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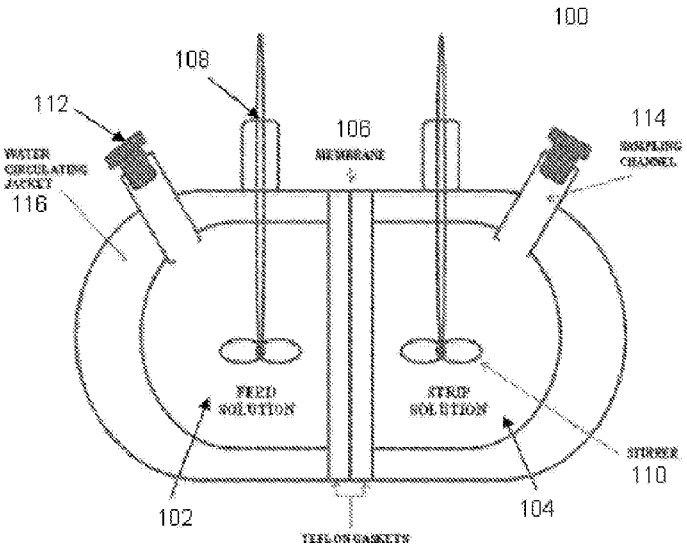
(54) **Title**: MEMBRANES FOR EXTRACTING GOLD

Figure 1



(57) **Abstract**: A method for extracting gold from an acidic solution that includes a gold containing anion and a counter-cation including: contacting the acidic solution with a polymer inclusion membrane to remove the gold containing anion and the counter-cation from the solution, the polymer inclusion membrane including: an acid resistant hydrophobic polymer matrix, and a bi-functional ion-exchanging ionic liquid that includes a hydrophobic cation to extract the gold containing anion and a hydrophobic anion to extract the counter-cation. Membranes for use in the invention are also provided.

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Membranes for extracting gold

Field of the invention

The present invention relates to a membrane to extract gold from solution and a method of using a membrane to extract gold from solution.

Background of the invention

There is an economic and environmental incentive to recover precious metals from scrap metal waste, such as scrap electronics. Scrap electronics in particular can contain gold in quantities that make it economically attractive to treat the waste to recover the gold. Presently, a range of mechanical, hydrometallurgical, pyrometallurgical, electrometallurigical, and biometallurgical processes have been used. However, these processes are not well suited to extraction of gold from waste metal such as scrap electronics. In many cases, these processes are slow, time consuming, and generally uneconomical particularly on a large scale.

The common process consists of thermal degradation, two-stage leaching with nitric acid solution to remove silver and other metals and dissolution of gold with aqua regia, followed by selective solvent extraction of gold (i.e. diethyl malonate, toluene with tetraoctylammonium bromide). This process is very lengthy and non-continuous in nature. It involves the use of large amounts of organic solvents, which are toxic, flammable and volatile and therefore are of considerable environmental and health concern.

Other approaches are based on the use of leaching solutions such as cyanide, halides, thiosulfate and thiourea. The leaching process is then followed by cementation, precipitation, liquid/solid ion-exchange and adsorption on activated carbon. Again, this process involves many steps and the use of highly toxic chemicals and is non-continuous in nature. This process is not highly selective for gold, therefore an addition step involving electrowinning is often used to obtain high purity gold.

Recently there has been research into the solvent extraction of gold using membrane separation technologies, and in particular the use of polymer inclusion membranes. A number of commercial solvent extraction reagents have been used successfully as carriers in polymer inclusion membranes for the selective extraction and transport of a large range of cations, anions and neutral molecules. The success of these carriers has

been largely due to their compatibility with common base-polymers such as poly(vinyl chloride) (PVC), cellulose triacetate (CTA) and poly(vinylidene) fluoride (PVDF).

More recently, ionic liquids have become of interest in solvent extraction. Solvent extraction systems involving ionic liquids have been used in the extraction of rare earths, palladium, cobalt, nickel, zinc, and iron. In addition, an ionic liquid impregnated resin has been used for Cr(VI) removal and it has been reported that a PVDF-based polymer inclusion membrane has been used for Cr(VI) transport.

Previously, PVC-based PIMs containing Aliquat 336 (a quaternary alkyl ammonium chloride salt) as the carrier were used in the extraction of Au(III) from 2.5 M hydrochloric acid. The chloride ion is of low molecular weight and hydrophilic (water soluble). In this case, it was shown that the membrane extracted gold from electronic scrap digested in aqua regia with a high selectivity for gold compared to copper. However, the stripping of Au(III) from the polymer inclusion membrane was difficult and inefficient.

Summary of the invention

The present invention is directed to providing a method for membrane extraction of gold from a solution that includes gold ions, and to a membrane for use in extracting gold ions from a solution that includes gold ions.

In one aspect of the invention there is provided a method for extracting gold from an acidic solution that includes a gold containing anion and a counter-cation including: contacting the acidic solution with a polymer inclusion membrane to remove the gold containing anion and the counter-cation from the solution, the polymer inclusion membrane including: an acid resistant hydrophobic polymer matrix, and a bi-functional ion-exchanging ionic liquid that includes a hydrophobic cation to extract the gold containing anion and a hydrophobic anion to extract the counter-cation. This is in contrast to prior art membranes such as Aliquat 336 which is an ionic liquid that has a chloride ion as the anion. Chloride is a low molecular weight hydrophilic anion and therefore increases the water solubility of Aliquat 336.

In a preferred embodiment, the method additionally includes the step of extracting gold from the polymer inclusion membrane using a stripping (receiving) solution.

Advantageously, the inventors have found that the use of a bi-functional ion-exchanging ionic liquid allows the extraction of the gold containing anion and the counter-cation simultaneously. This is thought to enhance the extraction of gold from an acidic solution

as both the gold containing anion and its counter-cation can be transported into the polymer inclusion membrane.

Additionally, the inventors have found that an ionic liquid in which both the anion and cation component of the ionic liquid are hydrophobic is advantageous as it mitigates loss of either component of the ionic liquid into either the acidic feed solution or into the stripping (receiving) solution.

In an embodiment, the hydrophobic cation has an equal and opposite charge to the gold containing anion to complex or form an ion-pair with the gold containing anion, and the hydrophobic anion has an equal and opposite charge to the counter-cation to complex or form an ion-pair with the counter-cation.

The inventors have found that this enhances the selectivity of the polymer inclusion membrane to the gold containing anions and the counter-cation. In certain embodiments additional metal species may be present in the acidic solution, for example copper. However, many of these metals when in the acidic solution, will be in a hydrated form or in the form of an anionic complex that has an absolute charge value that differs from the gold containing anion. As such, it is difficult for a complex or ion-pair to form between these metal species and the cationic or anionic components of the ionic liquid.

By way of example, in a preferred embodiment the gold containing anion is $AuCl_4^-$ and the counter-ion is H^+. The hydrophobic cationic component of the ionic liquid has a charge of +1 and the hydrophobic anionic component of the ionic liquid has a charge of -1. Therefore, an ion-pair can form between the $AuCl_4^-$ which has a -1 charge and the cationic component of the ionic liquid. Similarly, an ion-pair can form between the counter-cation H^+ which has a +1 charge and the anionic component of the ionic liquid. In contrast, other metals that may be present in the acidic solution which do not form a +1 or -1 charged ion will require multiple anionic or cationic components of the ionic liquid with which to form an ion-pair. For example if copper was present in the acidic solution it would be in the form $CuCl_4^{2-}$ and 2 cationic species would have been required to simultaneously bind $CuCl_4^{2-}$ prior to its extraction into the membrane which is more difficult than when in the case of monovalent ions. Thus, in a preferred embodiment, the hydrophobic cation has a +1 charge, and the hydrophobic anion has a -1 charge.

In an embodiment, the stripping solution includes a reducing agent to extract gold from the polymer inclusion membrane through a reduction reaction that reduces the oxidation state of the gold and regenerates the ionic liquid.

The inventors have determined that a stripping solution that includes a reducing agent is particularly useful as it provides efficient recovery of gold into the stripping solution, and also assists with the regeneration of the ionic liquid. Because the reducing agent regenerates the ionic liquid, the polymer inclusion membrane can be repeatedly used over many extraction cycles for batch extraction process, and/or for extended periods of time during a continuous extraction process.

Preferably, the reducing agent is an anionic sulfur species. More preferably, the anionic sulfur species is selected from sulfides, sulfites, thioureas, and thiosulfates. These anionic sulfur species have been found to be particularly useful for extracting gold from the polymer inclusion membrane and into the stripping solution. Even more preferably the reducing agent is Na_2SO_3, $Na_2S_2O_3$, or thiourea. Without wishing to be bound by theory, the inventors believe that these reducing agents provide a high extraction recovery of gold into the stripping solution.

It is also preferred that the stripping solution includes the reducing agent at a concentration of at least 0.05mol/L. More preferably the stripping solution includes the reducing agent at a concentration of at least 0.1mol/L. Even more preferably the reducing agent is at a concentration of at least 0.5mol/L. Alternatively or additionally, it is preferred that the stripping solution includes the reducing agent at a concentration of no more than 2.5mol/L. More preferably the stripping solution includes the reducing agent at a concentration of no more than 2mol/L. Even more preferably the reducing agent is at a concentration of no more than 1.5mol/L. Most preferably the stripping solution includes the reducing agent at a concentration of about 1mol/L ± 0.3mol/L. If the concentration of the reducing agent is too low, then the extraction of gold from the membrane can take a longer duration and the ultimate recovery may be lower. Conversely, if the concentration is too high then the process becomes more expensive for little gain in extraction rate or efficiency.

In an embodiment, the stripping solution has a pH of from about 7 to about 14. Preferably, the lower value of the pH range is at least 7.5 more preferably at least 8, even more preferably at least 8.5, most at least 9. Alternatively or in addition to, it is preferred that the upper value of the pH range is about 13, more preferably about 12, even more preferably about 11.5, and even more preferably about 11. Particularly preferred pH ranges are from about 8 to about 12, more preferably about 8.5 to about 11.5, even more preferably about 9 to about 11. Most preferably, the pH is 10 ± 0.5

units. The pH value is important for optimising the reaction environment in the stripping solution for the reduction of the gold containing anion and the regeneration of the ionic liquid.

In an embodiment, the recovery of gold into the stripping solution is at least 70% efficient. By a recovery efficiency of at least 70% it is meant that at least 70% of the gold in the acidic feed solution containing the digested electronic scrap was transferred to the stripping solution. Preferably the recovery of gold from the acidic feed solution is at least 80% efficient, more preferably at least 85% efficient, even more preferably at least 90% efficient. It is particularly preferred that the recovery of gold is at least 95% efficient, and most preferred that the recovery of gold is at least 99% efficient.

