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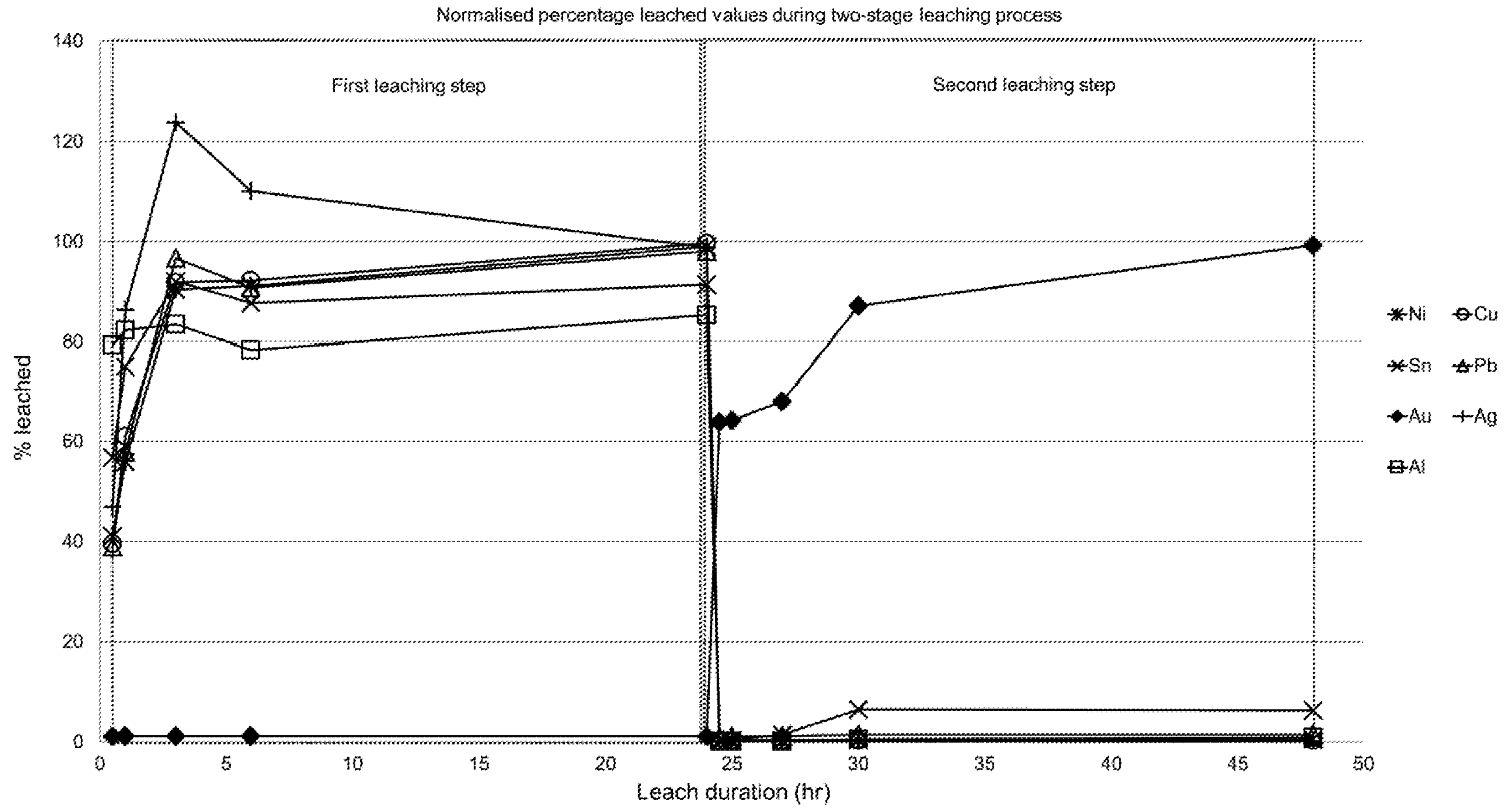
Figure 1:


Normalised percentage leached values during two-stage leaching process
First leaching step
Second leaching step
% leached
Leach duration (hr)
0
20
40
60
80
100
120
140
0
5
10
15
20
25
30
35
40
45
50
Ni
Cu
Sn
Pb
Au
Ag
Al

Compositions and processes for the extraction of metals using non-aqueous solvents

Field of the Invention

The present invention relates to compositions and processes for the extraction of metals from solid material using Deep Eutectic Solvents (DESs) and oxidisers. The processes and compositions of the present invention are useful for selectively extracting metals from solid material, particularly electronic waste material.

Background to the Invention

Deep Eutectic Solvents (DESs) are formed by the complexation of certain components to provide an homogeneous mixture that melts at a single temperature that is lower than the melting point of any of the constituent components. Examples of components that can be complexed to form DESs are quaternary ammonium salts and hydrogen bond donors.

Following their discovery, DESs found a number of applications, including in the dissolution of metal oxides and chlorides. In this regard, WO 02/26701 A2 discloses the preparation of a variety of DESs and their use as battery electrolytes, solvents for metal oxides, components for electropolishing and the electrodeposition of metals, and solvents for chemical reactions.

