Title: SELECTIVE GOLD EXTRACTION FROM COPPER ANODE SLIME WITH AN ALCOHOL

Abstract: The invention relates to a method for recovering gold from an acid digest of a gold-containing copper anode slime. The acid digest is selectively extracted with an alcohol having low miscibility with water. Gold is then recovered from the resulting alcoholic extract.
Selective Gold Extraction From Copper Anode Slime With An Alcohol

Technical Field

The present invention relates to recovery of gold from copper anode slimes.

Background of the Invention

Anode slimes derived from the electrowinning of anode copper contain significant amounts of gold and silver. The processing of the slimes is complicated by the impurities present such as Te, Se, Pb, As and Bi. The methods adopted in commercial operations for recovering gold and silver from such feeds depend largely on the individual feed compositions, but generally involve leaching to remove copper and in some cases tellurium. Roasting and/or smelting are commonly used to control lead and selenium. Silver is then recovered by electrolysis and gold is recovered last by electrowinning.

Oxidative chlorination of decopperised anode slimes is an attractive processing alternative, in that it offers the opportunity of separating silver and gold early in the processing, leading to decreased gold lock-up time and potentially to a simpler totally hydrometallurgical flowsheet. The oxidative chloride leach rejects most of the silver to the residue and produces a solution from which gold can be recovered by solvent extraction. This approach has been used in both the Kennecott chloride process (Hoffmann, J.E., Sutliff, K.E., Wells, B.A. and George, B.D. in Proceedings of COPPER 95 International Conference, Ed. W.C. Cooper, J.E. Dutrizac, H. Hein, G. Ugarte, The Metallurgical Society of CIM, vol III, pp 42) and the Minataur™ process (Feather, A., Sole, K.C. and Bryson, L.J., The Journal of the South African Institute of Mining and Metallurgy, July/August 1997, pp 169; Feather, A., Sole, K.C. and Bryson, L. J., Randol Gold Forum’97, Monterey, California, USA, 1997). In the Kennecott process, chlorination is applied to the decopperised slimes, and gold is extracted from solution by dibutyl carbitol, a solvent which suffers from some serious drawbacks, one of which is its high solubility in the aqueous phase. The Minataur™ Process has been applied to the gold mud, but has not been tested in solutions with the higher levels of impurities generated by direct treatment of decopperised slimes. A typical hydrometallurgical approach uses oxidative chloride leaching of decopperised slimes, which separates silver and gold at an early stage of processing, and allows recovery of gold from the leach liquor by solvent extraction. A simplified flowsheet is shown in Figure 1. This type of hydrometallurgical approach to anode slimes processing, has been implemented in
various refineries around the world. It is claimed that these types of process have significant advantages over conventional processes.

As noted above, DBC has been used for extraction of gold from liquors derived by hydrochloric acid digestion of copper anode slimes. DBC has high selectivity for gold but suffers from the following drawbacks:

- The phase separation in extraction for DBC is very slow, requiring very long settling rates;
- DBC has a high solubility in the aqueous phase (0.3% or 3000 mg/L). DBC needs to be recovered from the raffinate by steam distillation;
- Filtration of crud from the solvent extraction DBC circuit is recommended;
- Scrubbing of the organic in a DBC circuit is carried out by batch, due to the very long phase disengagement times, and
- gold can only be stripped from the solvent by reduction. This introduces solids in the strip circuit, which may result in crud and requires a three phase separation step. Furthermore, the recommended operating temperature for the reduction is 75-80°C.

There is therefore some incentive to develop a more practical solvent extraction process for the extraction of gold from liquors, such as chloride liquors derived from leaching of decopperised anode slimes.

**Object of the Invention**

It is the object of the present invention to substantially overcome or at least ameliorate one or more of the above disadvantages.

**Summary of the Invention**

In a first aspect of the invention there is provided a method for recovering gold from an acid digest of a gold-containing copper anode slime, said method comprising the steps of:

a) selectively extracting the acid digest with an alcohol to form an alcoholic extract comprising the gold, said alcohol having low solubility in water; and

b) recovering the gold from the alcoholic extract;

wherein the gold in the acid digest is in a form that is extractable into said alcohol.