In an embodiment, the acidic feed solution is an aqua regia solution. Aqua regia is particularly useful if the process includes an initial step of acid digestion of a metal or mixture of metals that includes at least gold. Aqua regia is able to dissolve most metals, forming an acidic aqueous solution that includes metal ions or metal ion complexes. Preferably the acidity of the diluted aqua regia is at least 2.5mol/L, more preferably at least 3mol/L, even more preferably at least 3.5mol/L. It is particularly preferred that the acidity of diluted aqua regia is at least 4mol/L, more particularly at least 4.5mol/L, and even more particularly at least 5mol/L. Most preferably the acidity of aqua regia is about 6 mol/L ± 0.5mol/L. The inventors have found that the present process can be operated at relatively high acidity of diluted aqua regia, preferably, if there is no dilution of the aqua regia during or after the acid digestion step.

Alternatively, depending on the origin of the gold containing anion, the acidic solution may be a hydrochloric acid solution. Preferably the concentration of hydrochloric acid is less than 6mol/L, more preferably less than 4mol/L, even more preferably less than 2 mol/L. Most preferably the concentration of hydrochloric acid is about 0.05 to about 1 mol/L.

In an embodiment, the gold containing anion in the acidic feed solution is $AuCl_4^-$ and the counter-cation is H^+.

In an embodiment, the ionic liquid is an ion-pair consisting of a hydrophobic cation (alkyl or aryl substituted phosphonium, ammonium, imidazolium group) and a hydrophobic anion.

In an embodiment, the hydrophobic anion can be protonated. Preferably the hydrophobic anion is selected from monovalent anions such as an alkyl or aryl group substituted phosphinate, phosphonate or carboxylate, an alkyl or aryl substituted sulfonate, imide or tosylate.

In an embodiment, the ionic liquid is selected from the group consisting of:

trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (CyphosIL104),

1-butyl-2,3-dimethylimidazolium tetrafluoroborate,

1-butyl-3-methylimidazolium methanesulfonate,

1,2,3-trimethylimidazolium methanesulfonate,

N-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide,

Tributyl(tetradecyl)phosphonium dodecylbenzenesulfonate (CyphosIL 201),

Trihexyl(tetradecyl)phosphonium dodecylbenzenesulfonate (CyphosIL 202),

Tributyl(tetradecyl)phosphonium methanesulfonate (CyphosIL 203),

Trihexyl(tetradecyl)phosphonium methanesulfonate (CyphosIL 204),

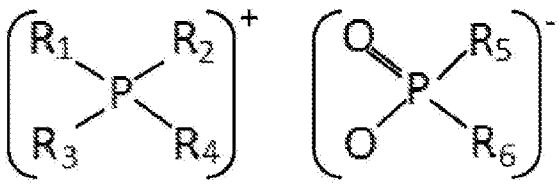
Trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)amide (CyphosIL 109), or

Trihexyl(tetradecyl)phosphonium decanoate (CyphosIL 103).

In an embodiment, the hydrophobic cation of the ionic liquid in the polymer inclusion membrane is an organic phosphonium cation.

In an embodiment, the hydrophobic anion of the ionic liquid in the polymer inclusion membrane is an organic phosphinate anion.

In an embodiment, the hydrophobic cation is an organic phosphonium cation and the hydrophobic anion is an organic phosphinate anion, such that the ionic liquid has the following general formula:



wherein R_1 to R_4 are organic groups that may be the same or different, and R_5 and R_6 are organic groups that may be the same or different.

In a preferred embodiment R_1 to R_4 are independently selected from alkyl, alkenyl, or alkynyl groups which may be branched or unbranched. It is preferred that R_1 to R_4 are unbranched alkyl, alkenyl, or alkynyl groups. Most preferably R_1 to R_4 are unbranched alkyl groups.

Preferably, R_1 to R_4 are independently C_1 to C_{30} alkyl, alkenyl, or alkynyl groups which may be branched or unbranched. More preferably R_1 to R_4 are independently C_2 to C_{24} alkyl, alkenyl, or alkynyl groups which may be branched or unbranched. Even more preferably, R_1 to R_4 are independently C_4 to C_{20} alkyl, alkenyl, or alkynyl groups which may be branched or unbranched. Most preferably, R_1 to R_4 are independently C_6 to C_{14} alkyl, alkenyl, or alkynyl groups which may be branched or unbranched.

In an alternative arrangement, R_1 to R_3 are the same and are selected from the group consisting of: C_1 to C_{20} alkyl, alkenyl, or alkynyl groups which may be branched or unbranched, and R_4 is different from R_1 to R_3 and is selected from the group consisting of C_8 to C_{30} alkyl, alkenyl, or alkynyl groups which may be branched or unbranched. Preferably, R_1 to R_3 are C_2 to C_{14}, more preferably C_3 to C_{12}, even more preferably C_4 to C_{10}, and most preferably C_5 to C_8 alkyl, alkenyl, or alkynyl groups which may be branched or unbranched. Preferably R_4 is C_{10} to C_{26}, more preferably C_{11} to C_{22} , even more preferably C_{12} to C_{18}, and most preferably C_{13} to C_{16} alkyl, alkenyl, or alkynyl groups which may be branched or unbranched.

Preferably R_5 and R_6 are independently selected from alkyl, alkenyl, or alkynyl groups which may be branched or unbranched. It is preferred that R_5 and R_6 are branched alkyl, alkenyl, or alkynyl groups. Most preferably R_5 and R_6 are branched alkyl groups.

Preferably, R_5 and R_6 are independently C_1 to C_{20} alkyl, alkenyl, or alkynyl groups which may be branched or unbranched. More preferably, R_5 and R_6 are independently C_2 to C_{16} alkyl, alkenyl, or alkynyl groups which may be branched or unbranched. Even more preferably, R_5 and R_6 are independently C_3 to C_{12} alkyl, alkenyl, or alkynyl groups which may be branched or unbranched. Most preferably, R_5 and R_6 are independently C_4 to C_8 alkyl, alkenyl, or alkynyl groups which may be branched or unbranched.

In an alternative arrangement R_5 and R_6 are the same.

Most preferably, the ionic liquid is trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)-phosphinate (Cyphos® IL 104).

Ionic liquids of the types discussed above are particularly advantageous as they are well retained within the polymer matrix with minimal loss into the acidic solution or into the stripping solution.

In an embodiment, the ionic liquid is present in the polymer inclusion membrane at from about 15 to about 40wt%. More preferably the lower value in the range is at least 20wt%, and even more preferably at least 25wt%. Alternatively, or additionally it is preferred that the upper value of the range is about 35wt%. Most preferably, the ionic liquid is present in the polymer inclusion membrane at from about 30wt% to about 35wt%.

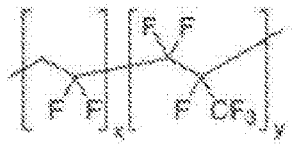
The polymer inclusion membrane may additionally include up to 5wt % of a plasticizer, such as 1-dodecanol. However, in alternative embodiments, the polymer inclusion membrane consists of the acid resistant hydrophobic polymer, the ionic liquid, and incidental inclusions that do not have a material effect on the extraction efficiency of the membrane. These incidental inclusions may consist of up to 5wt%, preferably up to 3wt%, more preferably up to 2wt%, most preferably less than 1wt%.

In an embodiment, the acid resistant hydrophobic polymer matrix is formed from a polymer that has resistance to aqua regia (1: 3 volume ratio of concentrated nitric acid to concentrated hydrochloric acid).

Additionally, or alternatively, the acid resistant hydrophobic polymer matrix is formed from a polymer that has resistance to hydrochloric acid at a concentration of at least 1mol/L, preferably at least 2mol/L, more preferably at least 3 mol/L, even more preferably at least 4 mol/L. Most preferably, the acid resistant hydrophobic polymer matrix is acid resistant to hydrochloric acid at a concentration of at least 6mol/L.

The acid resistant hydrophobic polymer matrix may be formed from a single polymer, or a polymer blend.

In an embodiment, the acid resistant hydrophobic polymer matrix is selected from the group consisting of poly(vinyl chloride) (PVC), poly(vinylidene diflouride) (PVDF), poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP), \other similar polymers, as well as blends thereof. More preferably, the acid resistant hydrophobic polymer matrix is formed from poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) shown below:



Poly(vinylidene fluoride-co-hexafluoropropene)
(PVDF-HFP)

This material is particularly advantageous as it is acid resistant, compatible with the ionic liquid, and exhibits long term stability.

In an embodiment the method is a continuous method for the extraction of gold from the acidic solution. Continuous processes are in many cases more economical and easier to scale up than batch or semi-batch processes. However, in alternative embodiments the method may be a batch or semi-batch process.

In an embodiment the polymer inclusion membrane includes a first side exposed to the acidic feed solution, and a second side exposed to the stripping solution, wherein the step of contacting the acidic solution with a polymer inclusion membrane includes continuously contacting the acidic solution with the first side of the polymer inclusion membrane, and the step of back-extracting gold from the polymer inclusion membrane includes continuously contacting the stripping solution with the second side of the polymer inclusion membrane.

Under this arrangement the method can be operated as either a continuous method for the extraction of gold or it may be operated in a batch type arrangement.

With a continuous process, the acidic feed solution rich in the gold containing anion is provided to the first side of the polymer inclusion membrane, as the feed solution passes over the first side of the polymer inclusion membrane the gold containing anions are removed from the acidic feed solution resulting in an acidic feed solution that is lean in the gold containing anion. The acidic feed solution that is lean in the gold containing anion may then be recycled, for example by possibly mixing it with fresh aqua regia solution to digest further metal (such as scrap metal or waste electronics or the like) that includes at least some gold. The gold containing anion removed from the acidic feed solution forms ion-pairs with the ions of the ionic liquid in the polymer inclusion membrane. The gold can be removed from the polymer inclusion membrane through use of a stripping solution that is applied to the second side of the polymer inclusion membrane. The stripping solution is provided to the second side of the polymer

inclusion membrane, as the stripping solution passes over the second side of the polymer inclusion membrane the gold is back-extracted from the polymer inclusion membrane into the stripping solution in an ionic form to form a stripping solution that is rich in gold. The stripping solution that is rich in gold can then undergo further processing to separate the gold from the stripping solution. The stripping solution may then be recycled for use by possibly mixing it with fresh reducing agent. In preferred forms, the continuous process is a counter-current continuous process to maximise the diffusive driving force for gold across the polymer inclusion membrane.

