

Method For High And Selective Extraction of Silver

Technical Field

5 The present invention relates to a composition comprising a weak acid, an oxidant and a metal complexing agent, wherein the composition has a pH in the range of 2 to 4. The present invention also relates to a method of preparing such a composition, and a method of extracting silver using such a composition.

Background Art

10 The demand for precious metallic silver (Ag) from the industries is rapidly increasing due to its use in the manufacture of numerous products. Silver is used extensively in electrical and electronic devices due to its superior electrical and heat conductivity. It also plays a key role in photovoltaics modules in the form of a conductive paste for efficient electricity generation. Owing to its malleability, ductility, high reflectivity and strength, silver is employed in the making of jewellery, silverware, solders and other industry applications. In addition, the photosensitive
15 nature of silver halides allows its use in photography. Silver is also utilised in medicine and consumer products because of its antimicrobial and non-toxic nature.

In order to meet the increasing demand for silver, it is essential that silver is recycled from secondary sources such as silver-coated printed circuit boards (PCBs) of discarded computers and mobile phones, metallic scraps and photographic films. In PCB for instance, silver can be present
20 in concentration of 50 to 3300 ppm depending on the manufacturer and year of production. With the large volumes of electronic waste generated every year i.e. estimated 50 million tonnes in 2019, considerable amount of silver is potentially available for recovery and re-use. As electrical and electronic wastes account for the bulk of secondary resources of silver, methods for extracting silver from such waste would need to take into consideration their complex matrix, which includes
25 a mixture of toxic heavy metals such as copper (Cu), zinc (Zn), aluminium (Al), tin (Sn), lead (Pb) etc., and hazardous organic components including brominated flame retardants, polybrominated biphenyls etc.

Currently, the most common approaches for silver extraction from silver-coated solid wastes are pyro-metallurgy and hydro-metallurgy. Pyro-metallurgy involves the application of heat in
30 furnaces or smelters to extract and refine metals from wastes under high temperature. During the process, dust, metal fumes and toxic gases like dioxins, furans, chlorine, bromine and sulphur dioxide are emitted. The flue gas would hence need to be treated to remove these noxious substances before discharging into the atmosphere. The pyro-metallurgy approach generally consumes high amounts of energy and requires high engineering capital costs as it is best suited
35 for large scale operation. These factors render it less economical and less environmentally-friendly compared to the hydro-metallurgy approach. Hydro-metallurgy extracts metals from solid wastes through contacting them with aqueous solutions that are formulated to promote the

dissolution of specific metals into the aqueous phase. The solutions are then subjected to separation and refining techniques, for example, precipitation and solvent extraction, to isolate and concentrate the metal of interest. This is followed by metal recovery from the solution via electro-winning, cementation, or chemical reduction. Hydro-metallurgy offers a way to recycle metals at a relatively low cost and at smaller scale, but optimum care should be taken to avoid the use of toxic and hazardous chemicals so that the waste streams resulting from the process do not adversely affect or damage organisms and the environment.

At present, however, strong corrosive acids such as nitric acid and highly toxic cyanide-based solutions are the most widely used solutions in the industry for extraction of silver from silver-coated solid wastes, attributed to their low cost and long history.

Nitric acid is a powerful oxidising acid at high concentrations ($> 5M$) that is capable of dissolving most metals including silver to form soluble metal nitrates. Studies investigating the leaching performance of nitric acid for silver extraction from PCB and photographic films yielded high efficiencies of 87% and 98% respectively. Due to its strong oxidising strength, leaching by nitric acid is non-selective as it oxidises not just silver but most of the other metals present in the wastes, causing a complex mixture of metal ions in the lixiviant that requires rigorous segregation and purification downstream. In addition, the concentrated form of nitric acid is difficult to handle, since it produces fumes and requires adequate exhaust system for safe operation.

In cyanide-based lixiviants, free cyanide ions (CN^-) act as a complexing agent to form a stable complex with silver at a pH of above 10. While the leaching is generally more selective than nitric acid towards precious metals such as silver, with minimal reagent loss during the process, reported extraction efficiencies from secondary sources such as pulverised waste PCBs was only about 60%. To improve recovery, a pre-treatment of the waste before cyanide leaching is often required to remove base metals such as copper. For instance, oxidative sulphuric acid leaching before cyanide leaching has been demonstrated to effectively aid in increasing overall silver recovery to 93%. Nevertheless, because of the highly toxic nature of cyanide, its use has been increasingly regulated or even prohibited in many countries, leading to the hunt for viable alternatives that are safer to handle, more environmentally-friendly and more economical.

Thiocyanate is one of the alternatives being examined as a replacement to cyanide. It has been shown to perform well under acidic conditions in the presence of an oxidant to achieve rather high extraction rates of silver. 99% silver leaching rate has been attained in a thiocyanate lixiviant with ferric ion as oxidant at pH 2 after 8 hours, using waste PCBs that have been pre-treated with sulphuric acid and hydrogen peroxide. Without pre-treatment, the leaching process using thiocyanate would need to be done at a higher temperature so as to achieve satisfactory leaching performance. For example, ammonium thiocyanate oxidative pressure leaching at pH 1.8, 120°C has been shown to facilitate extraction of 88% of silver from silver-rich residue after 3 hours. Operating at low pH and high temperatures indicate the need for high capital costs to accommodate such conditions, which could be why no large scale application of thiocyanate for precious metals recovery is known. Furthermore, under certain conditions, thiocyanate can decompose to form free cyanide, therefore stringent control of operating conditions is needed to

ensure safety. Similar to cyanide-based lixivants, it is also crucial to detoxify waste streams from thiocyanate leaching which further adds to operating costs.

Another potential alternative to cyanide is thiosulfate which is non-toxic. However, thiosulfate is intrinsically metastable and decomposes readily to sulphate via a series of sulphur-oxygen species (mainly tetrathionate) and sulphide. To reduce its decomposition, thiosulfate is utilised with ammonia and a delicately balanced concentration of copper ions since too much of copper can increase the decomposition of thiosulfate which in turn increases reagent consumption. Ammonium thiosulfate leaching conducted at pH 9 and 40°C on unprocessed PCBs waste only recorded 12% extraction of silver after 48 hours, but when the samples were milled prior to leaching, extraction increased significantly to 93% after 48 hours. To further reduce leaching duration, a pre-treatment step applied to remove base metals such as Cu, Ni, Zn in addition to size reduction of the samples has been proven to work well. 100% of silver has been shown to be successfully leached after 24 hours from waste PCBs that have been reduced to sizes less than 1 mm and pre-leached with sulfuric acid and hydrogen peroxide that removes over 95% of the base metals present. Nevertheless, the long reaction time remains a major drawback for this technology.

The feasibility of using thiourea-based lixiviant as a substitute for cyanide for precious metals extraction has been researched at a wider level compared to most of the others and even found large scale applications in Australia and China. Studies have shown the viability of using thiourea with ferric ion in diluted sulphuric acid medium for leaching of silver from secondary sources. For instance, it has been shown that 94% silver recovery from PCB waste after 2 hours of leaching with 10 g/L thiourea, 5 g/L ferric ions and 10 g/L sulphuric acid at pH 1, 20°C can be achieved. Reaction kinetics using thiourea leaching is fast and could be boosted with an increase in temperature or with the use of ultrasound as reported by Salim et al whom obtained a silver yield of 98.6% in just 24 minutes. However, thiourea leaching is highly sensitive to process conditions such as pH, temperature and reagent concentrations. Thiourea decomposes easily in the presence of an oxidant to form formamidine disulphide which further decomposes to produce cyanamide and elemental sulphur. This is detrimental since a passivating layer is formed on the precious metals surface and prevents further dissolution into the aqueous phase. The decomposition of thiourea not only increases reagent consumption but also makes the process difficult to control for optimum selectivity and recovery of silver. Furthermore, with thiourea classified as a suspected carcinogen, its use as a cyanide alternative becomes even less attractive.

Halides paired with their halogens i.e. bromide-bromine, iodide-iodine, have also been investigated as a potential replacement for cyanide for leaching of precious metals. In such systems, the halide acts as the complexing agent and the halogen the oxidant. Due to the corrosive and toxic nature of the halides/halogen, the leaching process is conducted within a closed system. While leaching rates are fast and extraction of silver can exceed 99%, the reagents are expensive and difficult to handle. Moreover, loss of the halides as insoluble precipitates would result in high reagent consumption and hence further increase reagent cost.

With the increasing demand for silver from the industry, there is a need for effective technologies to extract and recover silver from secondary sources so as to meet the demand. This is also

synchronous with the increasing regulations put up worldwide that mandates the recycling of electronic wastes, which accounts for the bulk of secondary sources of silver. The existing hydrometallurgy methods used in the industry currently are strong acid-based or cyanide-based techniques that are hazardous and highly toxic. Though several alternative non-cyanide systems
5 utilising thiourea, thiosulfate and halogen/halides have been examined and shown to perform well, there is limited demonstration of their large-scale application.