The acid digest may be an aqueous acid digest. The gold in the acid digest may be present as a gold species which is dissolved in said acid digest. This gold species may be extractable into the alcohol. The gold species may be capable of reacting with the alcohol to form a second gold species which is extractable into the alcohol.
The following options may be used in conjunction with the first aspect, either individually or in any appropriate combination.

The alcohol may have a solubility in water of less than about 0.2% w/w, v/v or w/v at 20°C. The alcohol may be a primary alcohol. It may be a branched chain alcohol. It may be for example 2-ethyl-1-hexanol, 8-methyl-1-nonanol or mixtures thereof. It may be capable of selectively extracting gold from an acid digest of anode slime.

The method may also comprise the step of digesting a gold-containing copper anode slime using acid to provide the acid digest. The step of digesting may comprise combining the anode slime with a concentrated mineral acid, e.g. a concentrated hydrohalic acid. The acid may be combined with the anode slime in a ratio sufficient to achieve an acid concentration of about 3N to about 5N (e.g. about 4N) in the acid digest. The method may comprise the step of digesting a gold-containing copper anode slime using acid and an oxidant to provide the acid digest. The step of digesting may comprise combining the anode slime with a concentrated mineral acid, e.g. a concentrated hydrohalic acid, and an oxidant, e.g. hydrogen peroxide. The acid may be combined with the anode slime in a ratio sufficient to achieve an acid concentration of about 3N to about 5N (e.g. about 4N) in the acid digest. The oxidant may be added to the anode slime in sufficient quantity to ensure dissolution of the gold in said slime, or to ensure dissolution of at least about 90% of the gold in the anode slime, under the conditions used.

The gold-containing copper anode slime may be a decopperised anode slime. Accordingly the acid digest may be an acid digest of a decopperised anode slime.

The acid digest may comprise a radioactive element (e.g. a radioactive metal) and said radioactive element may not be extracted into the alcohol. The radioactive element may for example be polonium. It may be polonium-210 or lead-210 or bismuth-210. There may be more than one radioactive element. None of the radioactive elements may be extracted into the alcohol. The acidity of the acid digest may be such that the gold is extracted into the alcohol and the radioactive element(s) is not extracted into the alcohol. Less than about 10% of the amount of the radioactive element(s) present in the acid digest may be extracted into the alcohol. The acidity of the acid digest may be such that at least about 90% of the gold present in the digest is extracted into the alcohol and less than about 10% of the amount of the radioactive element(s) present in the acid digest may be extracted into the alcohol.
The proportion of gold to total metals (or cations) in the acid digest prior to step a) may be about 4% or less by weight or by moles. This proportion may be taken to refer to ratios of metal atoms (or cations) in the acid digest.

Step a) of the method may comprise continuous countercurrent extraction. The method may additionally comprise the step of scrubbing the alcoholic extract. The scrubbing may be for the purpose of removing impurities from said extract. This step may be conducted between steps a) and b). The scrubbing may comprise scrubbing with a dilute mineral acid. In this context, impurities may be regarded as species comprising one or more of non-gold metals, metalloids and semimetals.

Step b) may comprise extracting the alcoholic extract with an aqueous extractant to provide a gold-containing aqueous extract. The aqueous extractant may be neutral or acidic. Prior to said extracting, the aqueous extractant may have a pH of greater than about 1. Prior to said extracting, it may have a pH of between about 5 and about 8.

The gold in the acid digest may be present as Au(III). The gold in the acid digest may be present as an Au(III) complex. It may be present as AuCl₄⁻ (e.g. HAuCl₄).

The method may comprise the step of reducing the gold in the aqueous extract to Au(0). The method may comprise the step of reducing the gold in the aqueous extract to Au(0) and separating gold metal (Au(0)) from the aqueous extract. The method may comprise further refining the Au(0).

The method may also comprise the step of recovering the alcohol from the alcoholic extract. The recovered alcohol may be reused in step a). It may be reused as an extractant in step a).

In an embodiment there is provided a method for recovering gold comprising the steps of:

- digesting a copper anode slime using acid and an oxidant to provide an acid digest;
- selectively extracting the acid digest with an alcohol to form an alcoholic extract comprising gold, said alcohol having low miscibility with water; and
- recovering the gold from the alcoholic extract.