It was later discovered that native metals such as gold, silver, copper, nickel, tin, lead, aluminium, iron etc. could be dissolved when the DES was combined with an oxidizer in the form of iodine (see Abbott *et al.*, Electrocatalytic recovery of elements from complex mixtures using deep eutectic solvents, *Green Chem.*, 2015, **17**, pp 2172-2179). Iodine is poorly soluble in water, making it unsuitable for most aqueous chemistries. However, it is highly soluble in DESs and, once solubilized, it is capable of oxidising a wide range of metals.

The ability of DESs to dissolve native metals has potential applications in the field of metal extraction where, currently, hydrometallurgical processes, which often use strong mineral acids or poisonous chemicals such as cyanide or mercury, and energy-intensive pyrometallurgical processes are used.

The use of DESs in combination with iodine to dissolve native metals does have disadvantages, however. These include the high cost of iodine, its relatively low metal selectivity due to its ability to oxidise a wide range of metals, and its sensitivity to additional water.

In the light of the above, there is a need for compositions comprising a DES and an oxidiser that addresses these disadvantages. Additionally, there is a need for processes for the extraction of metals from solid material that has improved selectivity for certain metals, thus simplifying the post-process recovery of these metals. This is particularly the case for the extraction of metals from high-value components of electronic waste (e-waste) such as printed circuit boards (PCBs), where recovery of the high-value metals such as gold is complicated by the presence of other metals.

Summary of the Invention

The present invention addresses and overcomes the disadvantages of the prior art by providing a composition for extracting metals from solid material comprising a DES and an oxidiser. This composition is capable of dissolving many metals, but may be incapable of dissolving some metals, including gold. The present invention also provides a process for the extraction of metals from solid material that uses this composition.

In addition to the above, the present invention provides a two-step process for the extraction of metals from solid material, in which the solid material is first contacted with a composition comprising a DES and a first oxidiser, and, in a second step, contacted with a composition comprising a DES and a second oxidiser, wherein the first oxidiser and the second oxidiser are different.

Viewed from a first aspect, the present invention is directed to a process for the extraction of one or more metals from a solid material, the process comprising:

(i) a first leaching step comprising contacting the solid material with a first leaching solution comprising:

a first deep eutectic solvent (DES) formed by the reaction of a first quaternary ammonium salt and a first hydrogen bond donor in a molar ratio of from 4:1 to 1:20; and,

a first oxidiser,

thereby providing a first leached solid material and a first liquid phase;

(ii) a second leaching step comprising contacting the first leached solid material with a second leaching solution comprising:

a second DES formed by the reaction of a second quaternary ammonium salt and a second hydrogen bond donor in a molar ratio of from 4:1 to 1:20; and,

a second oxidiser,

thereby providing a second leached solid material and a second liquid phase;

wherein the first oxidiser and the second oxidiser are different.

Preferable features of the present invention are set out in the dependent claims presented below.

Brief Description of the Figures

Figure 1 shows the normalised percentage of each metal leached during the leaching process described in Example 1.

Detailed Description of the Invention

The present inventors have identified a composition comprising a DES and an oxidiser and a process for the extraction of one or more metals from a solid material using this composition. This composition demonstrates high oxidiser solubility and is capable of dissolving many metals (including the majority of the metals that are commonly present in electronic solid waste material), but the composition is incapable of dissolving some metals, including gold. A process for the extraction of metals from solid material that uses this composition provides a gold-rich solid material after the solid material has been contacted with the composition.

The present inventors have additionally developed a two-step process for efficiently and selectively extracting metals from solid material, which comprises a first step of contacting the solid material with the composition comprising a DES and a first oxidiser. The material remaining after contacting the solid material with this composition is rich in the metals that are not dissolved in the first step. In the second step, the solid material from the first step is contacted with a composition comprising a DES and a second oxidiser, which is different from the first oxidiser. The second step may dissolve the metals that remained in the solid material after the first step.

DESs are non-aqueous solvents, which means that the compositions and processes of the present invention have very low water consumption. The low vapour pressure of DESs also means that the processes can be run at elevated temperatures without producing high quantities of volatile organic compounds or particulate emissions and with minimal loss of solvent due to evaporation. Their relatively benign nature means that DESs are user friendly.

The present invention achieves a low carbon, low energy and environmentally benign method for the processing of metal-containing solid material such as electronic-waste (e-waste) or waste electrical and electronic equipment (WEEE). The process can replace environmentally damaging hydrometallurgical processes, which often use strong mineral acids or poisonous chemicals such as cyanide or mercury, and energy-intensive pyrometallurgical processes that are commonly used to recycle such materials. Furthermore, the present invention achieves high metal recoveries from polymetallic feedstock and is capable of complex metal recovery at relatively low cost compared to capital-intensive pyrometallurgical processes.

In addition to the above advantages, the two-stage process of the present invention provides an efficient and selective process for the recovery of valuable metals contained within solid material and produces either single element metal products or mixed metal products that can be tailored to meet market needs.

Definitions

Oxidisers - When specific compounds are referred to herein as oxidisers (e.g. $FeCl_3$), this refers to the oxidiser in the form in which it is added to the composition, because the counterion (e.g. Cl^-) may change once the oxidiser has dissolved in the DES.