In view of the limitations of current methods for extraction of silver from solid wastes comprising silver, there is a need for development of a lixiviant that is non-toxic, user and environmentally friendly, economical, and capable of achieving selective extraction with high efficiencies, to
10 overcome or at least ameliorate, one or more of the disadvantages described above.

Summary

In an aspect, there is provided a composition comprising:

- i) a first weak acid;
- ii) an oxidant; and
- 15 iii) a metal complexing agent,

wherein the composition has a pH in the range of 2 to 4.

Advantageously, the disclosed composition is significantly less toxic and hazardous compared to conventional lixiviants since there is no highly corrosive or highly toxic reagents used. In particular, the composition does not comprise any cyanide, eliminating the safety, health and
20 environmental problems associated with the use and post-treatment of cyanide-based solutions. The composition further advantageously does not use any other highly toxic reagents, including strong corrosive acids. Therefore, the waste streams generated using these reagents would advantageously not require any specialised and costly treatment before discharging into the environment.

25 Advantageously, the composition may further comprise a catalyst. The catalyst may further enhance the rate of extraction of silver without compromising the other advantageous properties of the composition.

In another aspect, there is provided a method of preparing the composition according any one of the preceding claims, comprising the step of mixing:

- 30 i) a first weak acid;
- ii) an oxidant; and
- iii) an metal complexing agent,

wherein the composition has a pH in the range of 2 to 4.

Advantageously, the composition may be easily prepared by simply mixing the first weak acid, oxidant and metal complexing agent at room temperature and standard pressure. Further advantageously, since the method of preparation is so simple, up-scaling of the method may be easily done.

- 5 In another aspect, there is provided a method of extracting silver from a solid mixture comprising a plurality of metals comprising silver, the method comprising the step of contacting the composition as defined above with the solid mixture to form a leachate solution.

In another aspect, there is provided the use of the composition as defined above, to recover silver from a solid mixture comprising a plurality of metals comprising silver.

- 10 Advantageously, the disclosed method offers a simple, low cost and highly effective way of selectively extracting silver from silver-coated solid waste. Advantageously, the method allows the silver to be recovered at mild temperatures of $\leq 50^{\circ}\text{C}$, allowing for low energy consumption during the process. Advantageously, over 97% of silver may be extracted in a selective manner using the disclosed method, with silver constituting 84 to 98% of the metals in leachate, with
15 up to a saturation concentration of 3 to >15 g/L. The extraction of silver may therefore be achieved at a high yield, high selectivity and at a high rate. Further advantageously, the leached silver may be recovered from the leachate solution through facile conventional means such as precipitation and reduction.

- Further advantageously, the combination of the acidic medium, H_2O_2 and ethanolamine may be
20 essential for high yield and selectivity of silver leaching, as the deprivation of any one of these components may adversely affect the performance of the lixiviant. Further advantageously, the presence of the catalyst may further improve the rate of silver leaching. However, the concentration of reagents in the lixiviant as well as the extraction conditions such as pH and temperature, may be easily adjusted to improve the extraction performance of the lixiviant for
25 different types, sizes and surface area of waste materials. In addition, pre-treatment steps such as pre-leach to remove base metals, may be advantageously applied to enhance extraction rate.

- Further advantageously, since the components of the composition is significantly less toxic and hazardous the waste streams generated using during the method or use to extract silver would advantageously not require any specialised and costly treatment before discharging into the
30 environment. Moreover, as leaching proceeds, the oxidant is consumed, making the resulting leachate solution even less hazardous over time.

Definitions

The following words and terms used herein shall have the meaning indicated:

- "Alkyl" as a group or part of a group refers to a straight or branched aliphatic hydrocarbon group,
35 preferably a C_1 – C_{22} alkyl, more preferably a C_1 – C_{12} alkyl, most preferably C_1 – C_6 unless otherwise noted. Examples of suitable straight and branched C_1 – C_6 alkyl substituents include methyl, ethyl,

n-propyl, 2-propyl, n-butyl, sec-butyl, t-butyl, hexyl, and the like. The group may be a terminal group or a bridging group.

"Lower alkyl" as a group or part of a group refers to an alkyl group with fewer than six carbon atoms. The group may be a terminal group or a bridging group.

- 5 "Aryl" as a group or part of a group denotes (i) an optionally substituted monocyclic, or fused polycyclic, aromatic carbocycle (ring structure having ring atoms that are all carbon) preferably having from 5 to 12 atoms per ring. Examples of aryl groups include phenyl, naphthyl, and the like; (ii) an optionally substituted partially saturated bicyclic aromatic carbocyclic moiety in which a phenyl and a C₅₋₇ cycloalkyl or C₅₋₇ cycloalkenyl group are fused together to form a cyclic
10 structure, such as tetrahydronaphthyl, indenyl or indanyl. The group may be a terminal group or a bridging group. Typically an aryl group is a C₆-C₁₈ aryl group.

- "Alkylaryl" means an alkyl-aryl-- group in which the aryl and alkyl moieties are as defined herein. Preferred alkylaryl groups contain a C₁₋₁₂ alkyl moiety. The group may be a terminal group or a bridging group. If the group is a terminal group, it is bonded to the remainder of the molecule
15 through the aryl group.

"Alkyloxy" which can be used interchangeably with "alkoxy" refers to an alkyl group as defined herein that is singularly bonded to oxygen. The group may be a terminal group or a bridging group. If the group is a terminal group, it is bonded to the remainder of the molecule through the alkyl group. "

- 20 The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

- Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they
25 include recited elements but also permit inclusion of additional, unrecited elements.

- As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated
30 value.

- Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically
35 disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4,

from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

- 5 Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Detailed Disclosure of Optional Embodiments

There is provided a composition comprising:

- 10 i) a first weak acid;
- ii) an oxidant; and
- iii) a metal complexing agent,
- wherein the composition has a pH in the range of 2 to 4.

- 15 The pH may be in the range of about 2 to about 4, about 2 to about 2.5, about 2 to about 3, about 2 to about 3.5, about 2.5 to about 3, about 2.5 to about 3.5, about 2.5 to about 4, about 3 to about 3.5, about 3 to about 4, or about 3.5 to about 4. The pH may be maintained below 4.5 to maintain optimum stability of the oxidant.

- 20 The first weak acid may be a weak organic acid, a weak inorganic acid or a mixture thereof. Any acid which does not fully dissociate in water, with both the undissociated acid and its dissociation products being present, in solution, in equilibrium with each other, may be considered a weak acid.

- 25 The first weak acid may be selected from the group consisting of acetic acid, monochloroacetic acid, formic acid, benzoic acid, oxalic acid, sulfurous acid, methanoic acid, phosphoric acid, nitrous acid, , lactic acid, methanesulfonic acid, orthophosphoric acid, propionic acid, trichloroacetic acid, maleic acid, salicylic acid, phosphorous acid, citric acid, ethylenediaminetetraacetic acid, glycolic acid, levulinic acid, mercaptosuccinic acid, succinic acid, sulfamic acid, malonic acid, adipic acid and any mixture thereof.

The first weak acid may be a weak organic acid, and may be selected from acetic acid, monochloroacetic acid or a mixture thereof.

- 30 Where the first weak acid is a mixture of acetic acid and monochloroacetic acid, the acetic acid may have a concentration in a range of 0.2% w/v to about 1.5% w/v, about 0.2% w/v to about 0.5% w/v, about 0.2% w/v to about 1.0% w/v, about 0.5% w/v to about 1.0% w/v, about 0.5% w/v to about 1.5% w/v or about 1.0% w/v to about 1.5% w/v, based on the total volume of the

composition. Where the first weak acid is a mixture of acetic acid and monochloroacetic acid, the acetic acid may have a concentration of about 0.4% w/v.

Where the first weak acid is a mixture of acetic acid and monochloroacetic acid, the monochloroacetic acid may have a concentration in a range of about 0.1% w/v to about 1.0% w/v, about 0.1% w/v to about 0.5% w/v, about 0.1% w/v to about 0.2% w/v, about 0.2% w/v to about 0.5% w/v, about 0.2 % w/v to about 1.0% w/v or about 0.5% w/v to about 1.0% w/v based on the total volume of the composition.

The use of weak or milder acids such as organic acids including acetic acid and/or monochloroacetic acid may enhance the selectivity of silver extraction, as such acids may play a role in complexing silver. Further, monochloroacetic acid may additionally function to chelate silver, improving the selectivity of the lixiviant for silver extraction. By enhancing silver leaching, the oxidation of base metals such as Cu and Sn may be reduced.

The composition may comprise the first weak acid at concentration in a range of about 0.3% w/v to about 2.0% w/v, about 0.3% w/v to about 0.5% w/v, about 0.3% w/v to about 1.0% w/v, about 0.3% w/v to about 1.5% w/v, about 0.5% w/v to about 1.0% w/v, about 0.5% w/v to about 1.5% w/v, about 0.5% w/v to about 2.0% w/v, about 1.0% w/v to about 1.5% w/v, about 1.0% w/v to about 2.0% w/v or about 1.5% w/v to about 2.0% w/v, based on the total volume of the composition.