In another embodiment there is provided a method for recovering gold comprising the steps of:

- digesting copper anode slime using a concentrated mineral acid and an oxidant to provide an acid digest;
• selectively extracting the acid digest with an alcohol to form an alcoholic extract comprising gold, said alcohol having low miscibility with water; and
• extracting the gold from the alcoholic extract into an aqueous extractant having pH greater than about 1.

In another embodiment there is provided a method for recovering gold comprising the steps of:
• digesting copper anode slime using concentrated hydrochloric acid and hydrogen peroxide to provide an acid digest having a hydrochloric acid concentration of about 3N to about 5N;
• selectively extracting the acid digest with an alcohol to form an alcoholic extract comprising gold, said alcohol being selected from the group consisting of 2-ethyl-1-hexanol, 8-methyl-1-nonanol and mixtures thereof; and
• extracting the gold from the alcoholic extract into an aqueous extractant having pH greater than about 1.

In another embodiment there is provided a method for recovering gold comprising the steps of:
• digesting copper anode slime using concentrated hydrochloric acid and hydrogen peroxide to provide an acid digest having a hydrochloric acid concentration of about 3N to about 5N;
• selectively extracting the acid digest with an alcohol to form an alcoholic extract comprising gold, said alcohol being selected from the group consisting of 2-ethyl-1-hexanol, 8-methyl-1-nonanol and mixtures thereof;
• scrubbing the alcoholic extract with dilute hydrochloric acid; and
• extracting the gold from the alcoholic extract into an aqueous extractant having pH greater than about 1.

In another embodiment there is provided a method for recovering gold comprising the steps of:
• digesting copper anode slime at a temperature of greater than about 85°C using concentrated hydrochloric acid and hydrogen peroxide to provide an acid digest having a hydrochloric acid concentration of about 3N to about 5N;
• selectively extracting the acid digest with an alcohol to form an alcoholic extract comprising gold, said alcohol being selected from the group consisting of 2-ethyl-1-hexanol, 8-methyl-1-nonanol and mixtures thereof;
• scrubbing the alcoholic extract with dilute hydrochloric acid;
- extracting the gold from the alcoholic extract into an aqueous extractant having pH greater than about 1; and
- reducing the gold in the aqueous extractant to gold(0).

The invention also provides gold in the form of Au(0) (gold metal) recovered by the method of the first aspect. The gold metal may have a purity of greater than about 99.9% by weight.

In a second aspect of the invention there is provided the use of a primary alcohol for extracting gold species from an acid digest of copper anode slime. The primary alcohol may be a branched chain alcohol. The branched chain alcohol may comprise 2-ethyl-1-hexanol, 8-methyl-1-nonanol or a mixture thereof.

**Brief Description of the Drawings**

A preferred embodiment of the present invention will now be described, by way of an example only, with reference to the accompanying drawings wherein:

Figure 1 is a flow diagram for a hydrometallurgical method for recovery of gold from anode slimes;

Figure 2 is a flow diagram for a gold solvent extraction process for anode slimes digest; and

Figure 3 is a flow diagram for a wet process for recovery of various elements from anode slimes.

**Detailed Description of the Preferred Embodiments**

The present invention relates to the gold solvent extraction step of a gold recovery method. An example of a suitable overall process flow diagram is shown in Fig. 1. One use of the present method is to achieve effective control of radioactivity. The present specification describes a solvent extraction process to recover gold from copper anode slimes liquor arising from a wet chlorination leach. The steps preceding and proceeding solvent extraction, including decopperising, silver recovery, selenium recovery and dissolution of copper anode slimes in hydrochloric acid in the presence of an appropriate oxidant, are conventional technology and are well known in the art. These unit processes may be used in conjunction with the present gold solvent extraction method in a variety of ways.