Alternatively, the process may be operated as a batch process wherein the polymer inclusion membrane provides a physical separation between the acidic feed solution that includes a gold containing anion, and a stripping solution. The gold containing anion is removed from the acidic solution into the polymer membrane through contact between the gold containing anion in the acidic feed solution and the first side of the membrane. Gold is then back-extracted from the second side of the polymer membrane into the stripping solution. Recovery from the stripping phase may be conveniently done by electroplating.

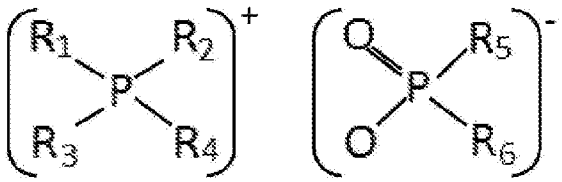
Many of the prior art extraction and recovery processes are batch processes. This limits their use in a commercial environment. In contrast, the inventors have found that the polymer inclusion membrane of the present invention can be used in a continuous process for gold extraction. This offers commercial advantages over the prior art processes as it is less costly to run and is easier to scale up.

In an embodiment, the acidic solution additionally includes copper ions. Preferably, the copper ions are present in solution at a concentration that is at least 1000 times the concentration of the gold anions. It is preferred that the method of the present invention is applied to recovering gold from scrap metal waste, such as scrap electronic components. In such systems, the concentration of copper generally exceeds the concentration of gold at least a thousandfold. Many of the prior art systems struggle to efficiently and effectively separate gold from a solution that contains this level of copper. In contrast with this, the present invention is able to readily select and extract gold from an acidic solution that includes an excess of copper ions, for example from acid digested scrap metal. Preferably the concentration of copper ions is at least 5000 times the concentration of the gold anions, more preferably 10,000 times the concentration of the gold anions, and most preferably 20,000 times the concentration of gold anions.

In an embodiment, the acidic solution that includes a gold containing anion and a counter-cation is formed through acid digestion of a metal or metals that include at least gold and copper.

In another aspect of the invention there is provided a polymer inclusion membrane to extract a gold containing anion and a counter-cation from an acidic solution, the polymer inclusion membrane including: an acid resistant hydrophobic polymer matrix, and a bi-functional ion-exchanging ionic liquid that includes a hydrophobic cation to extract the gold containing anion and a hydrophobic anion to extract the counter-cation, wherein the hydrophobic cation has an equal and opposite charge to the gold containing anion to form an ion-pair with the gold containing anion, and the hydrophobic anion has an equal and opposite charge to the counter-cation to form an ion-pair with the counter-cation.

In an embodiment, the ionic liquid has the following general formula:



wherein R_1 to R_4 are organic groups that may be the same or different, and R_5 and R_6 are organic groups that may be the same or different. Preferably, the ionic liquid is trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)-phosphinate (Cyphos® IL 104).

In an embodiment, the ionic liquid is present in the polymer inclusion membrane at from 20 to 35 wt%.

In an embodiment, the acid resistant hydrophobic polymer matrix is formed from poly(vinylidene fluoride-co-hexafluoropropene).

Brief description of the drawings

Figure 1: Schematic of a 2 compartment transport cell.

Figure 2: Schematic of PIM preparation using a Teflon casting knife.

Figure 3: Graph illustrating the effect of the PIM composition on the extraction of Au(III) in an embodiment of the invention (◆ 20 wt% Cyphos, 80 wt% PVDF-HFP; ■ 25 wt% Cyphos, 75 wt% PVDF-HFP; ● 30 wt% Cyphos, 70 wt% PVDF-HFP; △ 35 wt%

Cyphos, 65 wt% PVDF-HFP; ▲ 30 wt% Cyphos, 5 wt% 1-dodecanol, 65 wt% PVDF-HFP; O 30 wt% Cyphos, 5 wt% NPOE, 65 wt% PVDF-HFP). Experimental conditions: solution volume and composition: 100 mL, 100 mg L^{-1} Au(III), 2.5 mol L^{-1} HCl; membrane mass and thickness: 60 ± 3 mg, 30 ± 5 µm; shaking rate: 150 rpm. Data points are the average of 3 extraction experiments with an average standard deviation (SD) of 0.77.

Figure 4: Graph illustrating the effect of the HCl concentration on the extraction of Au(III) in an embodiment of the invention(◆ Digested aqua regia; ■ 6 mol L^{-1} HCl and O 0.05 mol L^{-1} HCl). Experimental condition as in Figure 3. Data points are the average of 3 extraction experiments with an average SD of 0.67.

Figure 5: Graph of the stoichiometry of the complex formed between Cyphos® IL 104 and Au(III) in an embodiment of the invention indicating a 1:1 ratio between Au(III) and Cyphos in their ion-pair. Experimental conditions - as in Figure 3. Data points are the average of 3 extraction experiments with an average SD of 0.13.

Figure 6: Graph showing the effect of the pH of the stripping solution in an embodiment of the invention(◆ pH 7; □ pH 8; ▲ pH9; ● pH 10). Experimental conditions: stripping solution volume and composition: 100 mL, 0.1 mol L^{-1} Na_2SO_3; membrane mass and thickness: 60 ± 3 mg, 30 ± 5 µm; membrane composition: 30 wt% Cyphos® IL 104 and 70 wt% PVDF-HFP; extraction solution volume and composition: 100 mL, 100 mg L^{-1} Au(III) in digested aqua regia (6 mol L^{-1}); shaking rate: 150 rpm. Data points are the average of 3 extraction experiments with an average SD of 1.57.

Figure 7: Graph showing the effect of the stripping solution concentration on an embodiment of the invention concentration (◆ 1.0 mol L^{-1}; ■ 0.5 mol L^{-1}; ▲ 0.1 mol L^{-1}; ● pH 10). Experimental conditions as in Figure 6, except for stripping solution pH 10. Data points are the average of 3 extraction experiments with an average SD of 1.67.

Figure 8: Graph showing five cycles of extraction of an embodiment of the invention (◆ 1^{st}; □ 2^{nd}; ▲ 3^{rd}; O 4^{th}; ● 5^{th}). Experimental conditions: feed solution volume and composition: 100 mL, 100 mg L^{-1} Au(III) in digested aqua regia (6 mol L^{-1}); membrane mass and thickness: 60 ± 3 mg, 30 ± 5 µm; membrane composition: 30 wt% Cyphos® IL 104 and 70 wt% PVDF-HFP; shaking rate: 150 rpm. Data points are the average of 3 experiments with an average SD of 0.74.

Figure 9: Graph showing five cycles of back-extraction of the embodiment of Figure 8(◆ 1st; □ 2nd; ▲ 3rd; O 4th; ● 5th). Experimental conditions: back-extraction solution volume and composition: 100 mL, 0.5 mol L^{-1} Na_2SO_3; membrane mass and thickness: 60 ± 3 mg, 30 ± 5 μm; membrane composition: 30 wt% Cyphos® IL 104 and 70 wt% PVDF-HFP; shaking rate: 150 rpm. Data points are the average of 3 experiments with an average SD of 1.57.

Figure 10: Comparison of the extraction performance of a fresh PIM (O) and PIM exposed for 24 h to an undiluted aqua regia solution (●). All remaining experimental conditions - as in Figure 8. Data points are the average of 3 extraction experiments with an average SD of 0.65.

Figure 11: Graph showing aqueous concentration of Au(III) in feed solution containing Au(III) in digested aqua regia(●) and Au(III) in stripping solution containing 0.5 M Na_2SO_3 (O) vs time of contact for 30 wt% Cyphos® IL 104/ 70 wt% PVDF-HFP membrane composition in the transport experiment. (Volume of solution in each compartment: 100 mL).

Figure 12: Graph showing the transient concentrations of Au(III) (●) and the major metallic constituents of electronic scrap (i.e. Al(III) (◆), Cd(II) (▲), Cu (△), Ni (■), and Zn (□)) in the corresponding feed aqua regia solution and transient percentage back-extraction of Au(III) (O) in the receiving solution containing 0.5 mol L^{-1} Na_2SO_3 during the transport experiment. The remaining experimental conditions are identical to those in Figs. 8 and 9.

Figure 13: Graph showing the transient concentrations of Au(III) (●), Ag(I) (△), Pt(II) (▲), and Pd(II) (□) in a feed aqua regia solution during extraction and the transient percentage back-extraction of Au(III) (O) in the receiving solution during subsequent back-extraction. The experimental conditions are identical to those in Figs. 8 and 9.

Detailed description of the embodiments

A polymer inclusion membrane (PIM) composed of Cyphos® IL 104 and poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) has shown a high selectivity for Au(III) from undiluted aqua regia solutions in the presence of a 1500-fold higher concentration of copper(II). The membrane has shown high stability in the extraction of Au(III) from aqua regia solutions and Au(III) can successfully be stripped from the membrane with a

Na_2SO_3 solution. The transport of Au(III) from undiluted aqua regia to Na_2SO_3 solution has also been demonstrated. The membrane has also been found to separate successfully Au(III) from aqua regia solutions containing additional metals such as Cu, and other noble metals such as Ag, Pt and Pd.

Dispersion of the PIM may be achieved by any convenient means and will depend on the form of the PIM (i.e., beads, hollow fibres, flat sheets, plates, etc). For instance if the PIM is in the form of beads, the PIM beads may be dispersed by mechanical agitation such as stirrers and the like or with the use of mixing pumps immersed in the aqueous solution, or by the use of gas (eg air) bubbled through the aqueous solution. Sufficient shear forces will need to be imparted on the solution to optimise dispersion of PIM beads.

In a preferred embodiment the PIM is presented in the form of PIM beads which have a diameter of less than 500 µM, and preferably in a range of from 20 µM to 450 µM. This size range provides a PIM which can be readily dispersed in an aqueous solution (eg water) and one which is suitable for subsequent separation from the aqueous solution. The size of the PIM beads may affect the kinetics of adsorption and the effectiveness of separation and stripping (ie the regeneration of the beads). The optimal size may be determined by routine experimentation. The beads may be solid PIM beads or beads which are produced by coating PIM unto a substrate (eg glass or another polymer). In one embodiment the PIM beads may be PIM coated glass beads.

In another embodiment the PIM is presented in the form of a hollow fibre membrane. The excellent mass-transfer properties provided for by the hollow fibre configuration means that such membranes can be used in large scale continuous extraction processes.

Typically, the amount of PIM used to substantially remove (ie >90%) from an acid feed solution that includes the gold containing anion will be in the range of from 1 to 4 g of PIM (in the form of beads) per litre of an aqueous solution which contains around from 50-100 mg/L of the gold containing anion. Although the person skilled in the art would appreciate the high concentrations of PIM may also be useful in removing higher concentrations of the gold containing anion, such higher concentrations allow shorter contact times and possibly more effective extraction.

The PIMs outlined above can be used for continuous on-line recovery of Au(III) from acid digest solutions that include membrane or packed-bed modules.