The composition may comprise the first weak acid at concentration in a range of 0.5 to 1.5% w/v based on the total volume of the composition, giving the composition a pH in the range of 2 to 4. At this concentration, the composition may be non-fuming and therefore easy to handle so that costly specialised equipment is not required.

The oxidant may be selected from the group consisting of a peroxide, a persulfate, a peroxy acid, an oxoacid acid, an oxyanion, a nitrate compound, a hexavalent chromium compound, permanganates, cerium (IV) compounds, sodium bismuthate, lead dioxide and any mixture thereof.

The oxidant may be selected from the group consisting of sodium nitrate, potassium nitrate, peroxydisulfuric acid, peroxymonosulfuric acid, hypochlorite, sodium hypochlorite, calcium hypochlorite, chlorite, sodium chlorite, chlorate, sodium chlorate, potassium chlorate, perchlorate, sodium perchlorate, potassium perchlorate, ammonium perchlorate, perchloric acid, chromic acid, dichromic acid, chromium trioxide, pyridinium chlorochromate, chromate compound, dichromate compound, sodium permanganate, potassium permanganate, ceric ammonium nitrate, ceric sulfate, sodium perborate, sodium percarbonate, sodium perphosphonate, sodium persulfate, urea peroxide, sodium bismuthate, lead dioxide and any mixture thereof.

The oxidant may be a peroxide. The oxidant may be selected from the group consisting of hydrogen peroxide, acetyl acetone peroxide, acetyl benzoyl peroxide, ascaridole, tert-butyl hydroperoxide, di-(1-naphthoyl)peroxide, diacetyl peroxide, ethyl hydroperoxide, iodoxy compounds, methyl ethyl ketone peroxide, methyl isobutyl ketone peroxide, peroxymonosulfuric

acid, peroxyntic acid, peroxyphosphoric acid, peroxydisulfate, hydroperoxyformic acid, sodium peroxide, potassium peroxide, urea peroxide, and any mixture thereof.

5 The oxidant may be hydrogen peroxide. Hydrogen peroxide may be a low-cost reagent and has been widely used in the industry over the years as bleach, oxidiser and disinfectant as it generally performs well and is more environmentally-friendly than many other alternatives such as chlorine and potassium permanganate, as hydrogen peroxide breaks down to produce only oxygen and water. In the case of precious metals extraction which typically uses highly corrosive or cyanide-based technologies subjected to stringent government regulations, the use of hydrogen peroxide would likely alleviate safety concerns and toxic waste treatment cost. Further, with the use of
10 stabilisers and an acidic medium, its consumption may be controlled and reduced relatively with ease to enable the extraction process to be economical.

The composition may comprise the oxidant at concentration in a range of about 3% w/v to 15 % w/v, about 3% w/v to about 6% w/v, about 3% w/v to about 9% w/v, about 3% w/v to about 12% w/v, about 6% w/v to about 9% w/v, about 6% w/v to about 12% w/v, about 6% w/v to about 15%
15 w/v, about 9% w/v to about 12% w/v, about 9% w/v to about 15% w/v, or about 12% w/v to about 15% w/v, based on the total volume of the composition.

The metal complexing agent may be any compound that may complex to a metal. The metal may be a precious metal. The metal may be a metal selected from group 10 or 11 of the Periodic Table of Elements. The metal may be selected from the group consisting of nickel, palladium, platinum,
20 copper, silver and gold. The metal may be silver, copper or silver and copper.

The metal complexing agent may comprise a nitrogen.

The metal complexing agent may comprise an amine group. Amines, being derivatives of ammonia which has been demonstrated to achieve high and selective leaching of silver, may be preferred to ammonia as they are easier to handle and generally have lower consumption than
25 volatile ammonia.

The amine group may be a primary tertiary or a secondary amine. The metal complexing agent may comprise 1, 2, 3, 4, 5 or 6 amine groups.

The metal complexing agent may further comprise an alcohol group. The metal complexing agent may comprise 1, 2, 3, 4, 5 or 6 alcohol groups

30 The metal complexing agent may be selected from the group consisting of ethanolamine, hexamethylenetetramine, ethylenediamine, N-(2-hydroxyethyl) ethylenediamine, N,N-Dimethylethylenediamine, ethylenediaminetetraacetic acid (EDTA), 5,5-dimethylhydantoin, ammonia, EDTA, nicotinic acid, 1,10-phenanthroline, 4,6-dimethylpyrimidine, 4,7-phenanthroline, benzo[c]cinnoline, 4-(2-pyridyl)pyrimidine and any mixture thereof.

35 The metal complexing agent may be selected from the group consisting of ethanolamine, hexamethylenetetramine, ethylenediamine, N-(2-hydroxyethyl) ethylenediamine, N,N-dimethylethylenediamine, and any mixture thereof.

By using a complexing agent that may form a stable complex with silver, the extraction of silver may be enhanced, which in turn may also reduce the oxidation of base metals such as Cu and Sn. The metal complexing agent comprising an amine group and monochloroacetic acid may both chelate silver to enhance the yield and selectivity in the extraction of silver. Base metals may be
5 common metals that tend to be more abundant and less costly, such as copper (Cu), zinc (Zn), aluminium (Al), tin (Sn), lead (Pb) and any mixture thereof. Base metals may generally be plated at the bottom layer of electronic components underneath precious metals such as silver (Ag), (Au), and/or (Pd).

The composition may comprise the metal chelating agent at a concentration in a range of about
10 0.05% w/v to about 2% w/v, about 0.05% w/v to about 0.1% w/v, about 0.05% w/v to about 0.2% w/v, about 0.05% w/v to about 0.5% w/v, about 0.05% w/v to about 1% w/v, about 0.1% w/v to about 0.2% w/v, about 0.1% w/v to about 0.5% w/v, about 0.1% w/v to about 1% w/v, about 0.1% w/v to about 2% w/v, about 0.2% w/v to about 0.5% w/v, about 0.2% w/v to about 1% w/v, about 0.2% w/v to about 2% w/v, about 0.5% w/v to about 1% w/v, about 0.5% w/v to about 2% w/v or
15 about 1% w/v to about 2% w/v based on the total volume of the composition.

The composition may further comprise a catalyst. The catalyst may enhance the extraction rate of silver to which the composition may be applied to, which may in turn reduce the duration of the extraction process.

The catalyst may be a base metal or a salt of a base metal. The salt of the base metal may comprise
20 a base metal cation and a counter anion.

The base metal may be selected from the group consisting of copper, nickel, cobalt, iron, chromium, aluminium, zinc, lead, manganese, titanium, and any mixture thereof.

The counter anion may be selected from the group consisting of acetate, nitrate, acetylacetonate, halide, oxide, hydroxide, oxalate, sulfate, carbonate, phosphate, hydrate and any mixture thereof.

25 The catalyst may be selected from the group consisting of a nickel salt, a copper salt, a cobalt salt, an iron salt, a chromium salt, an aluminium salt, a zinc salt, a lead salt, a manganese salt, a titanium salt, and any mixture thereof.

The catalyst may be nickel or a nickel salt, and may be selected from the group consisting of metallic nickel, nickel powder, anhydrous and hydrated salts of nickel(II), nickel(II) acetate,
30 nickel(II) hydroxide, nickel(II) nitrate, nickel(II) acetylacetonate, nickel(II) oxide, nickel(II) carbonate, nickel(II) sulfate, and any mixture thereof.

The catalyst may have a concentration in a range of about 0.01% w/v to about 0.3% w/v, about 0.01% w/v to about 0.05% w/v, about 0.01% w/v to about 0.1% w/v, about 0.01% w/v to about 0.2% w/v, about 0.05% w/v to about 0.1% w/v, about 0.05% w/v to about 0.2% w/v, about 0.05% w/v to about 0.3% w/v, about 0.1% w/v to about 0.2% w/v, about 0.1% w/v to about 0.3% w/v,
35 about 0.2% w/v to about 0.3% w/v, based on the total volume of the composition.

The composition may further comprise a surfactant. The surfactant may inhibit undesirable reactions on the surface of a solid mixture to which the composition may be applied to, to further improve the efficiency of silver recovery.

- 5 The surfactant may be a cationic surfactant, anionic surfactant, zwitterionic surfactant, nonionic surfactant, biological surfactant or any mixture thereof.

The surfactant may be selected from the group consisting of polysorbates such as polysorbate 20, polysorbate 40, polysorbate 60, and polysorbate 80, fatty alcohol alkoxylates, alkyl polyethylene glycol ethers, alkylphenol hydroxypolyethylenes such as octylphenol ethoxylates, including Triton® X-100 (2-[4-(2,4,4-trimethylpentan-2-yl)phenoxy]ethanol), Triton® X-114 (*t*-Oct-C₆H₄-(OCH₂CH₂)_xOH, x = 7-8), and Triton® X-405 (4-(1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol solution), sodium dodecyl sulfate, and any mixture thereof.

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The biological surfactant may be any surfactant that is produced by an organism. The biological surfactant may be peptone. Peptones may be any water-soluble mixture of polypeptides and/or amino acids formed by partial enzymatic or acidic hydrolysis of a protein.