The filtrate liquor from the oxidative chloride leach test may be used as the feed to solvent extraction method described herein. A flow diagram of a method according to the present invention is shown schematically in Fig. 2. A gold species is extracted from the chloride containing acid digest solution to a solvent phase comprising an active reagent
that selectively targets gold. The solvent may therefore be regarded as an active reagent or an active solvent or a selective solvent. The alcohol may react (e.g. by solvation) with a species that comprises the gold to form a gold complex or species. An example of such a complex is HAuCl₄·alcohol. The alcohol may solvate a species (which may be a complex) comprising the gold. The solvent may be selective for gold and may reject impurities commonly present in such liquors under the conditions (acidity, alcohol) used in the extraction. Importantly, the solvent may reject radioactive impurities such as polonium-210, or may reject the majority of the radioactive impurities such as polonium-210 present. The solvent may also be at least partially selective for gold species in the acid digest over selenium, tellurium, copper, zinc, lead, bismuth, antimony, tin, arsenic, nickel, palladium and platinum species and others therein. Scrubbing of the solvent phase with a separate aqueous solution may be required to further control/remove impurities from the solvent. The solvent loaded with gold is then moved to the strip circuit where gold is re-extracted into an aqueous solution. This loaded strip solution can be treated by reductive precipitation in a separate step. The stripped solvent may be recycled back to the extraction circuit. The inventor has shown that such a process can upgrade a solution containing gold to impurities ratio < 2% to >99.9% gold product which may be in the form of a gold species or gold complex. Primarily two solvents/reagents have been used for this purpose. They are 8-methyl-1-nonanol, commonly known as isodecanol, and 2-ethyl-1-hexanol, also known as isoctanol. These solvents include the following advantages:

- low solubility in the aqueous phase
- good phase separation characteristics
- capable of being stripped into an aqueous solution, and therefore the gold precipitation/recovery step can be separated from the solvent extraction step
- capable of being stripped into an aqueous solution at room temperature
- capable of being stripped with water
- selective for gold over all the major impurities present in the liquor, including Po-210, Bi-210 and Pb-210.

Other solvents displaying the above characteristics may be used in the present invention.

The inventor has, surprisingly, found that certain alcohols are able to selectively extract gold (gold species) from an acid digest of a copper anode slime and, in particular, may reject radionuclides such as Po-210. A suitable alcohol should have relatively low
solubility/miscibility with the acid digest. It may be characterised by its relatively low solubility or miscibility with water, or with the acid digest. Suitably, its solubility in water (or in the acid digest) may be less than about 0.2% w/w, v/v or w/v at 20°C, or less than about 0.15, 0.1, 0.09 or 0.08%. Its solubility in water may be for example about 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.15 or 0.2%. The alcohol may have at least about 7 carbon atoms, or at least about 8, 9 or 10 carbon atoms, or may have about 7 to about 14 carbon atoms, or about 7 to 12, 7 to 10, 8 to 12, 10 to 12, 10 to 14 or 8 to 10 carbon atoms, e.g. about 7, 8, 9, 10, 11, 12, 13 or 14 carbon atoms. It may be a straight chain alcohol. It may be a branched chain alcohol. It may have an alicyclic group. It may comprise one or more double bonds. It may comprise one or more triple bonds. The alcohol may be a liquid at 20°C. A mixture of alcohols may be used. The mixture of alcohols may be a liquid at 20°C. Each of the alcohols in said mixture may, independently, be as described above. Suitable alcohols include 2-ethyl-1-hexanol and 8-methyl-1-nonanol. Tridecyl alcohol or mixtures including tridecyl alcohol, may also be used. These alcohols have the advantage of being relatively inexpensive and relatively freely available.

The water solubility of 2-ethyl-1-hexanol has been reported as 0.07% at 20°C. This compares favourably (i.e. is substantially lower) with dibutyl carbitol, which has been reported as having solubility 0.3% at 20°C.

The extractant (i.e. the liquid used for selectively extracting the acid digest to form the alcoholic extract) used in step a) of the first aspect of the invention may comprise an alcohol or mixture of alcohols, as described above. It may consist essentially of said alcohol or mixture of alcohols. It may consist of said alcohol or mixture of alcohols. The extractant may comprise a diluent. The alcohol or mixture of alcohols may be soluble in, or miscible with, the diluent. The extractant may therefore consist, or consist essentially, of a mixture of the alcohol (or mixture of alcohols) and the diluent. The mixture of the alcohol (or mixture of alcohols) and the diluent may be a liquid at 20°C. The diluent may be an inert diluent. The diluent may be incapable of selectively extracting gold from the acid digest in the absence of an active or selective extractant such as the alcohols described above. The diluent may be a hydrocarbon diluent. It may be an aromatic hydrocarbon diluent. It may be an aromatic hydrocarbon diluent. It may be a mixture of aromatic and aromatic hydrocarbons. It may be a kerosene based diluent. The kerosene based diluent may have varying aromatic, paraffin and naphthenic content. The diluent may be (or comprise) some other type of inert diluent. The diluent may represent between
about 10 and about 95% of the extractant, or about 10 to 50, 10 to 20, 20 to 95, 50 to 95, 70 to 95, 90 to 95, 20 to 80, 30 to 70, 40 to 60, 20 to 50, 25 to 95 or 50 to 80% by weight or volume, e.g. about 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 80 or 95%.