When viewed from a first aspect, the present invention provides a process for the extraction of one or more metals from a solid material, the process comprising:

(i) a first leaching step comprising contacting the solid material with a first leaching solution comprising:

a first deep eutectic solvent (DES) formed by the reaction of a first quaternary ammonium salt and a first hydrogen bond donor in a molar ratio of from 4:1 to 1:20; and,

a first oxidiser,

thereby providing a first leached solid material and a first liquid phase;

(ii) a second leaching step comprising contacting the first leached solid material with a second leaching solution comprising:

a second DES formed by the reaction of a second quaternary ammonium salt and a second hydrogen bond donor in a molar ratio of from 4:1 to 1:20; and,

a second oxidiser,

thereby providing a second leached solid material and a second liquid phase;

wherein the first oxidiser and the second oxidiser are different.

Oxidisers

The oxidisers of the present invention may oxidise one or more metals in the solid material to an oxidised form, resulting in the dissolution of the metal in the DES. Accordingly, the oxidisers of the present invention are an additional component to the components that form the DES (which are described below) and the oxidisers do not form part of the DES *per se*. The oxidiser may be added to a leaching solution after the DES has formed from the quaternary ammonium salt and a hydrogen bond donor.

In the first aspect of the present invention, the first and second oxidisers are not particularly limited except in that they are different. The ability of an oxidiser to oxidise and/or dissolve a given metal may depend on the reduction potential of the oxidiser. Therefore, the first and the second oxidiser of the present invention may have different reduction potentials. For example, the reduction potential of the second oxidiser may be more positive than the reduction potential of the first oxidiser. The first oxidiser, having a less positive reduction potential, may not be able to oxidise (and therefore dissolve) certain metals. This allows for the selective dissolution of certain metals in each step of the process. For example, the first oxidiser may be an oxidiser that cannot or does not oxidise gold, while the second oxidiser may be an oxidiser that oxidises gold.

The reduction potential of the first oxidiser may be less than or equal to +0.50 V, optionally from -1.00 V to +0.50 V, optionally from 0 V to +0.50 V, optionally from 0 V to +0.49 V for example, 0 V, +0.1 V, +0.2 V, +0.3 V, 0.4 V, or +0.49 V. An oxidiser having a reduction potential in these ranges may not be able to oxidise (and therefore dissolve) certain metals, including gold. The reduction potential of the second oxidiser may be greater than or equal to +0.50 V, optionally from +0.50 V to +2.0 V, optionally from +0.51 V to +2.0V, optionally from +1.0 V to +2.0 V, for example, +1.0 V, +1.1 V, +1.2 V, +1.3 V, +1.4 V, +1.5 V, +1.6 V, +1.7 V, +1.8 V, +1.9 V or +2.0 V. An oxidiser having a reduction potential in these ranges may be able to oxidise (and therefore dissolve) certain metals, including gold.

The first oxidiser may be an Fe(III) salt, a Cu(II) salt, a Te(IV) salt, a Cr(III) salt, or a Mn(VII) salt. The first oxidiser may preferably be $FeCl_3$, FeF_3, $FeBr_3$, FeI_3, $Fe(CN)_6$, $Fe(SCN)_3$, $Fe(NO_3)_3$, $Fe(SO_4)_3$, $Fe(OH)_3$, $Fe(C_2H_3O_2)_3$, $CuCl_2$, CuF_2, $CuBr_2$, CuI_2, $Cu(NO_3)_2$, $CuSO_4$, CuO, $Cu(OH)_2$, $TeCl_4$, TeF_4, $TeBr_4$, TeI_4, TeO_2, or $KMnO_4$, more preferably wherein the first oxidiser is $FeCl_3$. These oxidisers may not be able to oxidise (and therefore dissolve) certain metals, including gold.

The first oxidiser of the present invention may be present at a concentration of 0.001 mol dm^{-3} to 2.5 mol dm^{-3}, preferably 0.01 mol dm^{-3} to 2 mol dm^{-3}, more preferably 0.1 mol dm^{-3} to 1.5 mol dm^{-3}, for example, 0.1 mol dm^{-3}, 0.25 mol dm^{-3}, 0.5 mol dm^{-3}, 0.75 mol dm^{-3}, 1 mol dm^{-3}, 1.25 mol dm^{-3}, or 1.5 mol dm^{-3}.

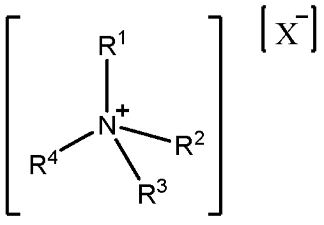
The second oxidiser may be I_2 or $SeCl_4$, SeF_4, $SeBr_4$, SeI_4, SeO_2, preferably wherein the second oxidiser is iodine (I_2). These oxidisers may be able to oxidise (and therefore dissolve) certain metals, including gold. When iodine is the second oxidiser, a further benefit of the two-stage process is that less of the DES and iodine composition (which is more expensive) is required compared to a process in which only the DES and iodine composition is used to extract the metals due to there being less overall metal to leach after the first stage. Recovery of gold from the DES in the second stage may also be greatly simplified as fewer or no other metals are contained in the DES at this stage. As gold recovery is an important economic driver for the extraction of metals, this is an important benefit of the process.

