), ammonium perchlorate (NH_4ClO_4), ammonium periodate (NH_4IO_3), ammonium persulfate ($(NH_4)_2S_2O_8$), ammonium hypochlorite (NH_4ClO), sodium persulfate ($Na_2S_2O_8$), sodium hypochlorite ($NaClO$)), potassium polyatomic salts (e.g., potassium iodate (KIO_3), potassium permanganate ($KMnO_4$), potassium persulfate, potassium persulfate ($K_2S_2O_8$), potassium hypochlorite ($KClO$), tetramethylammonium chlorite ($(N(CH_3)_4)ClO_2$), tetramethylammonium chlorate ($(N(CH_3)_4)ClO_3$), tetramethylammonium iodate ($(N(CH_3)_4)IO_3$), tetramethylammonium perborate ($(N(CH_3)_4)BO_3$), tetramethylammonium perchlorate ($(N(CH_3)_4)ClO_4$), tetramethylammonium periodate ($(N(CH_3)_4)IO_4$), tetramethylammonium persulfate ($(N(CH_3)_4)S_2O_8$), tetrabutylammonium peroxomonosulfate, peroxomonosulfuric acid, urea hydrogen peroxide ($(CO(NH_2)_2)H_2O_2$), peracetic acid ($CH_3(CO)OOH$), sodium nitrate, potassium nitrate, ammonium nitrate, and combinations thereof.

4. The leaching composition of any of the preceding claims, wherein the at least one oxidizing agent comprises a nitrate salt selected from the group consisting of nitric acid, sodium nitrate, potassium nitrate, ammonium nitrate, tetraalkylammonium nitrate, and combinations thereof, preferably nitric acid.

5. The leaching composition of any of the preceding claims, wherein the at least one halide comprises an alkaline chloride.

6. The leaching composition of any of the preceding claims, wherein the at least one halide comprises a chloride species selected from the group consisting of hydrochloric acid, sodium chloride, potassium chloride, rubidium chloride, cesium chloride, magnesium chloride, calcium chloride, strontium

chloride, ammonium chloride, quaternary ammonium chloride salts, and combinations thereof, with the proviso that the chloride species cannot include copper chloride, chlorine gas, or a second, different halide in the compound, preferably sodium chloride.

7. The leaching composition of any of the preceding claims, wherein the at least one acid is a sulfur-containing acid.

8. The leaching composition of any of the preceding claims, wherein the at least one acid comprises a species selected from the group consisting of sulfuric acid, sodium sulfate, potassium sulfate, rubidium sulfate, cesium sulfate, magnesium sulfate, calcium sulfate, strontium sulfate, barium sulfate, sulfonic acid, sulfonic acid derivatives, and combinations thereof, preferably sulfuric acid.

9. The leaching composition of any of the preceding claims, wherein the composition further comprises at least one of surfactants, defoamers, and combinations thereof.

10. The leaching composition of claim 1, wherein the composition comprises nitric acid, sodium chloride, sulfuric acid, and water.

11. The leaching composition of any of the preceding claims, wherein the composition further comprises at least one corrosion inhibitor.

12. The leaching composition of any of the preceding claims, wherein the leaching composition is substantially devoid of hydrogen peroxide, fluoride-containing compounds, $CuCl_2$, Cl_2, $BrCl_2^-$, hydroxide-containing compounds, ferrous ions, a sulfur compound comprising a sulfur atom with an oxidation state in the range of -2 to +5, and cyanides.

13. A method of removing noble metals from a source, said method comprising contacting said source under conditions with the leaching composition of any of claims 1-12, wherein said noble metals are dissolved or otherwise solubilized in the leaching composition.

14. The method of claim 13, wherein the noble metals are selectively removed relative to base metals also present in the source.

15. The method of claims 13 or 14, wherein the source is selected from the group consisting of ores, jewelry, scraps comprising noble metals, waste materials comprising noble metals, electronic waste materials comprising noble metals, alloys, catalyst materials, and industrial sources.

16. The method of any of claims 13-15, wherein the source is crushed, cracked, pulverized, shredded, or ground to expose the noble metals.

17. The method of any of claims 13-16, wherein the leaching composition and source are agitated such that the source is substantially exposed to the leaching composition.

18. The method of any of claims 13-17, wherein the conditions are selected from the group consisting of time of from about 1 min to about 120 minutes, temperature in a range of from about 20°C to about 100°C, and combinations thereof.

19. The method of any of claims 13-18, wherein the conditions comprise temperature of about 20°C to about 60°C.

20. The method of any of claims 13-19, further comprising reclaiming the noble metals from the leaching composition by electrochemical techniques such as electrowinning, or chemical reduction processes.

21. The method of any of claims 13-20, wherein the removal of noble metals from the source is effectuated at temperatures less than about 100°C, pressures not greater than atmospheric pressure, and without the use of electrodes.

22. The method of any of claims 13-21, wherein the noble metals comprise a species selected from the group consisting of gold, silver, ruthenium, osmium, rhodium, iridium, palladium, platinum, alloys comprising same, and combinations thereof.

23. The method of any of claims 14-22, wherein the base metals comprise a species selected from the group consisting of iron, nickel, zinc, copper, aluminum, tungsten, molybdenum, tantalum, magnesium, cobalt, bismuth, cadmium, titanium, zirconium, antimony, manganese, beryllium, chromium, germanium, vanadium, gallium, hafnium, indium, niobium, rhenium, thallium, alloys comprising same, and combinations thereof.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/017088

A. CLASSIFICATION OF SUBJECT MATTER

C22B 3/04(2006.01)i, C22B 3/06(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22B 3/04; C22B 11/04; C22B 11/04; C22B 13/04; C22B 003/00; C22B 11/00; C22B 59/00; C22B 3/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: recovery, leaching, oxidizing agent, chloride, acid and solvent

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0124213 A1 (HYDROMET MINERAL (UK) LIMITED) 07 November 1984 See page 2, line 32 - page 4, line 17; claims 1, 4, 11 and 15.	1-3,10
A	US 4244735 A (REYNOLDS et al.) 13 January 1981 See column 4, lines 22-56; claims 7 and 9.	1-3,10
A	US 2002-0112569 A1 (FARONE et al.) 22 August 2002 See paragraphs [0025]-[0027]; claim 19.	1-3,10
A	EP 0155250 B1 (BOLIDEN AKTIEBOLAG) 18 September 1985 See column 5, line 24 - column 6, line 41; claim 1.	1-3,10
A	US 6455018 B1 (CUIF, JEAN-PIERRE) 24 September 2002 See column 4, lines 35-64; claims 1, 2, 5 and 8.	1-3,10

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 26 May 2015 (26.05.2015)	Date of mailing of the international search report **27 May 2015 (27.05.2015)**
Name and mailing address of the ISA/KR International Application Division Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea Facsimile No. +82-42-472-7140	Authorized officer CHO, Han Sol Telephone No. +82-42-481-5580

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/017088

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 14
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 14 is unclear because it refers to multiple dependent claim 13 which does not comply with PCT Rule 6.4(a).

3. ☒ Claims Nos.: 4-9,11-13,15-23
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/017088

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