The volume ratio of extractant to acid digest in step a) may be between about 0.1 and about 10, or may be about 0.1 to 5, 0.1 to 2, 0.1 to 1, 0.1 to 0.5, 0.1 to 0.2, 0.3 to 0.5, 0.5 to 10, 1 to 10, 2 to 10, 5 to 10, 0.5 to 5, 0.5 to 2, 0.5 to 1, 1 to 5 or 1 to 2, e.g. about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 6, 7, 8, 9 or 10, or may be some other suitable ratio. Commonly the gold will be concentrated in the solvent phase. Thus an extractant to acid digest ratio of less than about 1, e.g. about 0.1 to about 1, may be preferred. The extractant may be used in sufficient quantity that the amount of the alcohol therein is sufficient to complex substantially all (e.g. at least about 80, 85, 90, 95 or 99%) of the gold present in the acid digest. The alcohol in the extractant may be present in a molar ratio relative to the gold in the acid digest of at least about 1, or at least about 1.1, 1.2, 1.3, 1.4, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 10, 20, 50 or 100. The method described herein may be capable of recovering at least about 80% of the gold present in the acid digest, or at least about 85, 90, 95, 96, 97, 98 or 99% thereof, or about 80 to about 99% thereof, or about 80 to 95, 80 to 90, 85 to 99, 90 to 99, 90 to 95 or 95 to 99% thereof. It may be capable of recovering about 80% of the gold present in the acid digest, or about 85, 90, 95, 96, 97, 98 or 99% thereof. It may for example be capable of recovering at least about 90% of the gold in the acid digest in a form that is at least about 99% pure on a weight or mole basis. The reagent concentration and/or solvent to aqueous ratio may be adjusted so as to extract the desired proportion (as described above) of the gold.

Thus the method of the present invention comprises a first step of selectively extracting an acid digest of copper anode slime with an extractant as described above. The gold is then recovered from the resulting alcoholic extract. The recovered gold may be metallic gold or may be a gold compound or complex. The acid digest may be an aqueous acid digest.

The acid digest may be obtained by digesting a gold-containing copper anode slime using acid. The digesting may use a concentrated mineral acid. A preferred acid is hydrochloric acid. The concentration of the acid may be at least about 5N, or at least about 6, 7, 8, 9 or 10N. It may be for example 5, 6, 7, 8, 9, 10, 11 or 12N. The acid may be combined with the liquor in a ratio sufficient to achieve a final acid concentration of
between about 3 and 6N, or about 3 to 5N, 3 to 4N or 4 to 5N, e.g. about 3, 3.5, 4, 4.5, 5, 5.5 or 6N. The digesting may be regarded as extracting or leaching the gold from the copper anode slime. The acid used for this may be regarded as a leach liquid or a digesting mixture. The gold-containing copper anode slime may comprise gold in an oxidation state less than 3, e.g. in an oxidation state of 0 or 1. It may comprise more than one gold species. It may comprise one or more Au(0) species and one or more Au(I) species. It may comprise gold in a form that is oxidisable to Au(III). It may optionally comprise gold in an oxidation state of 3 (i.e. Au(III)), either in addition to or instead of gold in an oxidation state less than 3.