The second oxidiser of the present invention may be present at a concentration of 0.001 mol dm^{-3} to 2.5 mol dm^{-3}, preferably 0.01 mol dm^{-3} to 2 mol dm^{-3}, more preferably 0.1 mol dm^{-3} to 1.5 mol dm^{-3}, for example, 0.1 mol dm^{-3}, 0.25 mol dm^{-3}, 0.5 mol dm^{-3}, 0.75 mol dm^{-3}, 1 mol dm^{-3}, 1.25 mol dm^{-3}, or 1.5 mol dm^{-3}.

Deep eutectic solvents

The deep eutectic solvents of the present invention are prepared by reacting, or combining, or complexing a quaternary ammonium salt and a hydrogen bond donor.

In the first aspect of the present invention, the first and second quaternary ammonium salts are not particularly limited and may be any that are capable of forming a DES with the hydrogen bond donors described below. The first and second quaternary ammonium salts may each independently be a compound of Formula (I):



(I)

wherein R^1, R^2, R^3, and R^4 are each independently: H; a substituted or unsubstituted C_1-C_5 alkyl group; a substituted or unsubstituted C_6-C_{10} cycloalkyl group; a substituted or unsubstituted C_6-C_{12} aryl group; a substituted or unsubstituted C_7-C_{12} alkaryl group; or,

wherein R^1 and R^2, taken together with the N atom to which they are attached, form a substituted or unsubstituted 5 to 11-membered ring, and R^3 and R^4 are as defined earlier;

wherein X^- is NO_3^-, F^-, Cl^-, Br^-, I^-, BF_4^-, ClO_4^-, $SO_3CF_3^-$, bitartrate, dihydrogen citrate, or $COOCF_3^-$, and,

wherein substituted means that the group may be substituted with one or more of the groups selected from: OH, SH, SR^5, Cl, Br, F, I, NH_2, CN, NO_2, COO^-, $COOR^5$, CHO, COR^5, and OR^5, wherein R^5 is H, a C_1-C_{10} alkyl or a C_1-C_{10} cycloalkyl group.

The first and second quaternary ammonium salts may each independently be a compound of Formula (I), wherein R^1, R^2 and R^3 are each independently: H, or an unsubstituted C_1-C_4 alkyl group and R^4 is a substituted or unsubstituted C_1-C_4 alkyl group and wherein the definitions of X^- and "substituted" are as above. More preferably wherein R^1, R^2 and R^3 are each independently: H, or an unsubstituted C_1 alkyl group and R^4 is a substituted or unsubstituted C_1-C_4 alkyl group, wherein substituted means that the group may be substituted with one or more of the groups selected from: OR^5, COO^-, and $COOR^5$, wherein R^5 is H, a C_1-C_{10} alkyl or a C_1-C_{10} cycloalkyl group and wherein X^- is as defined above.

For example, the first and second quaternary ammonium salts may each independently be choline chloride, choline hydroxide, choline acetate, choline bitartrate, choline dihydrogencitrate, betaine, betaine HCl, ammonium chloride, methylammonium chloride, ethylammonium chloride, tetra-butylammonium chloride, or ethanolamine hydrochloride, preferably wherein the first and second quaternary ammonium salts are choline chloride.

The first and second hydrogen bond donors of the present invention are not particularly limited and may be any that are capable of forming a DES with the quaternary ammonium salts described above. The first and second hydrogen bond donors may each independently be a compound of the formula R^6COOH, R^7R^8NH, R^9CZNH_2, $R^{10}OH$, or $HO–R^{11}–OH$ wherein:

R^6, R^7, R^8, and R^{10} are each independently H; a substituted or unsubstituted C_1-C_8 alkyl group; a substituted or unsubstituted C_1-C_8 alkenyl group, a substituted or unsubstituted aryl group; or, a substituted or unsubstituted C_7-C_{12} alkaryl group; and R^{11} is a substituted or unsubstituted C_1-C_{11} alkyl group;

wherein substituted means substituted with one or more groups selected from OH, SR_5, Cl, Br, F, I, NH_2, CN, NO_2, 3,4-dihydroxy-2*H*-furan-5-one, $CONR^5$, $COOR^5$, COR^5 and OR^5, wherein R^5 is H, a C_1 to C_{10} alkyl or a C_1-C_{10} cycloalkyl group;

R^9 is a group as defined for R^6, or NHR^{12} wherein R^{12} is H or a C_1-C_6 alkyl group; and, Z is O or S

The first and second hydrogen bond donors may each independently be a compound of the formula R^6COOH, R^9CZNH_2, or $HO–R^{11}–OH$, wherein R^6, R^9, Z and R^{11} are as defined above.

The first and second hydrogen bond donors may each independently be a compound of the formula R^6COOH, R^9CZNH_2, or $HO–R^{11}–OH$, wherein

R^6 is a substituted or unsubstituted C_1-C_6 alkyl group; a substituted or unsubstituted C_1-C_6 alkenyl group, or a substituted or unsubstituted aryl group;

R^9 is a substituted or unsubstituted C_1-C_6 alkyl group or a substituted or unsubstituted C_1-C_6 alkenyl group or NHR^{12} wherein R^{12} is H or a substituted or unsubstituted C_1-C_6 alkyl group; and, Z is O; and

R^{11} is a substituted or unsubstituted C_1-C_8 alkyl group;

wherein substituted means substituted with one or more groups selected from OH, $CONR^5$, $COOR^5$, COR^5 and OR^5, wherein R^5 is H, a C_1 to C_6 alkyl or a C_1-C_6 cycloalkyl group.