- 15 The surfactant may have a concentration in a range of about 0.05% w/v to about 0.3% w/v, about 0.05% w/v to about 0.075% w/v, about 0.05% w/v to about 0.1% w/v, about 0.05% w/v to about 0.15% w/v, about 0.05% w/v to about 0.2% w/v, about 0.075% w/v to about 0.1% w/v, about 0.075% w/v to about 0.15% w/v, about 0.075% w/v to about 0.2% w/v, about 0.075% w/v to about 0.3% w/v, about 0.1% w/v to about 0.15% w/v, about 0.1% w/v to about 0.2% w/v, about 0.1% w/v to about 0.3% w/v, about 0.15% w/v to about 0.2% w/v, about 0.15% w/v to about 0.3% w/v or about 0.2% w/v to about 0.3% w/v, based on the total volume of the composition.
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The composition may further comprise an oxidant stabilising agent. The oxidant stabilising agent may prevent excessive consumption of the oxidant.

- 25 The oxidant stabilising agent useful in the composition may be selected from the group consisting of citric acid, tartaric acid, phosphoric acid, dipicolinic acid (DPA), ethylene glycol, ethylenediamine tetra (methylene-phosphonic acid), ethylenediamine tetra acetic acid compounds (EDTA), amino tri-(lower alkylidene phosphonic acid) compounds such as sodium nitrilo tri-(methylene phosphonate), alkylidene-diphosphonic acid derivatives such as ethane-1-hydroxy-1,1-diphosphonate (EHDP), ethylenediamine tetra methylene phosphonic acid carboxylates (RCOOM) where R is a hydrocarbon chain of C₉-C₂₁ and M is an alkali metal including ammonium which includes soaps; the polyalkoxy carboxylates (R-(OCH₂CHR¹)-OR¹COOM, where R is as defined above, R¹ is hydrogen or lower alkyl and R² is lower alkyl and M is as defined above; the N-Acylsarcosinates (RCON(CH₃)CH₂COOM) wherein R and M are as defined above; acylated protein hydrolysates prepared by acylation of protein hydrolysates with fatty acids or fatty acid chlorides; alkyl, aryl or alkylaryl sulfonates and their alkali metal salts such as alkyl benzene sulfonates (R²C₆H₄SO₃M, where R² is an aliphatic group of from about 7 to about 15 carbon atoms and M is an alkali metal), alkyl arenesulfonates and their alkali metal and ammonium salts which include the salts of the sulfonates of toluene,
- 30
- 35

- xylene and isopropyl benzene; naphthalene sulfonates which include salts of naphthalene sulfonate, tetrahydronaphthalene sulfonate, alkyl naphthalene sulfonate and formaldehydenaphthalene condensation product sulfonate, olefin sulfonate salts, petroleum sulfonate salts, sulfonates with ester, amide or ether linkages such as dialkyl sulfosuccinates ($R^3O_2CCH_2CH(SO_3Na)CO_2R$, wherein R^3 is a hydrocarbon chain of C_7-C_{21}), amidosulfonates (N-acyl-N-Alkyl taurates, $RCONR^4CH_2CH_2SO_3M$, wherein M is as defined above, R is a hydrocarbon chain of C_9-C_{21} and R^4 is lower alkyl), sulfoethyl esters of fatty acids ($RCO_2CH_2CH_2SO_3M$) wherein R and M are as defined above, alcohol sulfates ($ROSO_3M$) wherein R and M are as defined above; ethoxylated and sulfated alcohols ($R-(OCH_2CH_2)_nOSO_3M$) wherein R and M are as defined above; ethoxylated and sulfated alkyl phenols ($RC_6H_4(OCH_2CH_2)_nOSO_3M$) wherein R and M are as defined above; sulfated natural oils and fats; mono and diesters of phosphoric acid ($R^5O)_n(OH)_{3-n}PO$) where n is 1 or 2 and R^5 is an alkyl of from about 1 to 22 carbon atoms, phenyl, alkyl phenyl, ethoxylated alkyl, ethoxylated phenyl, ethoxylated alkyl phenyl, glyceride ester, ethoxylates such as alcohol ethoxylates ($R^6(OCH_2CH_2)_{n_2}-OH$, wherein R^6 is an alkyl group having from about 1 to 22 carbons; alkyl phenol ethoxylates ($R^7C_6H_4(OCH_2CH_2)_{n_2}OH$ wherein n_2 is from about 1 to 70 and R^7 is an alkyl group having 1 to 22 carbons); glycerol esters of fatty acids; polyoxyethylene esters of rosin, tall oil and fatty acids, ethoxylated anhydrosorbitol esters; ethoxylated natural fats, oils and waxes; carboxylic amides; diethanolamine condensates; monoethanol amine condensates; polyoxyethylene fatty acid amides; polyalkylene oxide polymer and block copolymers, oxygen free mono and dialkyl amines; oxygen containing amines such as alkyl amine ethoxylates and alkyl amine oxides; rosin and aliphatic amine ethoxylates; 2-alkyl-1-(2-hydroxyethyl)-2-imidazolines; amines with amide linkages, quaternary ammonium salts, imidazolium derivatives; alkyl betaines; amidopropylbetaines; sulfobetaines; sulfotaines, phenyl acetic acid and its salts, salicylic acid and its salts, diethylene triamine pentaacetic acid and its salts, and methyl-3,4,5-trihydroxy benzoate, sulfosalicylic acid and its salts, polymeric phenyl sulfonate and any mixture thereof.

- The oxidant stabilising agent may be a sulfonate selected from the group consisting of alkyl, aryl or alkylaryl sulfonates and their alkali metal salts such as alkyl benzene sulfonates ($R^2C_6H_4SO_3M$, where R^2 is an aliphatic group of from about 7 to about 15 carbon atoms and M is an alkali metal), alkyl arenesulfonates and their alkali metal and ammonium salts which include the salts of the sulfonates of toluene, xylene and isopropyl benzene; naphthalene sulfonates which include salts of naphthalene sulfonate, tetrahydronaphthalene sulfonate, alkyl naphthalene sulfonate and formaldehydenaphthalene condensation product sulfonate, olefin sulfonate salts, petroleum sulfonate salts, sulfonates with ester, amide or ether linkages such as dialkyl sulfosuccinates ($R^3O_2CCH_2CH(SO_3Na)CO_2R$, wherein R^3 is a hydrocarbon chain of C_7-C_{21}), amidosulfonates (N-acyl-N-Alkyl taurates, $RCONR^4CH_2CH_2SO_3M$, wherein M is as defined above, R is a hydrocarbon chain of C_9-C_{21} and R^4 is lower alkyl) and any mixture thereof.

- The oxidant stabilising agent may be sodium phenol sulfonate ($C_6H_5NaO_4S$) or sodium nonanoyloxybenzenesulfonate (NOBS). The oxidant stabilising agent may be sodium phenol sulfonate. Sodium phenol sulfonate may advantageously be non-hazardous.

Sodium phenol sulfonate may minimise the degradation of hydrogen peroxide, and therefore help reduce the consumption of hydrogen peroxide.

- 5 The oxidant stabilising agent may have a concentration in a range of about 0.15 w/v to about 0.35% w/v, about 0.15% w/v to about 0.2% w/v, about 0.15% w/v to about 0.25% w/v, about 0.15% w/v to about 0.3% w/v, about 0.2% w/v to about 0.25% w/v, about 0.2% w/v to about 0.3% w/v, about 0.2% w/v to about 0.35% w/v, about 0.25% w/v to about 0.3% w/v, about 0.25% w/v to about 0.35% w/v or about 0.3% w/v to about 0.35% w/v, based on the total volume of the composition.

The composition may further comprise a second weak acid.

- 10 The second weak acid may be selected from the group consisting of acetic acid, monochloroacetic acid, formic acid, benzoic acid, oxalic acid, sulfurous acid, methanoic acid, phosphoric acid, nitrous acid, hydrofluoric acid and any mixture thereof.

The second weak acid may be monochloroacetic acid.

- 15 The second weak acid may have a concentration in a range of about 0.05% w/v to about 1.5% w/v, 0.05% w/v to about 0.75 % w/v, about 0.05% w/v to about 1.0% w/v, about 0.05% w/v to about 1.25% w/v, about 0.75% w/v to about 1.0% w/v, about 0.75% w/v to about 1.25% w/v, about 0.75% w/v to about 1.5% w/v, about 1.0% w/v to about 1.25% w/v, about 1.0% w/v to about 1.5% w/v or about 1.25% w/v to about 1.5% w/v, based on the total volume of the composition.

- 20 The composition may further comprise water. The water may be deionised water.

The total %w/v of the composition of the first weak acid, the oxidant, the metal complexing agent, water, optionally the surfactant, optionally the oxidant stabilising agent and optionally second weak acid, may be 100% w/v.

There is provided a composition comprising:

- 25 i) 0.3% w/v to 2.0% w/v of a first weak acid;
 ii) 3% w/v to 15 % w/v of an oxidant;
 iv) 0.05% w/v to 0.5% w/v of a metal complexing agent; and
 v) 82.5% w/v to 96.65% w/v of water,

- 30 wherein the composition has a pH in the range of 2 to 4, and the total %w/v of the composition is 100% w/v.