The acid used for digesting the gold-containing anode slime may comprise an oxidant. Suitable oxidants include hydrogen peroxide and chlorine. The oxidant may be added to the acid (or to the anode slime) as a concentrated solution, e.g. about 5 to about 27M, or about 5 to 20, 5 to 10, 10 to 20, 20 to 27 or 10 to 15, e.g. about 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26 or 27M. The oxidant may be a sufficiently strong oxidant to allow oxidation of any gold present in the slime in an oxidation state less than +3 to Au(III). It may be provided in a molar excess (e.g. a 10%, 20%, 50% or 100% excess) over that required for oxidation of any gold present in an oxidation state less than +3 to Au(III). The amount of oxidant used may need to accommodate the oxidation of other elements present in the slime as well. The step of digesting may comprise heating the anode slime with the acid, optionally containing the oxidant. The heating may be to a suitable temperature and for a suitable time for the gold in the anode slime to dissolve in the acid. At least about 90% of the gold may dissolve in the acid, or at least about 91, 92, 93, 94, 95, 96, 97, 98 or 99% of the gold may dissolve in the acid. The temperature may be a reflux temperature of the acid. It may be greater than about 70°C, or greater than about 75, 80, 85, 90 or 95°C. It may be between about 70 and about 110°C, or about 70 to 100, 70 to 90, 80 to 110, 90 to 110 or 90 to 100°C, e.g. about 70, 75, 80, 85, 90, 95, 100, 105 or 110°C. A suitable temperature is about 96°C. A suitable time for digestion is at least about 1 hour, or at least about 2, 3 or 4 hours, or about 1 to 10, 1 to 5, 1 to 2, 2 to 10, 4 to 10, 3 to 8 or 3 to 5 hours, e.g. about 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 hours.

It will be readily understood that if both acid and oxidant are used in digesting the copper anode slime, these may be added separately to the slime, or may be combined and then added to the slime.
The resulting acid digest may have a gold concentration of at least about 1g/L, or at least about 2, 3, 4 or 5g/L, or between about 1 and about 40g/L, or about 1 to 20, 1 to 10, 1 to 5, 5 to 40, 10 to 40, 20 to 40, 5 to 20 or 5 to 10g/L, e.g. about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35 or 40g/L.

Prior to extraction with the alcohol, the acid digest may be diluted to achieve the desired acid concentration. As noted elsewhere, the desired acid concentration may be about 3N to about 6N.

Thus the step of digesting a gold-containing copper anode slime using acid to provide the acid digest may comprise digesting the anode slime in a digesting mixture, said digesting mixture comprising a concentrated acid (e.g. hydrochloric acid) and an oxidant (e.g. hydrogen peroxide). It may comprise heating the anode slime in the digesting mixture. It may comprise heating the anode slime in the digesting mixture at a temperature and for a time sufficient to dissolve at least about 90% of the gold in the anode slime. It may additionally comprise diluting the resulting acid digest to an acid concentration of between about 3N and about 6N (or about 3 to 5N, 3 to 4N, 4 to 6N, 5 to 6N or 4 to 5N, e.g. about 3, 4, 5 or 6N).

The present method is suitable for selectively extracting gold from a copper anode slime or a decopperised anode slime, however it may also be used for extracting gold from other liquors or aqueous solutions having a low proportion of gold to total metals. In particular, the method may be capable of separating gold from acid digests of anode slimes that contain radioactivity, thereby separating the gold from the radioactivity. The radioactivity may be present in the acid digest in the form of one or more radioactive isotopes, e.g. polonium-210, lead-210, bismuth-210 etc. The method may extract less than about 10% of the radioactive isotopes (or of each radioactive isotope independently) present in the acid digest, or less than about 5, 2, 1, 0.5, 0.2 or 0.1% thereof. The method is particularly suitable for selectively extracting gold from an acid digest in which the gold is a minor proportion of the metals, metalloids and/or semimetsals in the acid digest, i.e. less than about 50%, or less than about 40, 40, 20, 10, 5 or 2% by weight or moles. Gold may represent about 0.01 to about 50% or about 0.01 to about 20% of the metals, metalloids and/or semimetsals, or about 0.01 to 10, 0.01 to 5, 0.01 to 2, 0.01 to 1, 0.1 to 20, 0.5 to 20, 1 to 20, 5 to 20, 10 to 20, 1 to 20, 5 to 20, 10 to 20, 1 to 10, 1 to 5, 1 to 2, 2 to 5 or 5 to 10%. It may represent about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 6, 7, 8, 9, 10, 15, 20, 30, 40 or 50% of the metals, metalloids and/or semimetsals in the acid digest. Other elements that may be present in the acid digest
include selenium, tellurium, silver, copper, zinc, lead, bismuth, antimony, tin, arsenic, nickel, palladium and platinum. These may be present in the acid digest in forms that are not extractable, or extractable to a very limited degree, into the alcohol. A typical copper refinery slime analysis is shown below.