The first and second hydrogen bond donors may each independently be a compound of the formula R^6COOH, R^9CZNH_2, or $HO–R^{11}–OH$, wherein

R^6 is a substituted or unsubstituted C_1-C_5 alkyl group; a substituted or unsubstituted C_1-C_4 alkenyl group, or a substituted or unsubstituted aryl group;

R^9 is a substituted or unsubstituted C_1-C_5 alkyl group or a substituted or unsubstituted C_1-C_4 alkenyl group or NHR^{12} wherein R^{12} is H or a C_1-C_6 alkyl group; and, Z is O; and

R^{11} is a substituted or unsubstituted C_1-C_5 alkyl group;

wherein substituted means substituted with one or more groups selected from OH, $CONR^5$, $COOR^5$, COR^5 and OR^5, wherein R^5 is H, or a C_1 to C_6 alkyl group.

The first and second hydrogen bond donors may each independently be a compound of the formula R^6COOH, or $HO–R^{11}–OH$, wherein

R^6 is a substituted or unsubstituted C_1-C_5 alkyl group; a substituted or unsubstituted C_1-C_4 alkenyl group, or a substituted or unsubstituted aryl group;

R^{11} is a substituted or unsubstituted C_1-C_5 alkyl group;

wherein substituted means substituted with one or more groups selected from OH, $CONR^5$, and $COOR^5$, wherein R^5 is H, or a C_1 alkyl group.

The first and second hydrogen bond donors may each independently be a compound of the formula $HO–R^{11}–OH$, wherein

R^{11} is a C_1-C_5 alkyl group, which may be substituted with one or more groups selected from OH and $COOR^5$, wherein R^5 is H, or a C_1 alkyl group.

For example, the first and second hydrogen bond donors may each independently be ethylene glycol, glycerol, 1,2-propanediol, 1,3-propandiol, 1,4-butandiol, 1,5-pentandiol, urea, oxalic acid, malonic acid, levulinic acid, lactic acid, citric acid, maleic acid, malonamide, acetamide, oxalic acid dihydrate, ascorbic acid, glutaric acid, glycolic acid, mandelic acid, succinic acid, tartaric acid or phenol, preferably wherein the first and second hydrogen bond donors are ethylene glycol.

The molar ratio of first quaternary ammonium salt to the first hydrogen bond donor is not particularly limited except that it must be a ratio that results in the formation of a DES when the first quaternary ammonium salt and the first hydrogen bond donor are combined. The molar ratio of first quaternary ammonium salt to the first hydrogen bond donor may be from 4:1 to 1:20, preferably 3.5:1 to 1:15, more preferably 2.5:1 to 1:10, more preferably 2:1 to 1:4, for example, 2:1, 1:1, 1:2, 1:3, or 1:4.

The molar ratio of the second quaternary ammonium salt to the second hydrogen bond donor is not particularly limited except that must be a ratio that results in the formation of a DES when the second quaternary ammonium salt to the second hydrogen bond donor are combined. The molar ratio of second quaternary ammonium salt to the second hydrogen bond donor may be from 4:1 to 1:20, preferably 3.5:1 to 1:15, more preferably 2.5:1 to 1:10, more preferably 2:1 to 1:4, for example, 2:1, 1:1, 1:2, 1:3, or 1:4.

The DES can be diluted with aqueous and/or organic solvents ranging from 0% diluent to a maximum 75% diluent (w/w). The diluent may be one or more selected from the group consisting of water, ethanol, acetonitrile, dichloromethane, or acetone.

Process parameters

The solid material may be any solid material that comprises metals. The solid material may be solid waste material such as electronic waste material, for example printed circuit boards. The metals in the solid material are not particularly limited and may be any metal known to the skilled person. For example, the metals may comprise one or more selected from the group consisting of aluminium, steel, copper, nickel, tin, lead, palladium, zinc, silver, chromium, cobalt, vanadium, indium, mercury, antimony, gallium, beryllium, molybdenum, cadmium, and gold.

The first liquid phase may comprise any or all of the above metals, or the first liquid phase may comprise any or all of the above metals except for gold. The second liquid phase may comprise any or all of the above metals, or the second liquid phase may only comprise gold.

Prior to performing the leaching steps, the solid material may be comminuted by crushing, grinding, or shredding to reduce its particle size. This may improve the efficiency of the leaching processes by reducing the amount of DES and oxidiser that is required to extract the metals. The solid material may be comminuted to a particle size of less than 10 mm, preferably less than 1.2 mm, for example 10 microns to 1 mm. Additionally, aluminium and steel may be removed prior to performing the leaching steps by, for example, gravimetric/eddy current/magnetic separation techniques. This may also improve the efficiency of the leaching processes.

In the first and second leaching steps, the ratio of DES plus the oxidiser to metal in the solid material may be from 1:50 to 100:1 (w:w), 1:40 to 75:1, 1:30 to 50:1, 1:25 to 25:1, or 1:20 to 10:1, for example 1:20, 1:15, 1:10, 1:5, 1:1, 5:1, or 10:1 (w:w).