There is provided a composition consisting essentially of:

- i) 0.3% w/v to 2.0% w/v of a first weak acid;

- ii) 3% w/v to 15 % w/v of an oxidant;
- iii) 0.05% w/v to 0.5% w/v of a metal complexing agent; and
- iv) 82.5% w/v to 96.65% w/v of water,

5 wherein the composition has a pH in the range of 2 to 4, and the total %w/v of the composition is 100% w/v.

There is provided a composition comprising:

- i) 0.3% w/v to 2.0% w/v of a first weak acid;
- ii) 3% w/v to 15 % w/v of an oxidant;
- iii) 0.05% w/v to 0.5% w/v of a metal complexing agent;
- 10 v) 0.05% w/v to 0.3% w/v of a surfactant;
- vi) 0.15% w/v to 0.35% w/v of an oxidant stabilising agent;
- vii) 0.05% w/v to 1.5% w/v of a second weak acid; and
- viii) 80.35% w/v to 96.4% w/v of water,

15 wherein the composition has a pH in the range of 2 to 4, and the total %w/v of the composition is 100% w/v.

There is provided a composition consisting essentially of:

- i) 0.3% w/v to 2.0% w/v of a first weak acid;
- ii) 3% w/v to 15 % w/v of an oxidant;
- iii) 0.05% w/v to 0.5% w/v of a metal complexing agent;
- 20 iv) 0.05% w/v to 0.3% w/v of a surfactant;
- v) 0.15% w/v to 0.35% w/v of an oxidant stabilising agent;
- vi) 0.05% w/v to 1.5% w/v of a second weak acid; and
- viii) 80.35% w/v to 96.4% w/v of water,

25 wherein the composition has a pH in the range of 2 to 4, and the total %w/v of the composition is 100% w/v.

The combination of the specific concentrations of the acidic medium, H₂O₂ and ethanolamine may be essential for high yield and selectivity of silver leaching, as the deprivation or use of any

one of these components at a different concentration may adversely affect the performance of the composition.

There is provided a composition comprising:

- i) 0.3% w/v to 2.0% w/v of a first weak acid;
- 5 ii) 3% w/v to 15 % w/v of an oxidant;
- ix) 0.05% w/v to 2.0% w/v of a metal complexing agent;
- x) 0.01% w/v to 0.3% w/v of a catalyst; and
- xi) 82.5% w/v to 96.65% w/v of water,

10 wherein the composition has a pH in the range of 2 to 4, and the total %w/v of the composition is 100% w/v.

There is provided a composition consisting essentially of:

- i) 0.3% w/v to 2.0% w/v of a first weak acid;
- ii) 3% w/v to 15 % w/v of an oxidant;
- iii) 0.05% w/v to 2% w/v of a metal complexing agent;
- 15 iv) 0.01% w/v to 0.3% w/v of a catalyst; and
- v) 82.5% w/v to 96.65% w/v of water,

wherein the composition has a pH in the range of 2 to 4, and the total %w/v of the composition is 100% w/v.

There is provided a composition comprising:

- 20 i) 0.3% w/v to 2.0% w/v of a first weak acid;
- ii) 3% w/v to 15 % w/v of an oxidant;
- iii) 0.05% w/v to 2.0% w/v of a metal complexing agent;
- iv) 0.01% w/v to 0.3% w/v of a catalyst;
- v) 0.05% w/v to 0.3% w/v of a surfactant;
- 25 vi) 0.15% w/v to 0.35% w/v of an oxidant stabilising agent;
- xii) 0.05% w/v to 1.5% w/v of a second weak acid; and
- xiii) 80.35% w/v to 96.4% w/v of water,

wherein the composition has a pH in the range of 2 to 4, and the total %w/v of the composition is 100% w/v.

There is provided a composition consisting essentially of:

- i) 0.3% w/v to 2.0% w/v of a first weak acid;
- 5 ii) 3% w/v to 15 % w/v of an oxidant;
- iii) 0.05% w/v to 2% w/v of a metal complexing agent;
- iv) 0.01% w/v to 0.3% w/v of a catalyst;
- v) 0.05% w/v to 0.3% w/v of a surfactant;
- vi) 0.15% w/v to 0.35% w/v of an oxidant stabilising agent;
- 10 vii) 0.05% w/v to 1.5% w/v of a second weak acid; and
- xiv) 80.35% w/v to 96.4% w/v of water,

wherein the composition has a pH in the range of 2 to 4, and the total %w/v of the composition is 100% w/v.

- 15 The presence of a catalyst in addition to the combination of the specific concentrations of the acidic medium, H₂O₂ and ethanolamine may further enhance the rate of silver leaching.

The composition may be a lixiviant (leaching medium) for extracting a metal from a solid mixture comprising the metal. The composition may be a lixiviant for extracting silver from a solid mixture comprising silver.

- 20 There is also provided a method of preparing the composition as defined above, comprising the step of mixing:

- i) a first weak acid;
- ii) an oxidant; and
- iii) an metal complexing agent,

wherein the composition has a pH in the range of about 2 to 4.

- 25 The method may further comprise the step of adding a catalyst to the composition.

The method may further comprise the step of adding a surfactant to the composition.

The method may further comprise the step of adding an oxidant stabiliser to the composition.

The method may further comprise the step of adding a second weak acid to the composition.

In an example, a solution containing the first weak acid, oxidant stabiliser, and surfactant may be prepared first, followed by the addition of the oxidant, and finally the addition of the amine additive.

- 5 In an example, a solution containing the first weak acid, oxidant stabiliser, and surfactant may be prepared first, followed by the addition of the oxidant and catalyst, and finally the addition of the amine additive.

The mixing or adding step may be performed at room temperature.

- 10 The surfactant may require mild heating at a temperature below 50 °C to dissolve. The surfactant may be heated to a temperature in the range of about 30 °C to about 50 °C, about 30 °C to about 40 °C or about 40 °C to about 50 °C to dissolve.

There is also provided a method of extracting silver from a solid mixture comprising a plurality of metals comprising silver, the method comprising the step of contacting the composition as defined above with the solid mixture to form a leachate solution.

The extraction may be selective for silver over other metals.

- 15 The contacting step may be performed at a temperature at or less than 50°C. The contacting step may be performed at a temperature at or less than 40°C. The contacting step may be performed at temperatures in the range of about 10°C to about 50 °C, about 10°C to about 20°C, about 10°C to about 30°C, about 10°C to about 40°C, about 20°C to about 30°C, about 20°C to about 40 °C, about 20°C to about 50°C, about 30°C to about 40°C, about 30°C to about 50 °C, or about 40°C to about 50°C. The contacting step may be performed at 40°C. The contacting step may be performed at room temperature.

- 25 The contacting step may be performed for a duration of less than 6 hours, less than 4 hours, less than 2 hours, less than 1 hour or less than 30 minutes. The contacting step may be performed for a duration in the range of 15 minutes to about 30 minutes, about 15 minutes to about 1 hour, about 15 minutes to about 2 hours, about 15 minutes to about 4 hours, about 15 minutes to about 6 hours, about 30 minutes to about 1 hour, about 30 minutes to about 2 hours, about 30 minutes to about 4 hours, about 30 minutes to about 6 hours, about 1 hour to about 2 hours, about 1 hour to about 4 hours, about 1 hour to about 6 hours, about 2 hours to about 4 hours, about 2 hours to about 6 hours or about 4 hours to about 6 hours.

- 30 The method may be applied to extract silver from the surface of the solid mixture, as well as silver embedded or integrated in the solid mixture.

The plurality of metals may be selected from the group consisting of silver, palladium, aluminium, gold, copper, iron, nickel, lead, tin, zinc and any mixture thereof.

The solid mixture may further comprise silica, silicates or an organic compound.

- 35 The silica or silicates may be in the form of a rock.

The solid mixture may be an ore comprising silver.

5 The solid mixture may further comprise an organic compound. The organic compound may be a polymer. The polymer may be selected from the group consisting of epoxide resin, acrylates, polyamides, poly(ethersulfone) (PES), polyetherimide (PEI), poly(phenylene sulfide) (PPS), polyethylene terephthalates and any mixture thereof. The organic compound may be a brominated flame retardant or a polybrominated polyphenyl.

10 The solid mixture may be electronic waste or industrial waste. The electronic waste may be selected from the group consisting of TV board scrap, PC board scrap, central processing units (CPU), mobile phone scrap, portable audio scrap, DVD player scrap, calculator scrap, PC mainboard scrap, printed circuit board (PCB) scrap, solar panel wafer, connectors, hull cell samples and lead frames and any mixture thereof. The industrial waste may be photographic films.

The solid mixture may be selected from the group consisting of silver-coated electronic wastes such as printed circuit boards (PCBs), connectors, hull cell samples and lead frames.

15 The method may further comprise the step of pre-treating the solid mixture before contacting with the composition as defined above.

The pre-treatment step may comprise the step of rinsing the solid mixture with an organic solvent and/or a strong acid before contacting with the composition.