1) Flat sheet or hollow fibre membrane modules

- Flow-through modules incorporating parallel plate flat sheet PIM stacks or spiral wound PIMs where the stripping solution and the feed acidic solution flow counter- or co-currently on the opposite sides of the flat sheet PIMs.
- Bundled hollow fibre modules where the stripping solution flows continuously through the fibres while the acid solution including the gold containing anion flows continuously around the fibres counter- or co-currently to the stripping solution flow. A configuration where the sides of the stripping solution and the acid feed solution are swapped is also possible.

In both types of modules outlined above the extraction and back-extraction (stripping) steps take place simultaneously.

2) Flow-through packed-bed modules

These are packed-bed reactors filled with packing which consist of the extracting polymer used for making PIMs or are coated with this material. An example of such packing is a load of beads which consist of the extracting polymer used for making PIMs or are coated with this material. The acid feed solution including the gold containing anion flows through these reactors until the extracting polymer is saturated with the gold containing anion after which a stripping solution is flown through the reactor to back-extract the retained gold containing anion and thus regenerate the extracting PIM.

Figure 1 illustrates a reactor 100 that may be used in a gold extraction process according to the present invention. The reactor 100 includes a first compartment 102 and a second compartment 104. A polymer inclusion membrane 106 separates the first compartment 102 from the second compartment 104. Acidic feed solution that includes a gold containing anion is introduced into the first compartment 102 where it contacts the membrane 106. The gold containing anion in the acidic feed solution forms an ion pair with ionic liquid in the polymer inclusion membrane. This process extracts the gold containing anion from the acidic feed solution resulting in an acidic feed solution that is depleted in the gold containing anion. The gold containing anion is transported across the membrane, where it is back-extracted from the membrane 106 through contact with stripping solution in the second compartment 104. This results in a stripping solution that is rich in the gold containing anion. Both the first compartment 102 and the second compartment 104 may be agitated via stirrers 108 and 110, respectively. The

concentrations of various reagents in the first compartment 102 and the second compartment 104 may be monitored via sampling channels 112 and 114 respectively. A water cooling jacket 116 is also used to control the temperature of the reaction environment. It will be appreciated that the reactor illustrated in Figure 1 is primarily operated in a batch mode. However, the reactor could also be operated as a continuous or semi-batch process by modifying the reactor to include inlet and outlet ports to and from the first compartment 102 and the second compartment 104.

Membrane preparation

PVC-based PIMs containing Cyphos® IL 104 (30 wt%) and PVC (70 wt%), with a total mass of 400 mg were prepared by the traditional casting method which in this case involved dissolving the 2 membrane components in approximately 8 mL of THF. The solution was poured into a glass ring with a diameter of 7.5 cm, which was positioned on a flat glass plate that was cleaned with acetone prior to casting. The mixture was covered with a filter paper and a watch glass to allow slow evaporation of the solvent over a 24-hour period leaving a transparent and flexible circular membrane. A circular membrane segment (mass 60±3 mg, thickness 50±5 μm) was used in the extraction experiments.

PVDF-HFP-based PIMs with various compositions of Cyphos® IL 104 (20 wt% - 35 wt%) and PVDF-HFP (65 wt% - 80 wt%) were prepared. In some cases, NPOE or 1-dodecanol (5 wt%) was added to the composition. The components were dissolved in THF with a ratio of 10 mL of THF to 1.0 g of PVDF-HFP by stirring the solution at room temperature for 1 h on an orbital shaker, which was followed by heating the stirred solution in a water jacketed beaker at 40°C for 2 h. The temperature of the water circulated through the jacketed beaker was adjusted at 40 ± 1.0°C in a thermostated bath fitted with a digital thermoregulator. The PIM casting solution was allowed to cool with stirring to room temperature for a further 1 h. Membranes were prepared using a homemade casting knife (Figure 2). This consisted of a Teflon block with a well for the membrane solution and a 50 μm channel at the bottom of the front edge sealed initially with a Teflon plate. This plate was raised and the block was drawn across the surface of a glass plate to form a thin layer of the PIM solution (Figure 2). This was then covered with an aluminum tray to allow slow evaporation of THF overnight. A flat sheet of a transparent and flexible PIM of 30 ± 5 μm thickness was removed. Circular pieces of 3.5

cm or 6.5 cm diameters were cut from the centre of the membrane using a circular steel punch and used in the extraction and transport experiments, respectively.

Membrane extraction and back-extraction

For extraction, membranes were immersed in glass jars containing 100 mg L^{-1} Au(III) in 100 mL HCl or digested aqua regia solutions. For back-extraction experiments, membranes containing Au(III) were immersed in different stripping solutions (100 mL). In each case, the jars were shaken using a platform orbital shaker at 150 rpm and samples of the solutions (0.2 mL) were removed at predetermined time intervals and diluted to 4 mL with deionized water. The Au(III) concentration was determined by atomic absorption spectrometry (AAS).

Membrane stability tests were carried out by repeated extraction and back-extraction experiments over multiple cycles and the membrane performance was monitored by sampling the solutions (0.2 mL) as outlined above.

Membrane masses were measured initially and after back-extraction. After back-extraction, membranes were rinsed with deionized water (10 mL), dried in air for 12 h and then weighed.

Determination of the stoichiometry of the Au(III) ion-pair with Cyphos® IL 104

The stoichiometry of the ion-pair formed between Au(III) and Cyphos® IL 104 in the membrane was studied using a variation of the method described by St. John et. al. (A.M. StJohn, R.W. Cattrall, S.D. Kolev, Extraction of Uranium(VI) from Sulfate Solutions Using a Polymer Inclusion Membrane Containing Di-(2-ethylhexyl)phosphoric Acid, J. Membr. Sci., 364 (2010) 354-361.) the contents of which are incorporated herein by reference Individual segments of the PIM containing Cyphos® IL 104 (30 wt%) with masses varying between 8 and 125 mg were placed in jars containing 50 mL of a solution containing 50 mg L^{-1} Au(III) and 2.5 mol L^{-1} HCl. The mole ratio of Cyphos® IL 104 in the PIM to Au(III) in the solution in these experiments was in the range 0.2:1 - 3:1. The jars were agitated using an orbital shaker at 150 rpm for 5 days to allow the PIM/solution systems to reach equilibrium. The equilibrium concentration of Au(III) in each jar was measured by AAS.

Transport experiments

Au(III) transport experiments were carried out using a two compartment glass cell with a volume of each compartment of 100 mL. The membrane with an internal diameters of

4.8 cm was sandwiched between the two compartments. The cell was thermostated at 25°C and each compartment was stirred. The temperature of the water circulated through the jacketed compartments of the transport cell was adjusted at 25 ± 0.10°C in the thermostated bath used in the heating of the PIM casting solution. The feed solution was a digested aqua regia solution of Au(III) or an aqua regia solution of digested electronic scrap and the receiving solution contained 0.50 mol L^{-1} Na_2SO_3. The transient Au(III) concentration in the feed and receiving solutions was monitored in the same way as in the PIM extraction and back-extraction experiments. In the transport experiments involving digested electronic scrap, the determination of other metal ions was carried out using inductively coupled plasma – optical emission spectrometry (ICP-OES).

Digestion of electronic scrap

Electronic scrap was obtained from old computer parts (total mass 17.0 g) and was broken into small pieces with a hammer. The digestion was carried out using 200 mL of aqua regia (3:1 HCl: HNO_3 (v/v)) heated on a hot plate at 100°C for 6 h. All the metals parts were dissolved and only a small amount of plastic particles remained in the solution. The digested solution was allowed to cool to room temperature and then filtered. The volume of the solution was slightly reduced after digestion and so was adjusted to 200 mL using deionized water. The total mass of the dissolved metal parts was 7.42 g.

Initial flux calculation

The calculation of the initial flux (J_0, mol m^{-2} s^{-1}) was made according to Fick's first law by fitting the transient concentration with an exponential decay function ($\bar{C} = \alpha_1 + \alpha_2 e^{-\alpha_3 t}$) the first derivative of which $(d\bar{C}/dt)_{t=0}$ is used to calculate J_0 according to Eq. (1)

$$J_0 = \frac{V}{S} \cdot \left[\frac{dC}{dt}\right]_{t=0} \qquad (1)$$

where V is the volume of the solution (m^3), S is the surface area of the membrane (m^2) and t is time (s).

Optimization of the membrane composition

Initially, PIMs containing Cyphos® IL 104 were prepared by the casting method with PVC as the base polymer. Although the PIMs after preparation appeared transparent,

flexible and homogenous, their longer term stability was very poor particularly since back-extraction of the Au(III) required the use of solutions with pH values greater than 3. Hence, PVC-based membranes were not studied further. Also, the use of PVDF as the base polymer was unsuccessful. Because of these findings, PVDF-HFP copolymer was investigated for its suitability as a base polymer since it is less prone to dehydrofluorination under acidic conditions than PVDF and is easier to dissolve in volatile solvents such as THF. However, PVDF-HFP-based PIMs prepared by the traditional casting method appeared to shrink inside the glass ring to produce membranes with variable thickness. Because of this, PVDF-HFP based PIMs were prepared using the casting knife technique, outlined above.

PIMs made with this method were transparent, homogeneous, flexible and retained their shape provided the amount of Cyphos® IL 104 was 35 wt% or lower. Higher concentrations of Cyphos® IL 104 resulted in membranes with crystalline regions due to the incompatibility of the Cyphos® IL 104 at high concentration with the base polymer. The effect of adding common plasticizers such as NPOE or 1-dodecanol (5 wt%) to the PIM composition was also investigated.

The PIMs were studied for their ability to extract Au(III) from 2.5 mol L^{-1} HCl solutions. Figure 3 shows the concentration of Au(III) in the solution with time for the various PIM compositions studied. As expected, the extent and rate of extraction increased with increase in the concentration of Cyphos® IL 104 in the membrane up to 30 wt%. A further increase in the concentration of Cyphos® IL to 35 wt% showed only a very slight improvement in the extraction properties. Figure 3 also shows that the addition of 5 wt% NPOE or 1-dodecanol to the membrane composition does not improve its extraction properties and, in fact, the rate and extent of extraction become lower than those for the PIM containing only 30 wt% Cyphos® IL 104.

From these studies, the PIM containing 30 wt% Cyphos® IL 104 and 70 wt% PVDF-HFP was selected for further study.

Effect of the HCl concentration

The effect of the concentration of HCl on the extraction of Au(III) was studied by varying the concentration of HCl from 0.05 to 9.0 mol L^{-1} and the results are shown in Figure 4. It can be seen there is little difference in the extraction performance for the different concentrations of HCl. Even in a 0.05 mol L^{-1} HCl solution Au(III) exists as the

tetrachloroaurate(III) species and it is proposed that the species extracted by the bi-functional carrier Cyphos® IL 104 is $H^+[AuCl_4]^-$.