TABLE 1: TYPICAL COPPER REFINERY SLIMES COMPOSITIONAL RANGES {ACCORDING TO HOFFMANN, J. E., THE WORLD'S MOST COMPLEX METALLURGY - REVISITED. PROCEEDINGS OF EUROPEAN METALLURGICAL CONFERENCE EMC 2007, VOL. 2, PP. 555-570}

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (%)</th>
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<tbody>
<tr>
<td></td>
<td>Low</td>
</tr>
<tr>
<td>Sb</td>
<td>0.50</td>
</tr>
<tr>
<td>As</td>
<td>0.50</td>
</tr>
<tr>
<td>Bi</td>
<td>0.10</td>
</tr>
<tr>
<td>Cu</td>
<td>6</td>
</tr>
<tr>
<td>Au</td>
<td>0.10</td>
</tr>
<tr>
<td>Ag</td>
<td>0.02</td>
</tr>
<tr>
<td>Pb</td>
<td>5</td>
</tr>
<tr>
<td>Ni</td>
<td>0.10</td>
</tr>
<tr>
<td>Pd</td>
<td>0.005</td>
</tr>
<tr>
<td>Pt</td>
<td>0.0005</td>
</tr>
<tr>
<td>Se</td>
<td>4</td>
</tr>
<tr>
<td>Te</td>
<td>0.50</td>
</tr>
</tbody>
</table>

There is a great variety of chemical forms in which these and other elements exist in the slimes obtained in the copper electrolysis.

The fraction of gold and silver released during copper electrorefining process reports to the residue as very small metallic particles. Gold, having a strong affinity for selenium, nucleates on the Ag-Se selenide inclusions. Another part of gold is dissolved in the sulfate solution during the refining process and, along with silver, later precipitates as a minor component of the oxidate phase. A large fraction of gold appears in the discrete Ag-Au-Cu selenide phase (for example, in form of intermetallic AgAuSe, Ag_{2-x}Au_{x}Se).

Silver from the copper anode is soluble in the acidic electrolyte solution to some extent. Part of this dissolved silver reacts with copper selenide, Cu_{2}Se, and forms individual and intermetallic Ag-Cu and Ag-Au selenide species (for example, silver selenide, Ag_{2}Se and silver copper(I) selenide, AgCuSe).
Like Se, tellurium has preferential binding with Au and Ag and is primarily found in Cu-Ag selenide-telluride phase as well as in the forms of other individual and intermetallic tellurides, such as, for example, Ag₂Te, Au₂Te.

In addition, arsenic, antimony and bismuth are dissolved during the electrolytic process and a fraction of metals precipitates as Pb-Sb-As-Bi oxides. Lead is also detected in the form of lead sulfate, PbSO₄.

Precipitated copper exists in the numerous forms, mostly as intermetallic compounds, chalcogenides: for example, copper silver selenide, AgCuSe, copper selenide(s), Cu₂-ₙSeₙ (where n≤1), copper telluride, Cu₂Te and copper sulfide, Cu₂S. Copper also reports to the oxide phase and is found in the form of sulfate or arsenate.

The extraction of step a) of the method may comprise batchwise extraction, e.g. repeated batchwise extraction. It may comprise continuous extraction, e.g. continuous countercurrent extraction. There may be one countercurrent extractor. There may be more than one countercurrent extractor, e.g. 2, 3, 4 or 5 or more than 5 countercurrent extractors. In the case of more than one countercurrent extractor, one mode of operation may involve fresh extractant used in the final extractor, then passing to the penultimate extractor, and so on to the first extractor, so that the extractant passes through the series of extractors in the opposite direction to the acid digest.

The extractant used in the present invention is selective for gold species in the acid digest. The gold may be present in the acid digest as a gold complex prior to the extracting. The gold complex may be a gold(III) complex. It may be a gold halide complex. It may be present as AuX₄⁻, where is a halogen, e.g. chlorine, bromine or iodine (or a mixture of two or more of these). It may be present as AuCl₄⁻. The extractant may be selective for the gold complex. It may be sufficiently selective that the gold is present in the alcoholic extract at a percentage of total metals, metalloids and semimetals in the extract of at least about 70% on a weight or molar basis, or at least about 75, 80, 85, 90 or 95%, e.g. about 75, 80, 80, 85, 90, 91, 92, 93, 94, 95, 96, 97, 98 or 99%.