20 The organic solvent may be selected from the group consisting of methanol, ethanol, propanol, acetone, chloroform, dichloromethane, dimethylsulfoxide, dimethylformamide, toluene, tetrahydrofuran, acetone, acetonitrile and any mixture thereof.

The strong acid may be selected from the group consisting of hydrochloric acid, nitric acid, sulfuric acid, hydrobromic acid, hydroiodic acid, perchloric acid, chloric acid and any mixture thereof.

25 Where the solid mixture comprises an organic compound, the pre-treating step may comprise the step of separating the solid mixture into the organic compounds and the plurality of metals to form a solid metal mixture.

The pre-treating step may comprise a size-reduction step, wherein the solid mixture or the solid metal mixture may be crushed or cut.

30 Those skilled in the art will recognise that the solid mixture or the solid metal mixture may be ground to particle or a particular average size through various well known crushers or grinders, such as hammer mills, ball mills, ring mills and shredders or a combination of two or more such implements. By way of example, the grinding step may include a cutting stage followed by a two-step grinding and crushing stage. The particle size may be reduced to be in the mm to cm range. The particle size may be reduced to less than 10 cm, less than 5 cm, less than 2 cm or less than 1
35 cm. The particle size may be reduced to an average of about 1 mm to about 10 cm, about 1 mm to about 2 mm, about 1 mm to about 5 mm, about 1 mm to about 1 cm, about 1 mm to about 2

- cm, about 1 mm to about 5 cm, about 2 mm to about 5 mm, about 2 mm to about 1 cm, about 2 mm to about 2 cm, about 2 mm to about 5 cm, about 2 mm to about 10 cm, about 5 mm to about 1 cm, about 5 mm to about 2 cm, about 5 mm to about 5 cm, about 5 mm to about 10 cm, about 1 cm to about 2 cm, about 1 cm to about 5 cm, about 1 cm to about 10 cm, about 2 cm to about 5 cm, about 2 cm to about 10 cm, or about 5 cm to about 10 cm.

The size reduction step may follow the separation step.

The pre-treating step may comprise a priming step, wherein the optionally crushed or cut solid mixture or the solid metal mixture may be contacted with a strong acid. The strong acid may be sulfuric acid.

- 10 The priming step may follow the size reduction step.

The pre-treating step may comprise a washing step, wherein the optionally crushed, cut or primed solid mixture or the solid metal mixture may be rinsed with water.

The washing step may follow the priming step.

- 15 The method may further comprise the step of contacting the leachate solution with an anion to precipitate the silver as a silver salt. The anion may be any anion, provided that it is not nitrate, fluoride or acetate. The anion may be bromide, chloride, or iodide. The silver salt may be silver chloride.

There is also provided the use of the composition as defined above, to extract silver from a solid mixture comprising a plurality of metals comprising silver.

20 **Brief Description of Drawings**

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

25 **Fig. 1**

[Fig. 1] shows images of silver-coated waste materials used for leaching tests: (a), (b) connector, (c) hull cell, (d) lead frame.

Fig. 2

- 30 [Fig. 2] shows images of silver-coated waste materials with specific dimensions used for testing selectivity of lixiviant: (a) connector and (b) hull cell.

Fig. 3

[Fig. 3] shows a graph showing the effect of increasing ethanolamine concentration against concentration of Ag leached (304) and %Ag in leachate (302).

Fig. 4

- 5 [Fig. 4] shows samples with Cu layer exposed after leaching of residual Ag in 3M HNO₃: (a), (b) connector, and (c) hull cell.

Fig. 5

[Fig. 5] shows an image showing silver recovered as shiny pellets (502).

Fig. 6

- 10 [Fig. 6] shows a schematic diagram showing the process of silver recovery from a solid mixture comprising a plurality of metals comprising silver

Examples

- Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.
- 15

Example 1: Lixiviant

- Acetic acid (glacial, min 99.8%), hydrogen peroxide (min 30% wt), peptone (microbiology grade, total nitrogen min 15%), nickel(II) acetate tetrahydrate (min 99%), sodium phenol sulfonate (min 98.5%) and hexamethylenetetramine (min 99.5%) were obtained from
- 20 Sinopharm Chemical Reagent Co. Ltd. Monochloroacetic acid ($\geq 99.0\%$) and ethanolamine ($\geq 98\%$) were obtained from Sigma-Aldrich. Ethylenediamine (99%), N-(2-hydroxyethyl) ethylenediamine (99%) and N-N'-dimethylethylenediamine (95%) were obtained from Alfa Aesar.

- Essentially, the cyanide-free lixiviant developed for extraction of silver from silver-coated solid wastes as disclosed herein, is an acidic aqueous system (pH 2 to 4) comprising:
- 25

- i) 0.5 to 1.5% w/v of acetic acid (CH₃COOH) and monochloroacetic acid (C₂H₃ClO₂) that provides an acidic medium for reagent dissolution and also acts as a complexing agent,
- ii) 0.1% w/v of peptone functioning as surfactant to prevent the surfaces of the electronic waste from which the silver is to be extracted from, from undergoing undesirable reactions
- 30 during the process,
- iii) 6 to 9% w/v of hydrogen peroxide (H₂O₂) as oxidant,

iv) 0.25% w/v of sodium phenol sulfonate ($\text{C}_6\text{H}_5\text{NaO}_4\text{S}$) as stabilising agent for H_2O_2 to minimise degradation,

v) 0.1 to 0.2% w/v of an amine additive, preferably ethanolamine ($\text{C}_2\text{H}_7\text{NO}$), hexamethylenetetramine ($(\text{CH}_2)_6\text{N}_4$), ethylenediamine ($\text{C}_2\text{H}_4(\text{NH}_2)_2$), N-(2-hydroxyethyl) ethylenediamine ($\text{C}_6\text{H}_{16}\text{N}_2\text{O}_2$), or N,N-dimethylethylenediamine ($\text{C}_4\text{H}_{12}\text{N}_2$), as complexing ligand to enhance silver extraction, and in turn minimise base metal (e.g. Cu) dissolution.

The lixiviant was prepared using 5% v/v (i.e. 50 ml/L) of a stock solution consisting of 80 g/L acetic acid, 20.4 g/L monochloroacetic acid, 20.4 g/L peptone, 50 g/L sodium phenol sulfonate, and then adding in 20 to 30% v/v of 30% H_2O_2 , 0.1 to 0.2% w/v (i.e. 1 to 2 g/L) of amine additive, and an additional 0.1 to 1.0% w/v (i.e. 1 to 10 g/L) of monochloroacetic acid. The remainder of the lixiviant was made up of deionised water.

Acetic acid, monochloroacetic acid, peptone and the sodium phenol sulfonate were mixed at room temperature to prepare a solution, before addition of the hydrogen peroxide, followed by the amine additive. The surfactant may require some mild heating at a temperature below 50 °C to dissolve.

The formulation was used in the extraction of silver coatings on discarded electronic waste, including connectors (Fig. 1a and Fig. 1b), hull cell samples (Fig. 1c) and lead frames (Fig. 1d) obtained from manufacturers of electrical components and recyclers of electronics waste. The major base metals in these electronic waste are Cu, Ni, Zn and Sn. Before leaching, the waste materials were rinsed with ethanol to remove any organic layer present, followed by 10% H_2SO_4 to remove any oxide layer present that may interfere with the extraction, then washed with water and dried.

Example 2: Selectivity

To demonstrate the selective leaching of silver using the lixiviant, 3 pieces each of connector (Fig. 2a) and hull cell samples (Fig. 2b) with specific dimensions were immersed in 100mL of several combinations of the lixiviant formulation with varying amounts of ethanolamine as an additive. Leaching was conducted at 40°C for 20 minutes, after which the concentration of the metal ions in the leachates were analysed by inductively coupled plasma-optical emission spectrometry using an inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo Scientific ICAP 6300 Duo) with axial and radial configuration. The radio frequency source (27.12 MHz) provided a power of 1.15 kW with nebulizer gas flow at 0.60 L/min, auxiliary gas flow at 1.0 L/min, flush pump rate and analysis pump rate at 50 rpm, using an axial plasma view. Readings were repeated 3 times and averaged. The metals were analysed at the corresponding wavelengths (λ/nm): Ag 328.0, Cu 324.7, Ni 231.6, Sn 283.9, Zn 213.8. Effervescence as well as formation of oxygen foam could be observed during the leaching process.

Table 1 shows the results obtained from the selectivity tests and Fig. 3 shows the effect of increasing concentration of the additive ethanolamine on the amount of silver leached (304), as well as its proportion in the leachate (302). It can be observed that with increasing concentration

of ethanolamine, the amount of silver leached within 20 minutes decreased, indicating a decreasing leaching rate which is likely attributable to the higher pH. However, the proportion of silver in the leachate increased, and the increase was most notable for ethanolamine concentration of 0.1 to 0.2% w/v, which achieved a proportion of 70 to 88% silver in the leachate compared to 57% when no ethanolamine was present. While the amount of silver leached decreased slightly for the lixiviants with 0.1 to 0.2% w/v ethanolamine, the amount of base metals leached was drastically reduced, signifying that the addition of ethanolamine promoted more selective leaching of silver from the samples. Nevertheless, excessive amount of ethanolamine at 0.5 to 1.0% w/v caused the pH rise above 4.5 and this may have resulted in higher decomposition of H_2O_2 , consequently slowing leaching and decreasing the amount of silver leached.