It was observed that the extraction of Au(III) from 9.0 mol L^{-1} HCl was possible without deterioration in the membrane performance. In previous studies using PVC/Aliquat 336 PIMs, such high acid concentrations led to membrane damage and for this reason applying a PVC-based PIM to the extraction of Au(III) from electronic scrap digested in an aqua regia solution required the dilution of this solution to an acid concentration of around 2.5 mol L^{-1}. Therefore, it was of interest to investigate if a PVDF-HFP-based membrane could be used for the extraction of Au(III) directly from digested aqua regia solution without prior dilution. The acid concentration of aqua regia after digestion was determined to be close to 6.0 mol L^{-1} by titration with a standard solution of NaOH. Figure 4 shows that the membrane extracts Au(III) well from digested aqua regia solutions although the rate and extent of extraction of Au(III) are slightly lower than those for 6.0 mol L^{-1} HCl solutions. This can be explained by the presence of some residual nitric acid in the digested aqua regia solution which competes with the extraction of $H^+[AuCl_4]^-$. This was confirmed by the IR spectrum of the PIM which showed the presence of the antisymmetric stretching peak of NO_3^- at 1248 cm^{-1}.

Stoichiometry of the extracted Au(III)- Cyphos® IL 104 ion-pair

The stoichiometry of the extracted Au(III) ion-pair with Cyphos® IL 104 was studied using a variation of the method described by St. John et. al. (A.M. St John, R.W. Cattrall, S.D. Kolev, Extraction of Uranium(VI) from Sulfate Solutions Using a Polymer Inclusion Membrane Containing Di-(2-ethylhexyl)phosphoric Acid, J. Membr. Sci., 364 (2010) 354-361.). Different masses of membrane segments with a composition of 30 wt% Cyphos® IL 104 and 70 wt% PVDF-HFP were immersed in 100 mL of a 100 mg L^{-1} Au(III) solution in 2.5 mol L^{-1} HCl. The chosen masses of the segments allowed to vary the initial mole ratio of Cyphos® IL 104 in the PIM to Au(III) in the solution between 0.2:1 to 3:1. The equilibrium concentration of Au(III) extracted into each PIM segment was determined and the ratio of the number of moles of Cyphos® IL 104 to Au(III) in the PIM segment was calculated and plotted against the initial mole ratio of Cyphos® IL 104 in the PIM to Au(III) in the solution (Figure 5). Figure 5 shows that when the number of moles of Au(III) in the solution exceeds significantly the number of moles of Cyphos® IL 104 in the PIM, the mole ratio of Au(III) to Cyphos® IL 104 in the PIM is 1:1. This means that the PIM segment is fully loaded with Au(III) and there is only a negligible amount of

free Cyphos® IL 104 remaining. However, as the ratio of the number of moles of Cyphos® IL 104 to Au(III) in the solution becomes greater than 1:1, the number of moles of free Cyphos® IL 104 rapidly increases. These results confirm a 1:1 ratio for the stoichiometry of the extracted ion-pair.

The proposed mechanism for the extraction process is described by Eq. (2) which demonstrates the bi-functional behavior of Cyphos® IL 104 which acts as an anion exchanger for the $AuCl_4^-$ anion and as a cation exchanger for the H^+ ion. The PIM loading capacity was calculated from the fully loaded membrane data as equal to 0.38 meq g^{-1}.

$$\mathbf{[P]^+\,[PO_2]^-_m + H^+[AuCl_4]^-_{aq} \leftrightharpoons [P]^+\,[AuCl_4]^-\,H^+\,[PO_2]^-_m} \qquad \mathbf{(2)}$$

where $\mathbf{[P]^+}$ and $\mathbf{[PO_2]^-}$ refer to the trihexyl(tetradecyl)phosphonium cation and the bis(2,4,4-trimethylpentyl)phosphinate anion, respectively, and **m** and **aq** refer to membrane and aqueous, respectively.

Back-extraction of Au(III)

The back-extraction of Au(III) from the membrane was studied using various stripping reagents of concentration 0.10 mol L^{-1}. It should be noted that for these back-extraction experiments, the PIM was loaded with Au(III) using 100 mL digested aqua regia solution (acidity 6 mol L^{-1}) containing 100 mg L^{-1} Au(III). The results showing the percentage back-extraction after 25 h and the initial back-extraction flux are summarized in Table 1. The three stripping reagents with reducing properties, i.e. Na_2SO_3, $Na_2S_2O_3$ and thiourea, showed relatively high back-extraction efficiencies with Na_2SO_3 being the best and yielding 100% back-extraction of Au(III) with a relatively high initial flux. The remaining stripping reagents studied (Table 1) showed low back-extraction efficiencies which was due to their inability for reducing Au(III). The back-extraction mechanism in this case involved simple anion exchange between the reagent anion in solution and the $AuCl_4^-$ ion in the membrane. Na_2SO_3 was selected for further studies because of its high-back extraction efficiency. Interestingly, it was observed that after exposing a used membrane to ambient air for several days, a small number of pink spots appeared on the membrane surface, however, this did not affect the reusability of the membrane.

Table 1. Percentage back-extraction and initial flux values for the stripping reagents studied. Values are the average of 3 back-extraction experiments conducted for each reagent with an average SD of 1.39.

Stripping reagents	%Back-extraction	Initial flux (mol m^{-2} s^{-1})
NaCl	11.5	1.05
HCl	7.72	5.31×10^{-1}
KNO_3	16.1	6.81×10^{-1}
HNO_3	5.30	5.35×10^{-1}
KSCN	23.3	1.74
Na_2SO_3	100.0	1.31
$Na_2S_2O_3$	98.1	7.51×10^{-1}
Thiourea	75.7	7.40
Na_2SO_4	13.8	6.01×10^{-1}
H_2SO_4	2.74	4.60×10^{-1}
$NaClO_4$	37.7	1.87
KBr	8.73	5.67×10^{-1}

A possible mechanism for the back-extraction process using Na_2SO_3 is described by Eq. (3). According to this mechanism, Au(III) is reduced to Au(I) which forms a complex with the sulfite anion in the stripping solution and Cyphos® IL 104 reverts back to its original ionic liquid form. Support for this mechanism is seen in a decrease in the pH of the stripping solution. However, there is, of course, another possibility in which the phosphonium ion of Cyphos® IL 104 is converted to the chloride or even the sulfate form. The latter seems unlikely since it would lead to a very bulky ion-pair in the membrane. To test for the presence of chloride or sulfate in the stripped PIM, the membrane was conditioned in 0.25 mol L^{-1} nitric acid and the solution was spot tested with $AgNO_3$ and $BaCl_2$ solutions and analyzed using IC. No anion other than nitrate was detected.

$$[P]^+[AuCl_4]^- \cdot H^+[PO_2]^-_m + 3SO_3^{2-}{}_{aq} + H_2O \leftrightharpoons [P]^+[PO_2]^-_m + [Au(SO_3)_2]^{3-}{}_{aq} + 3H^+_{aq} + 4Cl^-_{aq} + SO_4^{2-}{}_{aq} \quad (3)$$

Effect of the stripping solution pH

The natural pH of freshly prepared Na_2SO_3 solutions in deionized water is close to 10 and at this pH the SO_3^{2-} species is dominant. At pH values as low as 7, protonated species also exist and so it was of interest to see if the initial pH of the Na_2SO_3 solution had an effect on the stripping efficiency. The results shown in Figure 6 indicate that there is a negligible effect of the initial pH in the pH range between 7 and 10. Thus, Na_2SO_3 in deionized water (pH 10) was chosen as the stripping solution.

Effect of the stripping solution concentration

The influence of the concentration of the stripping solution, varied from 0.05 mol L^{-1} to 1.0 mol L^{-1}, on the stripping efficiency and rate is presented in Figure 7. The results show that the rate of stripping of Au(III) increased as the concentration of Na_2SO_3 increased though 100% stripping efficiency was reached for all concentrations studied. The stripping rate for 0.5 mol L^{-1} and 1.0 mol L^{-1} Na_2SO_3 are approximately the same and therefore 0.5 mol L^{-1} was chosen as the optimal concentration value.

Membrane stability

One of the crucial factors determining the suitability of PIMs in analytical, environmental and industrial separation is the membrane stability and hence its reusability and so the stability of the PVDF-HFP/ Cyphos® IL 104 membrane was examined. This was carried out by subjecting the PIM to 5 cycles of extraction and back-extraction and monitoring its performance, assuming that deterioration in membrane performance was an indication of instability. The results presented in Figure 8 show an overall stable extraction performance with a slight deterioration in extraction efficiency at the 5th cycle. The back-extraction results (Figure 9) show a relatively small decrease in the rate of back-extraction after the first cycle which suggests a slight loss of the membrane liquid phase which was confirmed by a decrease of approximately 3% in the membrane mass. However, beyond the second back-extraction, there was little change in performance and the average mass of the membranes did not change. The results of these experiments in which extraction was carried out from digested aqua regia (6 mol L^{-1}) demonstrate the high stability of the PIM proposed in this study.

The stability of the membrane was further tested by immersing it in a fresh undiluted aqua regia solution overnight. The membrane was then rinsed with deionized water and used for Au(III) extraction from a digested aqua regia solution. The results, shown in

Figure 10, indicate that the PIM extraction performance was virtually identical to that of a fresh PIM. This demonstrates the high stability of the proposed PIM even after immersion in undiluted aqua regia solutions.

Transport studies

A preliminary transport experiment using the proposed PIM was carried out with an Au(III) solution in digested aqua regia (acidity, 6.0 mol L^{-1}) as the feed solution and a receiving solution containing 0.50 mol L^{-1} Na_2SO_3. The transient Au(III) concentration curves for the feed and receiving solutions are shown in Figure 11.

A similar transport experiment was also carried out using an undiluted aqua regia solution of electronic scrap with composition listed in Table 2 along with the molar metal:Au ratio.

Table 2: ICP-OES analysis of the undiluted aqua regia solution of electronic scrap.