In the first and second leaching steps, the solid material may be leached at a temperature of 10° C to 120° C, optionally 40° C to 110° C, optionally 50° C to 100° C, for example, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 or 100° C. In the first and second leaching steps, the solid material may be leached for 5 minutes to 240 hours, preferably 1 hour to 144 hours, more preferably 6 hours to 96 hours, more preferably 12 hours to 48 hours, more preferably 18 hours to 36 hours, for example, 18, 24, 30 or 36 hours. In an embodiment, the solid material is leached at a temperature of 10° C to 120° C for 5 minutes to 240 hours, preferably at 80° C for 24 hours.

In a particular embodiment of the first aspect of the present invention, the first and second quaternary ammonium salts may each independently be choline chloride, choline hydroxide, choline acetate, choline bitartrate, choline dihydrogencitrate, betaine, betaine HCl, ammonium chloride, methylammonium chloride, ethylammonium chloride, tetra-butylammonium chloride, or ethanolamine hydrochloride; preferably wherein the first and second quaternary ammonium salts are choline chloride;

the first and second hydrogen bond donors may each independently be ethylene glycol, glycerol, 1,2-propanediol, 1,3-propandiol, 1,4-butandiol, 1,5-pentandiol, urea, oxalic acid, malonic acid, levulinic acid, lactic acid, citric acid, maleic acid, malonamide urea, acetamide, oxalic acid dihydrate, ascorbic acid, glutaric acid, glycolic acid, mandelic acid, succinic acid, tartaric acid or phenol, preferably wherein the first and second hydrogen bond donors are ethylene glycol;

the molar ratios of the first and second quaternary ammonium salts to the first and second hydrogen bond donors may be from 4:1 to 1:20, preferably 2:1 to 1:4;

the reduction potential of the first oxidiser may be less than or equal to +0.50 V and/or the first oxidiser may be an Fe(III) salt, a Cu(II) salt, a Te(IV) salt, a Cr(III) salt, or a Mn(VII) salt, preferably wherein the first oxidiser is $FeCl_3$; and,

the reduction potential of the second oxidiser may be greater than or equal to +0.50 V and/or the second oxidiser may be I_2 or $SeCl_4$, SeF_4, $SeBr_4$, SeI_4, SeO_2, preferably wherein the second oxidiser is I_2.

The processes of the present invention may further comprise a step of recovering one or more metals from the first liquid phase; and/or recovering one or more metals from the second liquid phase. The processes for recovering metals from solution according to the present invention are not particularly limited and may be any of those known to the skilled person. Metals may be recovered individually or together with other metals. The recovery processes may include solvent extraction, precipitation (for example cementation), and/or processes whereby the metals are recovered from solution by means of electrolytic chemical reaction (for example electrowinning). In a particular embodiment, gold is recovered by the addition of activated carbon (e.g. Jacobi PICAGOLD® G210AS).

During the leaching steps, the oxidisers oxidise the metals in the solid material, which may cause the oxidiser to be reduced such that it is no longer able to oxidise. Accordingly, the processes of the present invention may further comprise a step of regenerating the oxidisers. The step of regenerating may be performed after a leaching step or it may be performed simultaneously with the leaching step so that the oxidiser is regenerated *in situ*. The oxidisers may be regenerated by any means known to the skilled person. For example, the oxidiser may be regenerated by bubbling oxygen into a leaching solution or a liquid phase that results from a leaching step. This method may be particularly advantageous if the oxidiser is an Fe(III) salt, a Cu(II) salt, a Te(IV) salt, a Cr(III) salt, or a Mn(VII) salt, for example if the oxidiser is $FeCl_3$. The oxidisers may be regenerated by means of electrolytic chemical reaction, for example, by inserting electrodes into a leaching solution or a liquid phase that results from a leaching step and applying a voltage.

The processes of the present invention may further comprise steps of filtering, and/or cleaning and/or drying the solid material after each of the leaching steps. These additional steps may improve the efficiency of any subsequent leaching steps.

Examples

Reduction potentials

The reduction potentials of oxidisers recited in the present application were measured as a formal reduction potential in the respective DES using an Ag reference electrode in AgCl (0.1 M).

Leaching efficiencies

Leaching efficiencies (i.e. the percentage of each metal that is recovered during a leaching stage) were determined by leaching the solid material remaining following the leaching step in *aqua regia* for 24 hours to dissolve all remaining metal. The concentration of the metals in the *aqua regia* was determined via Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

<u>*Example 1*</u>

Pre-treatment of electronic waste prior to extraction

Comminution of the electronic waste material: The material was comminuted to a particle size of below 1.2 mm.

Removal of steel: Steel was removed by magnetic separation techniques.

Extraction using Deep Eutectic Solvents

Stage 1 Leach: Electronic waste solid material containing copper, nickel, tin, lead, silver and gold was sent into the first leach tank in which it was contacted with a DES formed from choline chloride (1 mol. equiv.) and ethylene glycol (2 mol. equiv.), with $FeCl_3$ (1 mol dm^{-3}) as the oxidiser. The ratio of DES + $FeCl_3$ to solid material was 15:1 w/w. Contacting the solid material with the DES + $FeCl_3$ formulation at 80 °C for 24 hrs resulted in efficient metal recoveries: Cu: 99.7%, Ni: 99%, Sn: 92%, Pb: 98%, Ag: 99%. 0% Au is leached using this formulation, resulting in an Au-rich solid material. The leached solid material from this stage was filtered, washed and dried. The liquid phase comprising the leached metals was transferred to a separate tank for metal recovery.