This was further apparent when the acidic medium was completely removed and H_2O_2 was observed to rapidly decompose and retard the leaching process. This illustrates that the combination of the acidic medium, H_2O_2 and ethanolamine is essential for high yield and selective silver leaching, as the deprivation of any one of these components would adversely affect the performance of the lixiviant. From the selectivity tests, the optimum amount of amine additive to be used is 0.1 to 0.2% w/v. The performance of the formulation remained relatively unchanged even when left overnight, as seen from the results of both formulations having 0.1% w/v of ethanolamine, thereby demonstrating the stability of the lixiviant.

Table 1. Experimental results from selectivity tests at 40°C with 20 minutes immersion

Formulation ^(a)	pH	Concentration in Leachate (ppm)					% Ag	% Base Metals ^(b)
		Ag	Cu	Ni	Sn	Zn		
5% v/v stock, 6% w/v H_2O_2	2.37	379.7	180.7	0	2.99	102.3	57.04	42.96
5% v/v stock, 6% w/v H_2O_2 , 0.1% w/v ethanolamine	3.54	365.3	93.28	0	0.83	52.68	71.34	28.66
5% v/v stock, 6% w/v H_2O_2 , 0.1% w/v ethanolamine (left overnight)	3.44	335.6	70.65	0	0.51	41.73	74.83	25.17
5% v/v stock, 6% w/v H_2O_2 , 0.2% w/v ethanolamine	4.15	341.9	28.26	0	2.33	16.51	87.89	12.11
5% v/v stock, 6% w/v H_2O_2 , 0.5% w/v ethanolamine	5.05	107.6	6.73	0	1.45	3.86	89.94	10.06
5% v/v stock, 6% w/v H_2O_2 , 1.0% w/v ethanolamine	9.13	71.52	4.16	0	1.11	0.33	92.74	7.26
6% w/v H_2O_2 , 0.2% w/v ethanolamine	9.29	6.48	0.03	0	0.49	0	92.70	7.30

Note: (a) 5% v/v stock solution constitutes 0.5% w/v of CH_3COOH and $C_2H_3ClO_2$, 0.1% w/v of peptone and 0.25% w/v of $C_6H_5NaO_4S$ to the lixiviant (b) Base metals include Cu, Ni, Zn, Sn

Example 3: Extraction Rate

To obtain the saturation point and extraction rate of the lixiviant, mixtures of samples shown in Fig. 1 were immersed in batches into the lixiviant at 40°C. Samples were removed and replaced with another batch once effervescence ceased. This was repeated until the solution was saturated and no longer produced effervescence upon immersion of new samples, indicating complete consumption of the H₂O₂ oxidant. All the leached samples were subjected to a second leaching in 3M HNO₃ at 40°C, during which the base layer Cu metal was exposed in the connector (Fig. 4a and 4b) and hull cell sample (Fig. 4c), to obtain the amount of residual silver that remained after the first leach. The concentration of metal ions in all leachates were analysed by ICP-OES and the data substituted into Equation 1 for determination of extraction efficiency of the present invention.

Equation 1. Determination of extraction rate

$$\begin{aligned}
 &\text{Extraction rate (\%)} \\
 &= \frac{\text{Mass of Ag extracted in 1st leach}}{\text{Total Mass of Ag extracted in 1st \& 2nd leach}} \\
 &= \frac{\text{Ag Concentration } \left(\frac{\text{g}}{\text{L}}\right) \times \text{Volume (L) in 1st leach}}{\left(\text{Ag Concentration } \left(\frac{\text{g}}{\text{L}}\right) \times \text{Volume (L) in 1st leach}\right) + \left(\text{Ag Concentration } \left(\frac{\text{g}}{\text{L}}\right) \times \text{Volume (L) in 2nd leach}\right)}
 \end{aligned}$$

Table 2 presents the experimental data obtained from leaching tests performed at 40°C using 5% v/v of the stock solution, 6 to 9% w/v of H₂O₂ oxidant, 0.1 to 0.2% w/v of ethanolamine as additive, and an additional 0.5 to 1.0% w/v of monochloroacetic acid to boost silver concentration at saturation. The lixiviant developed was able to leach 3 to >15 g/L of silver within 1.5 to 6 hours with an extraction rate of over 97%. This is relatively fast compared to most existing technologies that can achieve similarly high extraction efficiencies. For example, thiocyanate leaching may have an extraction rate of 99% but only after 8 hours and thiosulfate leaching may have an extraction rate of 93% but only after 48 hours. In addition, the proportion of silver in the leachate ranged from 84% to 98% depending on sample matrix, showing that extraction was selective towards silver.

Table 2. Experimental results from saturation leaching tests at 40°C using 5% v/v stock solution^(a)

Concentration of Oxidant, Amine Additive and Additional Acid Component	Vol (mL)	Metal Concentration at Saturation (g/L)		Duration (hr)	Mass of Ag Extracted (mg)	Mass of Residual Ag (mg)	Extraction Rate
		Ag	Base metals ^(b)				
6% w/v H ₂ O ₂ , 0.1% w/v ethanolamine	50	2.97 (98.1%)	0.057 (1.9%)	1.5	148.6	ND ^(c)	ND
6% w/v H ₂ O ₂ , 0.2% w/v ethanolamine	50	3.18 (97.9%)	0.069 (2.1%)	1.5	158.8	1.0	99.4%
9% w/v H ₂ O ₂	100	5.04	0.29	3.5	503.5	ND	ND

0.1% w/v ethanolamine	50	(94.5%) 4.93 (84.3%)	(5.5%) 0.92 (15.7%)	2.0	246.6	1.2	99.5%
9% w/v H ₂ O ₂ , 0.1% w/v ethanolamine, 0.5% w/v monochloroacetic acid	50	11.20 (96.9%)	0.36 (3.1%)	6.0	559.8	ND	ND
9% w/v H ₂ O ₂ , 0.2% w/v ethanolamine, 1% w/v monochloroacetic acid	50	>15.21 ^(d) (96.6%)	0.54 (3.4%)	5.5	760.5	21.8	97.2%

Note: (a) 5% v/v stock solution constitutes 0.5% w/v of CH₃COOH and C₂H₃ClO₂, 0.1% w/v of peptone and 0.25% w/v of C₆H₅NaO₄S to the lixiviant (b) Base metals include Cu, Ni, Zn, Sn, (c) ND: not determined, (d) Solution was not yet saturated when leaching was stopped after 5.5 hours

Example 4: Effect of Amine Additive

- 5 Other than ethanolamine, hexamethylenetetramine, ethylenediamine, N-(2-hydroxyethyl) ethylenediamine, or N,N-Dimethylethylenediamine may be used as the amine additive. Unsaturated leaching tests conducted on silver-coated lead frames (2.0 x 1.5 cm, 2 samples in each formulation) using 0.05 to 0.1% w/v of these additives revealed comparable performance to ethanolamine. In all instances, silver was completely extracted at a high selectivity, with the proportion of silver in the leachate being approximately 90% or more for this sample type (Table 3). Nevertheless, ethanolamine is still the preferred option owing to its less hazardous nature.
- 10

Table 3. Extraction performance of various amine additives in unsaturated leaching tests at 40°C using 5% v/v stock solution^(a) and 9% w/v H₂O₂

Amine Additive	Concentration (% w/v)	% Ag in Leachate	% Base Metals ^(b) in Leachate	Extraction Rate
Ethanolamine	0.1	93.4	6.6	100
Hexamethylenetetramine	0.1	92.2	7.8	100
Ethylenediamine	0.05	89.7	10.3	100
N-(2-hydroxyethyl) ethylenediamine	0.1	92.2	7.8	100
N,N-Dimethylethylenediamine	0.1	90.8	9.2	100

Note: (a) 5% v/v stock solution constitutes 0.5% w/v of CH₃COOH and C₂H₃ClO₂, 0.1% w/v of peptone and 0.25% w/v of C₆H₅NaO₄S to the lixiviant (b) Base metals include Cu, Ni, Zn, Sn

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Example 5: Recovery of Silver Metal

Recovery of silver from the leachate can be carried out via conventional methods such as precipitation and reduction. Following the method reported in literature, 1M sodium chloride

solution was added to the leachate to precipitate silver in the form of silver chloride (AgCl). Over 99% of silver leached was precipitated as AgCl. After drying, AgCl was reduced to metallic silver by sodium borohydride (NaBH₄). The experimental data obtained from the recovery process is presented in Table 4. Approximately 90% of silver was recovered from the leachate in the form of shiny pellets (Fig. 5, 502) with purity $\geq 95\%$ based on X-ray fluorescence (XRF) analysis. XRF analysis was performed using an energy dispersion fluorescence X-ray spectrometer (EDXRF, Shimadzu EDX-720). Energy calibration and position check was performed using aluminium 750 standard. The pellets were placed in a sample cup supported by SPEXTM 3525 Ultralene thin film and SPEXTM 3524 Micro-porous Teflon as the sample window. Analysis was conducted under the following parameters: 15-50 kV, 100 μ A, max 40 keV, vacuum, 1-10 mm collimator, measurement range from Na to U.