Metal	Concentration (mg L^{-1})	Mole ratio of metal : Au
Al	1660	214
Au	56.7	1.00
Cd	184	5.68
Co	8.49×10^{-1}	5.00×10^{-2}
Cr	4.30×10^{-2}	2.87×10^{-3}
Cu	2.73×10^{4}	1493
Fe	3.02	1.88×10^{-1}
Ni	713	42.2
Pb	4.86×10^{-1}	8.14×10^{-3}
Zn	1200	63.7

As expected, relative to Au very high concentrations of Al, Cd, Cu, Ni and Zn were found in the electronic scrap solution and any separation process for the recovery of the Au must eliminate these potential interferents. The transient normalized concentrations of these metals, as well as those of the other metals (Co, Cr, Fe and Pb) present in lower concentrations in the feed electronic scrap solution (Table 2), and the transient

percentage back-extraction of Au(III) in the receiving solution are shown in Figure 12. Only Au(III) was found to be transported across the proposed PIM from the feed to the receiving solution. The transport of the all other metal ions present in the feed solution (Table 2) was found to be negligible and therefore the corresponding transient back-extraction curves are not shown in Figure 12. At first glance, this is surprising since one group of metal ions present in high concentrations in the electronic scrap solution (e.g. Cu^{2+}, Cd^{2+} and Zn^{2+}) readily form anionic chlorocomplexes in the presence of high concentration of chloride. However, the dominant anionic chlorocomplexes formed with these metal ions have a charge of 2- and so it is proposed that the ion-pairs formed with Cyphos® IL 104 will be very bulky and hence extraction into the PIM will be unfavorable compared to the singly negatively charged $AuCl_4^-$ ion. Another group of metal ions present in the electronic scrap solution (e.g. Ni^{2+} and Al^{3+}) do not form anionic chlorocomplexes and the extraction of these metal cations by the phosphinate group will be unfavorable due to their high charges as well as due to competition with the H^+ ion.

The results presented in Figure 12 demonstrate that the selectivity of the membrane for $[AuCl_4]^-$ was very high, especially with over 1500-fold higher concentration of Cu(II) in the solution. It should be noted that the rate of transport of Au(III) from the aqua regia digest of electronic scrap was slower than from the aqua regia solution containing only Au(III) (Figure 11). This was due to the presence of high concentration of other metals, and especially copper, compared to the $[AuCl_4]^-$ concentration which caused the slower rate of extraction. For example, the Cu(II) ion is known to slow the rate of extraction of Au(III) by Aliquat 336 due to ion-pairing with $[AuCl_4]^-$. However, this membrane has shown very high selectivity toward Au and the stability of the membrane makes it promising for efficient gold recovery on industrial scale without the use of too much fresh water for dilution.

Separation of Au(III) from aqua regia solutions of Ag(I), Pt(II) and Pd(II)

PIMs with optimal compositions were exposed to aqua regia solutions containing the same concentration of Au(III), Ag(I) and platinum group metal ions Pt(II) and Pd(II). The results presented in Figure 13 show that Au(III) was the only metal ion extracted from the aqua regia solution and its was successfully stripped from the membrane (Figure 13) using 0.5 M Na_2SO_3.

It will be understood that the invention disclosed and defined in this specification extends to all alternative combinations of two or more of the individual features mentioned or evident from the text or drawings. All of these different combinations constitute various alternative aspects of the invention.

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CLAIMS

1. A method for extracting gold from an acidic solution that includes a gold containing anion and a counter-cation including:

contacting the acidic solution with a polymer inclusion membrane to remove the gold containing anion and the counter-cation from the solution, the polymer inclusion membrane including:

an acid resistant hydrophobic polymer matrix, and

a bi-functional ion-exchanging ionic liquid that includes a hydrophobic cation to extract the gold containing anion and a hydrophobic anion to extract the counter-cation.

2. The method of claim 1, wherein the method further includes the step of extracting gold from the polymer inclusion membrane using a stripping solution.

3. The method of claim 2, wherein the stripping solution includes a reducing agent to extract gold from the polymer inclusion membrane through a reduction reaction that reduces the oxidation state of the gold and regenerates the ionic liquid.

4. The method of claim 3, wherein the reducing agent is an anionic sulfur species.

5. The method of claim 4, wherein the anionic sulphur species is selected from sulfides, sulfites, thioureas, and thiosulfates.

6. The method of any one of claims 3 to 5 wherein the stripping solution includes the reducing agent at a concentration of at least 0.05mol/L.

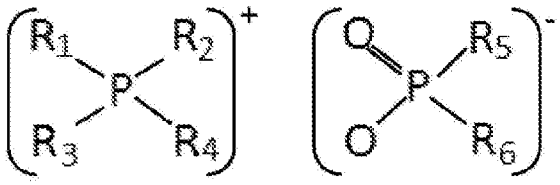
7. The method of any one of the preceding claims, wherein the hydrophobic cation has an equal and opposite charge to the gold containing anion to form an ion-pair with the gold containing anion, and the hydrophobic anion has an equal and opposite charge to the counter-cation to form an ion-pair with the counter-cation.

8. The method of any one of the preceding claims wherein the hydrophobic cation has a +1 charge, and the hydrophobic anion has a -1 charge.

9. The method of any one of the preceding claims, wherein the gold containing anion is $AuCl_4^-$ and the counter-cation is H^+.

10. The method of any one of the preceding claims, wherein the acidic solution is an aqua regia solution.

11. The method of any one of the preceding claims wherein the ionic liquid has the following general formula:



wherein R_1 to R_4 are organic groups that may be the same or different, and R_5 and R_6 are organic groups that may be the same or different.

12. The method of claim 11, wherein the ionic liquid is trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)-phosphinate (Cyphos® IL 104).

13. The method of any one of the preceding claims wherein the ionic liquid is present in the polymer inclusion membrane at from 20 to 35 wt%.

14. The method of any one of the preceding claims, wherein the acid resistant hydrophobic polymer matrix is formed from poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP).

15. The method of any one of the preceding claims wherein the polymer inclusion membrane includes a first side exposed to the acidic solution, and a second side exposed to the stripping solution.

16. The method of claim 15, wherein the method is a continuous method for the extraction of gold from the acidic solution, and

the step of contacting the acidic solution with a polymer inclusion membrane includes continuously contacting the acidic solution with the first side of the polymer inclusion membrane, and

the step of extracting gold from the polymer inclusion membrane includes continuously contacting the stripping solution with the second side of the polymer inclusion membrane.

17. The method of any one of the preceding claims wherein the acidic solution additionally includes copper ions.

18. The method of claim 17 wherein copper ions are present in solution at a concentration that is at least 1000 times the concentration of the gold anions.

19. The method of any one of the preceding claims wherein the acidic solution that includes a gold containing anion and a counter-cation is formed through acid digestion of a metal or metals that include at least gold and copper.

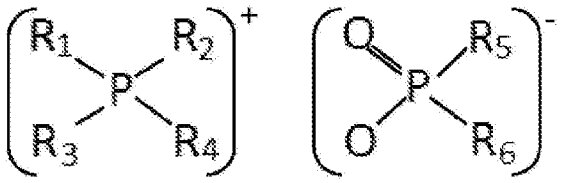
20. A polymer inclusion membrane to extract a gold containing anion and a counter-cation from an acidic solution, the polymer inclusion membrane including:

an acid resistant hydrophobic polymer matrix, and

a bi-functional ion-exchanging ionic liquid that includes a hydrophobic cation to extract the gold containing anion and a hydrophobic anion to extract the counter-cation.

21. The polymer inclusion membrane of claim 20, wherein the hydrophobic cation has an equal and opposite charge to the gold containing anion to form an ion-pair with the gold containing anion, and the hydrophobic anion has an equal and opposite charge to the counter-cation to form an ion-pair with the counter-cation.

22. The polymer inclusion membrane of claim 20 or 21, wherein the ionic liquid has the following general formula:



wherein R_1 to R_4 are organic groups that may be the same or different, and R_5 and R_6 are organic groups that may be the same or different.

23. The polymer inclusion membrane of claim 22, wherein the ionic liquid is trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)-phosphinate (Cyphos® IL 104).

24. The polymer inclusion membrane of claim of any one of claims 20 to 23, wherein the ionic liquid is present in the polymer inclusion membrane at from 20 to 35 wt%.

25. The polymer inclusion membrane of claim any one claims 20 to 24, wherein the acid resistant hydrophobic polymer matrix is formed from poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP).

26. The polymer inclusion membrane of any one of claims 20 to 25, wherein the PIM is in the form of flat sheets or hollow fibre membranes.

27. The method of any one of claims 1 to 19 wherein the polymer inclusion membrane is in the form of hollow fibre membranes.