Stage 2 Leach: The cleaned and dried leached solid material was transferred into a second leach tank in which it was contacted with a DES formed from choline chloride (1 mol. equiv.) and ethylene glycol (2 mol. equiv.), with I_2 (0.5 mol dm^{-3}) as the oxidiser. The ratio of DES + I_2 to solid material was 3:1 w/w. The purpose of this second leach is to recover Au from the solid material. Contacting the solid material with the DES + I_2 formulation at 80 °C for 24 hrs resulted in 99% Au recovery and was also able to recover any residual metals contained within the solid residue. The leached solid material from this stage was filtered, washed and sent for waste. The liquid phase comprising the leached metals was transferred to a separate tank for metal recovery. Data from this leaching process can be seen in Fig. 1.

CLAIMS:

1. A process for the extraction of one or more metals from a solid material, the process comprising:

(i) a first leaching step comprising contacting the solid material with a first leaching solution comprising:

a first deep eutectic solvent (DES) formed by the reaction of a first quaternary ammonium salt and a first hydrogen bond donor in a molar ratio of from 4:1 to 1:20; and,

a first oxidiser,

thereby providing a first leached solid material and a first liquid phase;

(ii) a second leaching step comprising contacting the first leached solid material with a second leaching solution comprising:

a second DES formed by the reaction of a second quaternary ammonium salt and a second hydrogen bond donor in a molar ratio of from 4:1 to 1:20; and,

a second oxidiser,

thereby providing a second leached solid material and a second liquid phase;

wherein the first oxidiser and the second oxidiser are different.

2. The process according to claim 1, wherein the first and the second oxidiser have different reduction potentials.

3. The process according to any one of the preceding claims, wherein the reduction potential of the second oxidiser is more positive than the reduction potential of the first oxidiser.

4. The process according to any one of the preceding claims, wherein the reduction potential of the first oxidiser is less than or equal to +0.50V, preferably from -1.00 V to +0.50 V.

5. The process according to any one of the preceding claims, wherein the reduction potential of the second oxidiser is greater than or equal to +0.50 V, preferably from +0.50 V to +2.0 V.

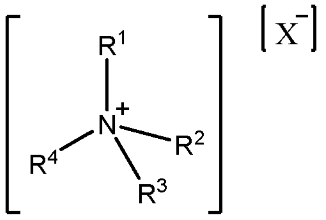
6. The process according to any one of the preceding claims, wherein the first oxidiser cannot oxidise Au(0).

7. The process according to any one of the preceding claims, wherein the second oxidiser oxidises Au(0).

8. The process according to any one of the preceding claims, wherein the first oxidiser is an Fe(III) salt, a Cu(II) salt, a Te(IV) salt, a Cr(III) salt, or a Mn(VII) salt, preferably wherein the first oxidiser is $FeCl_3$, FeF_3, $FeBr_3$, FeI_3, $Fe(CN)_6$, $Fe(SCN)_3$, $Fe(NO_3)_3$, $Fe(SO_4)_3$, $Fe(OH)_3$, $Fe(C_2H_3O_2)_3$, $CuCl_2$, CuF_2, $CuBr_2$, CuI_2, $Cu(NO_3)_2$, $CuSO_4$, CuO, $Cu(OH)_2$, $TeCl_4$, TeF_4, $TeBr_4$, TeI_4, TeO_2, or $KMnO_4$, more preferably wherein the first oxidiser is $FeCl_3$.

9. The process according to any one of the preceding claims, wherein the second oxidiser is I_2 or $SeCl_4$, SeF_4, $SeBr_4$, SeI_4, SeO_2, preferably wherein the second oxidiser is I_2.

10. The process according to any one of the preceding claims, wherein the first and second quaternary ammonium salts are each independently a compound of Formula (I):



(I)

wherein R^1, R^2, R^3, and R^4 are each independently: H; a substituted or unsubstituted C_1-C_5 alkyl group; a substituted or unsubstituted C_6-C_{10} cycloalkyl group; a substituted or unsubstituted C_6-C_{12} aryl group; a substituted or unsubstituted C_7-C_{12} alkaryl group; or,

wherein R^1 and R^2, taken together with the N atom to which they are attached, form a substituted or unsubstituted 5 to 11-membered ring, and R^3 and R^4 are as defined earlier;

wherein X^- is NO_3^-, F^-, Cl^-, Br^-, I^-, BF_4^-, ClO_4^-, $SO_3CF_3^-$, bitartrate, dihydrogen citrate, or, $COOCF_3^-$, and,

wherein substituted means that the group may be substituted with one or more of the groups selected from: OH, SH, SR^5, Cl, Br, F, I, NH_2, CN, NO_2, COO^-, $COOR^5$, CHO, COR^5, and OR^5, wherein R^5 is H, a C_1-C_{10} alkyl or a C_1-C_{10} cycloalkyl group.