Recovery rate could potentially improve with minimisation of losses during filtration and washing.

Table 4. Results for recovery of silver from leachate

Initial concentration of Ag in leachate	5.090 g/L
Final concentration of Ag in leachate	0.00157 g/L
Percentage precipitated	99.97%
Volume of leachate used	41 mL
Theoretical mass of silver present	41 mL x 5.090 g/L = 0.2087 g
Mass of metallic silver obtained	0.19 g
Purity of metallic silver obtained	98.71 %
Actual mass of silver recovered	98.71 % x 0.19 g = 0.1876 g
Percentage recovery	(0.1876/0.2087) = 89.9 %

The overall recovery process is shown in a flow chart in Fig. 6, where a solid mixture (602) comprising a plurality of metals comprising silver and optionally silica, silicates and/or an organic compound undergoes pre-treatment (604) which may comprise size-reduction, priming and washing steps, then contacted with the inventive lixiviant (606). The mixture is separated into the leachate comprising silver (608) and the waste (610) which includes base metals and optionally organic compounds. The leachate then undergoes precipitation (612) to yield the metallic silver (614).

The lixiviant of the present disclosure has been demonstrated at a laboratory scale but it would be easily conceivable to a person skilled in the art that the lixiviant and its use may be scaled up to industrial scale.

Example 6: Effect of Catalyst

To demonstrate the effect of catalyst on leaching of silver in order to further enhance the silver concentration at saturation, a cyanide-free lixiviant further comprising a catalyst in an acidic aqueous system (pH 2 to 4) was prepared.

- 5 In addition to the components as indicated in Example 1, 0.01 to 0.3% w/v of nickel(II) acetate tetrahydrate ($\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$) was included in the composition as catalyst.

- 10 The lixiviant was prepared using 5% v/v (i.e. 50 ml/L) of a stock solution consisting of 80 g/L acetic acid, 20.4 g/L monochloroacetic acid, 20.4 g/L peptone, 50 g/L sodium phenol sulfonate, and then adding in 3 to 15% v/v of 30% H_2O_2 , 0.01 to 0.3% w/v $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, 0.05 to 2.0% w/v (i.e. 1 to 2 g/L) of amine additive, and an additional 0.1 to 1.0% w/v (i.e. 1 to 10 g/L) of monochloroacetic acid. The remainder of the lixiviant was made up of deionised water.

Acetic acid, monochloroacetic acid, peptone and the sodium phenol sulfonate were mixed at room temperature to prepare a solution, before addition of the hydrogen peroxide and nickel(II) acetate tetrahydrate, followed by the amine additive.

- 15 The composition comprising the catalyst was used in the same manner as described in Example 1.

- 20 Table 5 summarizes the experimental results obtained by varying the concentration of oxidant, acid and catalyst. Compared to Bath A, the addition of 0.02% w/v $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ catalyst in Bath B improved the extraction rate from 75.4% to 91.9%, without significantly affecting the silver concentration at saturation. The addition of more oxidant (H_2O_2) and acid in Bath C further boosted the silver concentration at saturation by 18%, from 8.511 g/L (in Bath B) to 10.073 g/L, but this compromised the extraction rate from 91.9% to 72.5%. Furthermore, by increasing the concentration of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ catalyst from 0.02% w/v in Bath C to 0.06 w/v in Bath D, the silver concentration at saturation improved by 27% to 12.771 g/L, while the extraction rate improved by 23% to 89.4%.

This illustrates that the addition of catalyst, while adding more oxidant and acid, may improve yield and extraction rate of silver leaching, as the removal of any one of these components may adversely affect the true performance of the lixiviant.

Table 5. Experimental results from saturation leaching tests at 40°C using stock solution^(a) with monochloroacetic acid and ethanolamine.

Bath	Concentration of Oxidant, Additional Acid, and Catalyst ^(c)	Metal Concentration at Saturation (g/L)		Duration (hr)	Mass of Extracted Ag (mg)	Mass of Residual Ag (mg)	Extraction Rate
		Ag	Base metals ^(b)				
A	7.5% w/v H ₂ O ₂ ,	8.639 (88.2%)	1.009 (11.8%)	2.25	863.9	281.6	75.4%
B	7.5% w/v H ₂ O ₂ , 0.02% w/v Ni(OAc) ₂ ·4H ₂ O	8.511 (84.7 %)	1.349 (15.3%)	4.5	851.1	74.7	91.9%
C	9.0% w/v H ₂ O ₂ , acetic acid, 0.02% w/v Ni(OAc) ₂ ·4H ₂ O	10.073 (88.4%)	1.244 (11.6%)	3	1007.3	382	72.5%
D	9.0% w/v H ₂ O ₂ , acetic acid, 0.06% w/v Ni(OAc) ₂ ·4H ₂ O	12.771 (84.6%)	2.240 (15.4%)	2.5	1277.1	151.4	89.4%

Note: (a) 5% v/v stock solution constitutes 0.5% w/v of CH₃COOH, and C₂H₃ClO₂, 0.1% w/v of peptone and 0.25% w/v of C₆H₅NaO₄S to the lixiviant (b) Base metals include Cu, Ni, Zn, Sn,

Industrial Applicability

5 This invention may be used for recovery of silver from electronic and industrial wastes such as printed circuit boards, connectors, CPUs, photographic films, solar panel wafer, in the recycling and waste management industry, as well as extraction of silver from silver-containing ores in the mining industry.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A composition comprising:
 - i) a first weak acid;
 - ii) an oxidant; and
 - 5 iii) a metal complexing agent,wherein the composition has a pH in the range of 2 to 4.
2. The composition according to claim 1, wherein the first weak acid is a weak organic acid.
3. The composition according to claim 1 or 2, wherein the first weak acid has a concentration in a range of 0.3% w/v to 2.0% w/v, based on the total volume of the composition.
- 10 4. The composition according to any one of the preceding claims, wherein the oxidant is selected from the group consisting of a peroxide, a persulfate, a peroxy acid, an oxoacid acid, an oxyanion, a nitrate, a hexavalent chromium compound, permanganates, cerium (IV) compounds, sodium bismuthate, lead dioxide and any mixture thereof.
- 15 5. The composition according to any one of the preceding claims, wherein the oxidant has a concentration in a range of 3% w/v to 15 % w/v, based on the total volume of the composition.
6. The composition according to any one of the preceding claims, wherein the metal complexing agent comprises a nitrogen.
- 20 7. The composition according to any one of the preceding claims, wherein the metal complexing agent comprises an amine group.
8. The composition according to any one of the preceding claims, wherein the metal chelating agent has a concentration in a range of 0.05% w/v to 2.0% w/v, based on the total volume of the composition.
- 25 9. The composition according to any one of the preceding claims, further comprising a catalyst.
10. The composition according to claim 9, wherein the catalyst has a concentration in a range of 0.01% w/v to 0.3% w/v, based on the total volume of the composition.
11. The composition according to any one of the preceding claims, further comprising a surfactant.
- 30 12. The composition according to claim 11, wherein the surfactant has a concentration in a range of 0.05% w/v to 0.3% w/v, based on the total volume of the composition.

13. The composition according to any one of the preceding claims, further comprising an oxidant stabilising agent.
14. The composition according to claim 13, wherein the oxidant stabilising agent has a concentration in a range of 0.15 w/v to 0.35% w/v, based on the total volume of the composition.
15. The composition according to any one of the preceding claims, further comprising a second weak acid.
16. The composition according to claim 15, wherein the second weak acid has a concentration in a range of 0.05% w/v to 1.5% w/v, based on the total volume of the composition.
17. A method of preparing the composition according any one of the preceding claims, comprising the step of mixing:
- i) a first weak acid;
 - ii) an oxidant; and
 - iii) an metal complexing agent,
- wherein the composition has a pH in the range of 2 to 4.
18. The method according to claim 17, further comprising the step of adding a catalyst, a surfactant, an oxidant stabiliser and/or a second weak acid to the composition.
19. A method of extracting silver from a solid mixture comprising a plurality of metals comprising silver, the method comprising the step of contacting the composition according to any one of claims 1 to 16 with the solid mixture to form a leachate solution.
20. The method according to claim 19, wherein the solid mixture further comprises silica, silicates, an organic compound or any mixture thereof.
21. The method according to claim 19 or 20, wherein the contacting step is performed at a temperature at or less than 50°C or for a duration of less than 6 hours.
22. The method according to any one of claims 19 to 21, further comprising a pre-treatment step, wherein the solid mixture is rinsed with an organic solvent and/or a strong acid before contacting with the composition.
23. The method according to any one of claims 19 to 22, further comprising the step of contacting the leachate solution with an anion to precipitate the silver as a silver salt.
24. The use of the composition according to any one of claims 1 to 16, to recover silver from a solid mixture comprising a plurality of metals comprising silver.