Figure 1

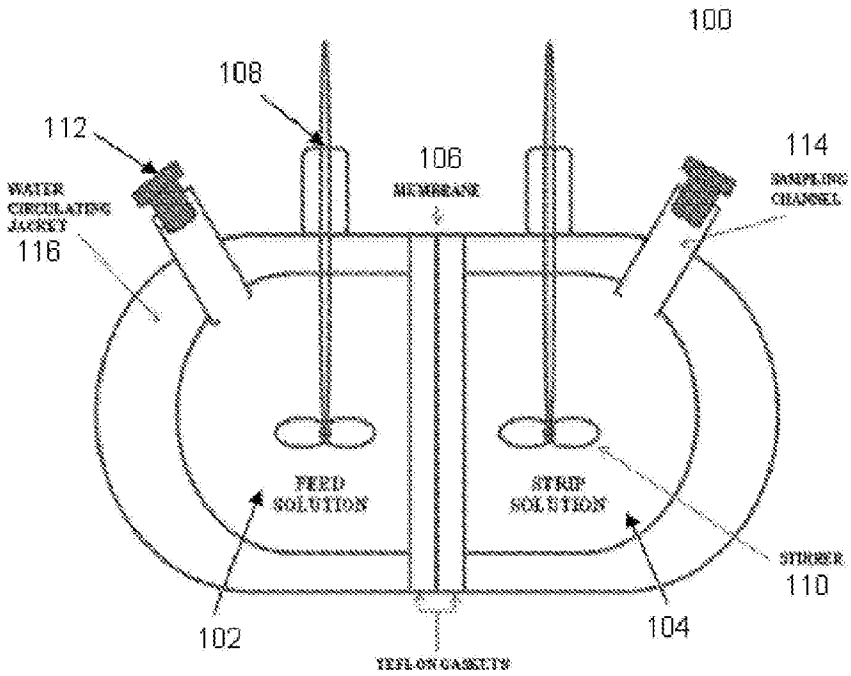
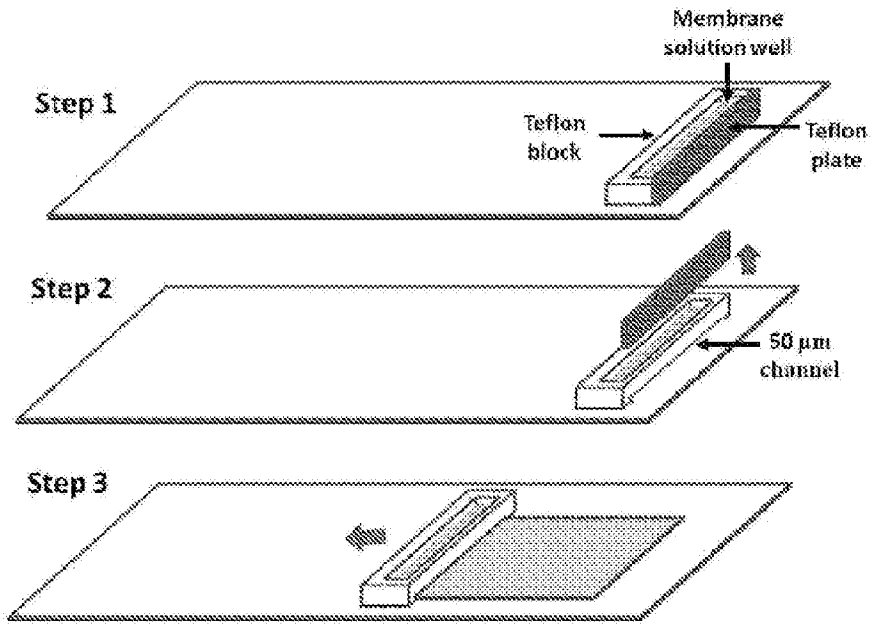
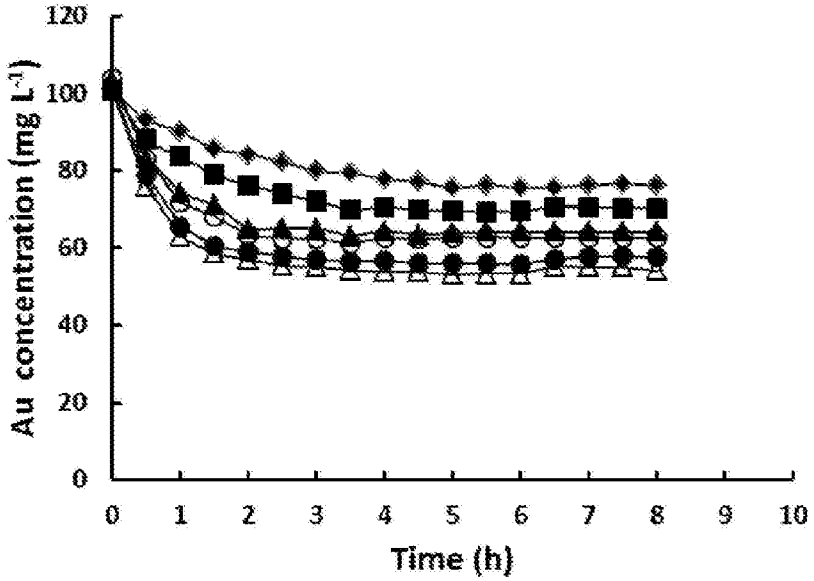

100
108
112
106
114
116
FEED SOLUTION
STRIP SOLUTION
STIRRER
110
102
104

Figure 2


Membrane solution well
Step 1
Teflon block
Teflon plate
Step 2
50 µm channel
Step 3

5

Figure 3


Au concentration (mg L-1)
120
100
80
60
40
20
0
0
1
2
3
4
5
6
7
8
9
10
Time (h)

5

Figure 4

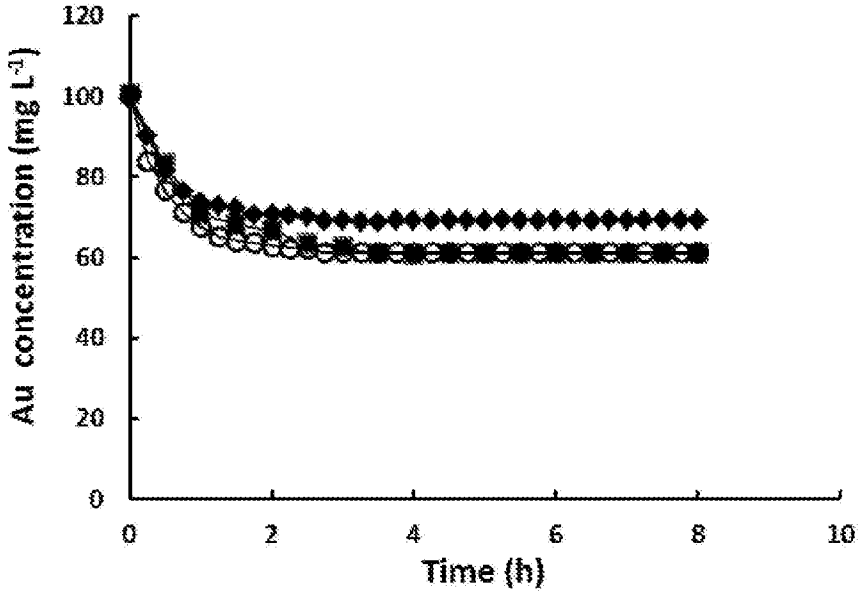


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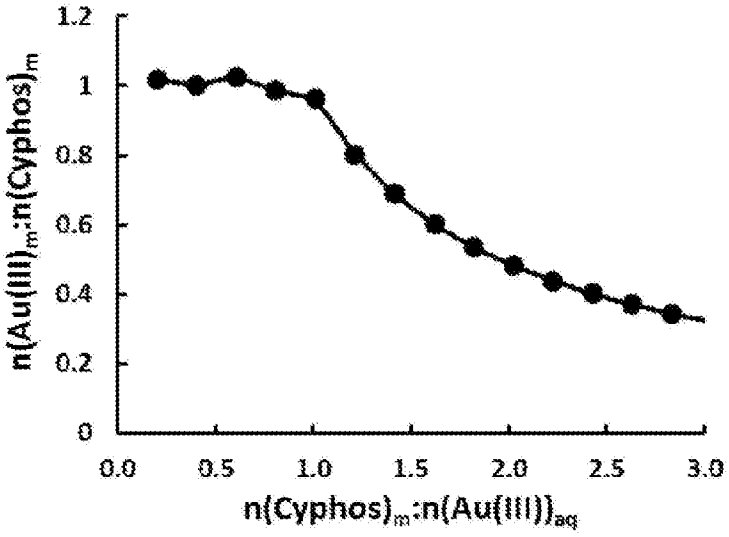
Figure 5


1.2
1
0.8
0.6
0.4
0.2
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
n(Au(III))m:n(Cyphos)m
n(Cyphos)m:n(Au(III))aq