11. The process according to any one of the preceding claims, wherein the first and second quaternary ammonium salts are each independently choline chloride, choline hydroxide, choline acetate, choline bitartrate, choline dihydrogencitrate, betaine, betaine HCl, ammonium chloride, methylammonium chloride, ethylammonium chloride, tetra-butylammonium chloride, or ethanolamine hydrochloride, preferably wherein the first and second quaternary ammonium salts are choline chloride.

12. The process according to any one of the preceding claims, wherein the first and second hydrogen bond donors are each independently a compound of the formula R^6COOH, R^7R^8NH, R^9CZNH_2, $R^{10}OH$, or $HO–R^{11}–OH$ wherein:

R^6, R^7, R^8, and R^{10} are each independently H; a substituted or unsubstituted C_1-C_8 alkyl group; a substituted or unsubstituted C_1-C_8 alkenyl group; a substituted or unsubstituted aryl group; or a substituted or unsubstituted C_7-C_{12} alkaryl group; and R^{11} is a substituted or unsubstituted C_1-C_{11} alkyl group

wherein substituted means that the group may be substituted with one or more groups selected from OH, SR_5, Cl, Br, F, I, NH_2, CN, NO_2, 3,4-dihydroxy-2*H*-furan-5-one, $CONR^5$,$COOR^5$, COR^5 and OR^5, wherein R^5 is H, a C_1 to C_{10} alkyl or a C_1-C_{10} cycloalkyl group;

R^9 is a group as defined for R^6, or NHR^{12}, wherein R^{12} is H or a C_1-C_6 alkyl group; and, Z is O or S

R^{11} is a substituted or unsubstituted C_1-C_{11} alkyl group

13. The process according to any one of the preceding claims, wherein the first and second hydrogen bond donors are each independently ethylene glycol, glycerol, 1,2-propanediol, 1,3-propandiol, 1,4-butandiol, 1,5-pentandiol, urea, oxalic acid, malonic acid, levulinic acid, lactic acid, citric acid, maleic acid, malonamide, acetamide, oxalic acid dihydrate, ascorbic acid, glutaric acid, glycolic acid, mandelic acid, succinic acid, tartaric acid or phenol, preferably wherein the first and second hydrogen bond donors are ethylene glycol.

14. The process according to any one of the preceding claims, wherein the molar ratio of first quaternary ammonium salt to the first hydrogen bond donor is from 4:1 to 1:20, preferably 2:1 to 1:4.

15. The process according to any one of the preceding claims, wherein the molar ratio of second quaternary ammonium salt to the second hydrogen bond donor is from 4:1 to 1:20, preferably 2:1 to 1:4.

16. The process according to any one of the preceding claims, wherein the first oxidiser is present at a concentration of 0.001 mol dm^{-3} to 2.5 mol dm^{-3}, preferably 1 mol dm^{-3}.

17. The process according to any one of the preceding claims, wherein the second oxidiser is present at a concentration of 0.001 mol dm^{-3} to 1.5 mol dm^{-3}, preferably 0.5 mol dm^{-3}.

18. The process according to any one of the preceding claims, wherein, in the first leaching step, the ratio of DES plus the first oxidiser to metal in the solid material is from 1:50 to 100:1 (w:w).

19. The process according to any one of the preceding claims, wherein, in the second leaching step, the ratio of DES plus second oxidiser to metal in the solid material is 1:50 to 100:1 (w:w).

20. The process according to any one of the preceding claims, wherein, in the first and second leaching steps, the solid material is leached at a temperature of 10° C to 120° C for 5 minutes to 240 hours.

21. The process according to any one of the preceding claims, wherein the first and second quaternary ammonium salts are each independently choline chloride, choline hydroxide, choline acetate, choline bitartrate, choline dihydrogencitrate, betaine, betaine HCl, ammonium chloride, methylammonium chloride, ethylammonium chloride, tetra-butylammonium chloride, or ethanolamine hydrochloride; preferably wherein the first and second quaternary ammonium salts are choline chloride;

wherein the first and second hydrogen bond donors are each independently ethylene glycol, glycerol, 1,2-propanediol, 1,3-propandiol, 1,4-butandiol, 1,5-pentandiol, urea, oxalic acid, malonic acid, levulinic acid, lactic acid, citric acid, maleic acid, malonamide urea, acetamide, oxalic acid dihydrate, ascorbic acid, glutaric acid, glycolic acid, mandelic acid, succinic acid, tartaric acid or phenol, preferably wherein the first and second hydrogen bond donors are ethylene glycol;

wherein the molar ratios of the first and second quaternary ammonium salts to the first and second hydrogen bond donors are preferably from 4:1 to 1:20, more preferably 2:1 to 1:4;

wherein the reduction potential of the first oxidiser is less than or equal to +0.50 V, preferably wherein the first oxidiser is $FeCl_3$; and,

wherein the reduction potential of the second oxidiser is greater than or equal to +0.50 V, preferably wherein the second oxidiser is I_2.

22. The process according to any one of the preceding claims, further comprising a step of:

recovering one or more metals from the first liquid phase; and/or,

recovering one or more metals from the second liquid phase.

23. The process according to any one of the preceding claims, further comprising filtering, cleaning and drying the first leached solid material before the second leaching step.