5

Figure 6

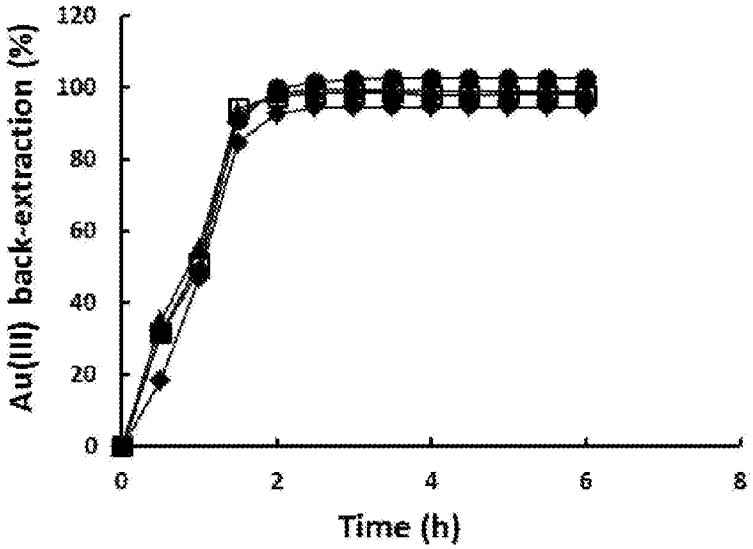


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Figure 7

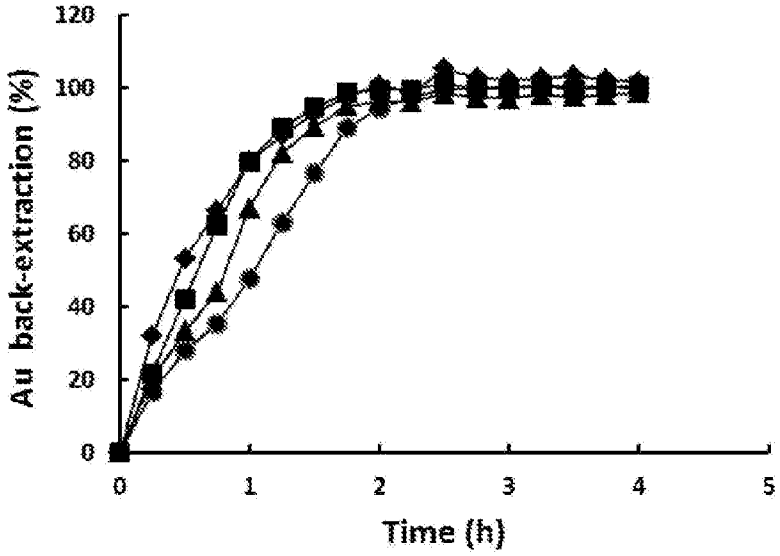

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Figure 8

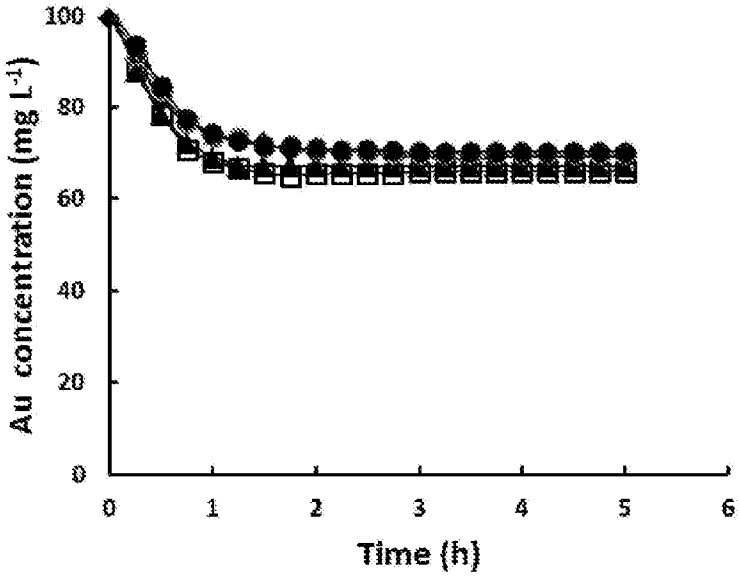

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Figure 9

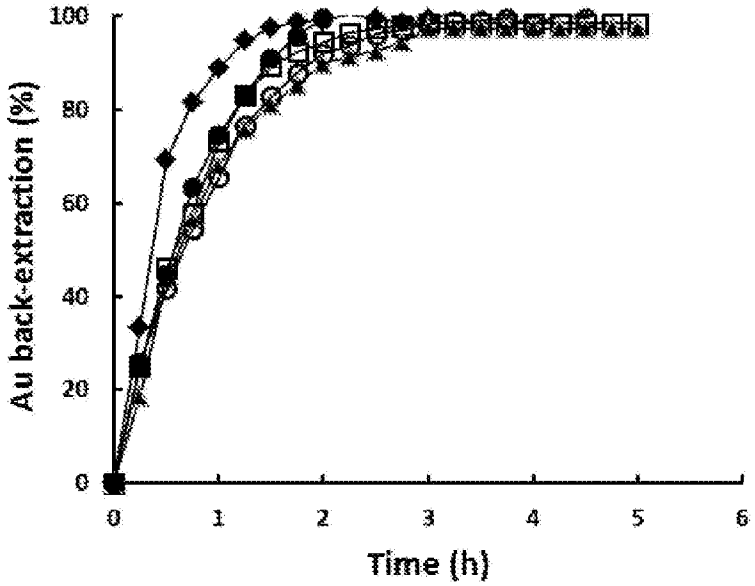

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Figure 10

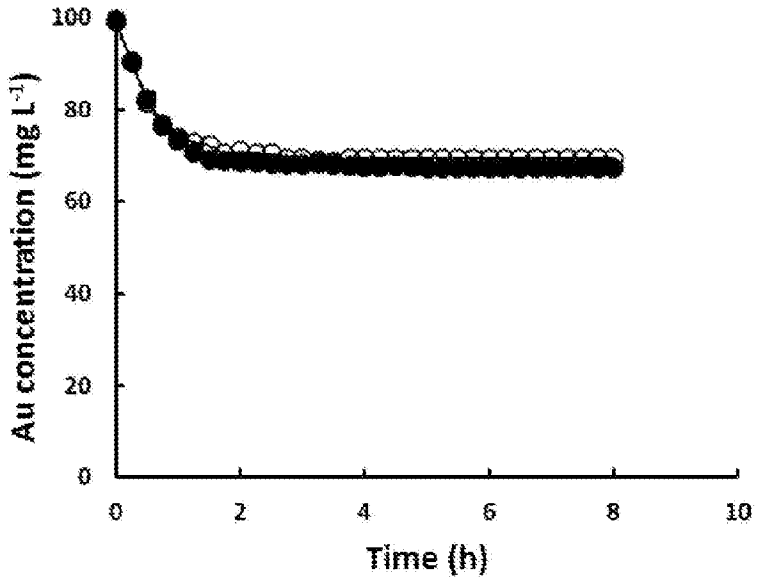

Figure 11

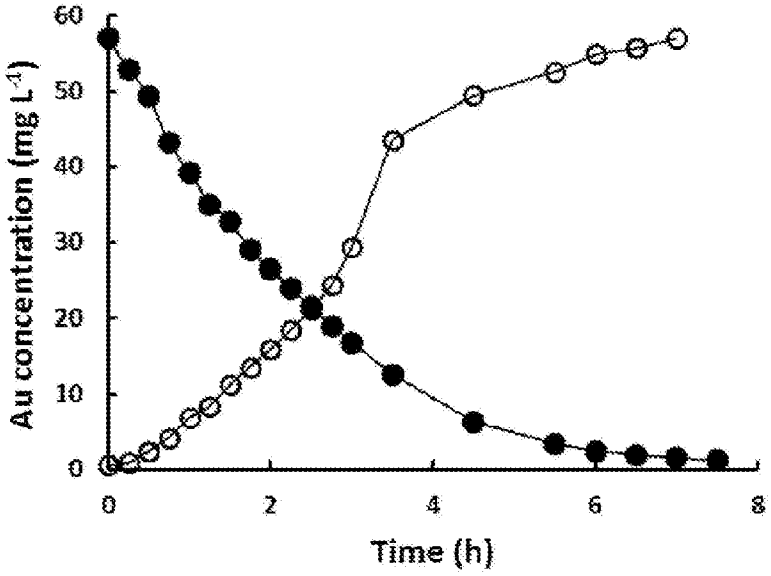

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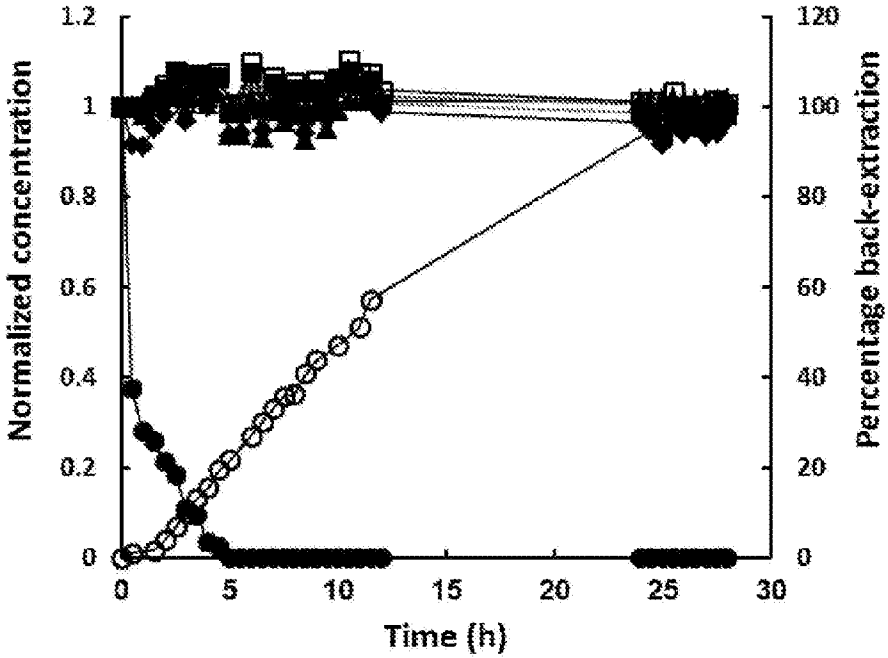
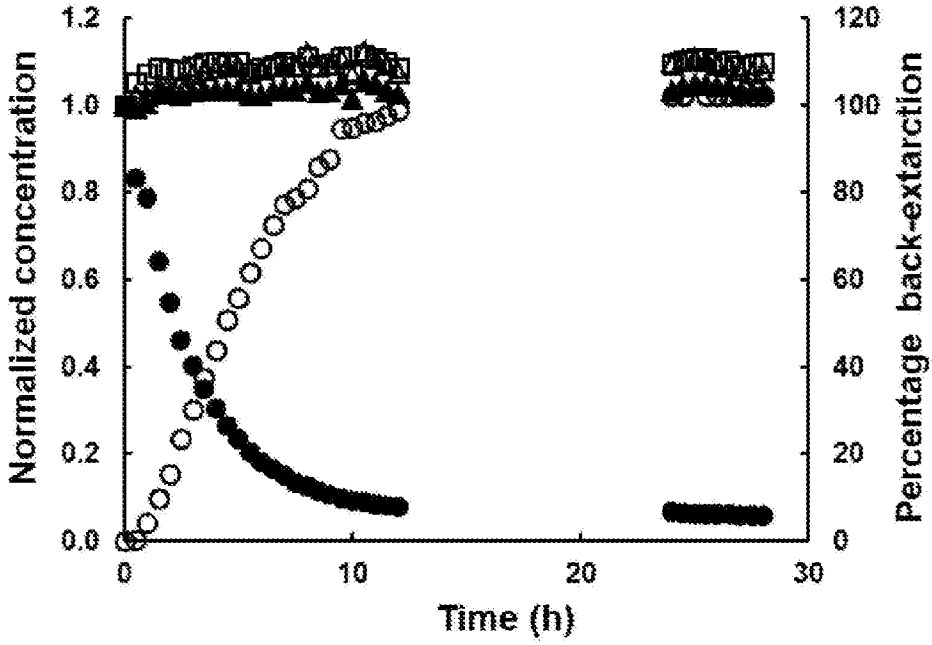
Figure 12


Normalized concentration
Percentage back-extraction
Time (h)
0
0.2
0.4
0.6
0.8
1
1.2
0
20
40
60
80
100
120
0
5
10
15
20
25
30

5

Figure 13


Normalized concentration
Percentage back-extarction
Time (h)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
20
40
60
80
100
120
0
10
20
30

5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2014/050033

A. CLASSIFICATION OF SUBJECT MATTER

C22B 3/42 (2006.01) C22B 11/00 (2006.01) C22B 7/00 (2006.01) C01G 7/00 (2006.01) B01J 47/12 (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

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

EPODOC and WPI:/IC/CN C22B11 or C22B3 or C22B7 or C01G7/00 or B01D61 or B01D63 or B01D71 or B01J47/12 and Keywords (gold, inclusion_membrane, ionic_liquid, extract) & like terms.

Cluster - $PATEN-English full text databases TXTAU1 TXTCA1 TXTEP1 TXTGB1 TXTSG1 TXTUS0 TXTUS1 TXTUS2 TXTUS3 TXTUS4 TXTUS5 TXTWO1 WPI EPODOC and Keywords (gold, inclusion_membrane, ionic_liquid, extract) & like terms.

CAPLUS and keywords (gold?, polymer()inclusion()membrane?, ionic()liquid?, extract?).
GoogleScholar search and keywords ("polymer inclusion membrane" "ionic liquid" gold acid)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [ ] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 June 2014	23 June 2014
Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	John Deuis AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262832146

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	**PCT/AU2014/050033**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	"Recent trends in extraction and transport of metal ions using polymer inclusion membranes (PIMs)"; M. Ines G.S. Almeida, Robert W. Cattrall, Spas D. Kolev; Journal of Membrane Science 415-416 (2012) 9-23. See sections: Abstract; 2.1 Basic carriers and Table 1.	1, 20
A	"Preparation of Poly(vinylidene fluoride-co-tetrafluoroethylene)-Based Polymer Inclusion Membranes Using Bifunctional Ionic Liquid Extractant for Cr(VI) Transport"; Lin Guo, Jianping Zhang, Dongli Zhang, Yinghui Liu, Yuefeng Deng and Ji Chen; Ind. Eng.Chem. Res. 2012, 51, 2714-2722. See sections: Title and Abstract.	1, 20
A	"The use of sonication to increase extraction rate in polymer inclusion membranes. An application to the extraction of gold(III)"; Ya Ya Nutchapurida Bonggotgetsakul, Muthupandian Ashokkumar, Robert W. Cattrall, Spas D. Kolev; Journal of Membrane Science 365 (2010) 242-247. See sections: Abstract.	1, 20