It will be understood however that higher purity than is provided by the extraction step may in some cases be required. In this case the method may comprise the step of scrubbing the extract with a scrubbing agent in order to remove impurities from said extract. A suitable scrubbing agent is a dilute mineral acid. The dilute mineral acid may comprise the same mineral acid as used for digesting the anode slime, or may comprise a different mineral acid. It may comprise a mixture of mineral acids. It may for example be dilute hydrochloric acid. The dilute mineral acid may be about 0.01 to 4N mineral acid, or
about 0.01 to 3, 0.01 to 1, 1 to 4, 2, to 4, 1 to 3, 0.5 to 2, 0.05 to 1, 0.1 to 1, 0.5 to 1, 0.01 to 0.5, 0.01 to 0.1, 0.01 to 0.05, 0.05 to 0.5 or 0.05 to 0.2, e.g. about 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.5, 2, 2.5, 3, 3.5 or 4N. The scrubbing may comprise extracting the alcoholic extract with the scrubbing agent. This may be conducted in a continuous countercurrent fashion or may be conducted batchwise. The scrubbing may raise the percentage of gold in the alcoholic extract as a percentage of total metals, metalloids and semimetals to at least about 90%, or at least about 95 or 99%, e.g. about 90, 91, 92, 93, 94, 95, 96, 97, 98 or 99%. The scrubbing agent may be at least partially selective for metals other than gold.

The gold may be obtained from the alcoholic extract, optionally from the scrubbed alcoholic extract, by extraction with an aqueous extractant. The aqueous extractant may have a pH greater than about 1. It may be at approximately neutral pH. The pH of the aqueous extractant may be greater than about 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5 or 7. It may be about 1 to 8, 1 to 7, 1 to 5, 1 to 3, 1 to 2, 2 to 8, 4 to 8, 6 to 8, 7 to 8, 2 to 3, 3 to 4, 4 to 5, 5 to 7 or 6 to 7, e.g. about 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5 or 8. The aqueous extractant may be a dilute acid, e.g. dilute hydrochloric acid. The dilute acid may be between about 0.01 and about 0.1N, or about 0.01 to 0.5, 0.5 to 0.1, 0.02 to 0.08, 0.03 to 0.07 or 0.04 to 0.06, e.g. about 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09 or 0.1N. The aqueous extractant may be water. The water may be at least about 99% pure, or at least about 99.5 or 99.9% pure.

Any or all of the above described extraction steps may, independently, be conducted at room temperature or at some other convenient temperature. The temperature may be for example about 10 to about 30°C, or about 10 to 20, 20 to 30 or 15 to 25°C, e.g. about 10, 15, 20, 25 or 30°C, or may in some circumstances be conducted at some other temperature, e.g. 35, 40, 45, 50, 55 or 60°C.

As an alternative to obtaining the gold from the alcoholic extract by extraction, the gold may be obtained by direct reduction from the alcoholic extract. This may for example be achieved by treating the gold-containing alcoholic extract with a reducing agent such as oxalic acid.

The method may comprise the step of reducing the gold in the aqueous extract to Au(0). The Au(0) may be in the form of metallic gold. Such reductions are well known in the art. The reduction may comprise reacting the gold in the aqueous extract with a reducing agent. Suitable reducing agents include sulfur dioxide, sulfites, oxalates and
oxalic acid. The method may comprise further refining the Au(0). Again, such methods are well known in the art and include for example the Miller process (in which chlorine gas is passed through the gold which is in a molten state) and electorefining. The step of reducing the gold to Au(0) may provide additional purification (i.e. removal of impurities such as non-gold metals, metalloids and/or semimetals). This may raise the purity of the gold to greater than about 99% on a weight or molar basis, or at least about 99.1, 99.2, 99.3, 99.4, 99.5, 99.6, 99.7, 99.8 or 99.9%, e.g. about 99, 99.1, 99.2, 99.3, 99.4, 99.5, 99.6, 99.7, 99.8, 99.9, 99.91, 99.92, 99.93, 99.94, 99.95, 99.96, 99.97, 99.98, 99.99, 99.995 or 99.999%.

The gold species in the aqueous extract may be further purified prior to reduction and (optionally) further refining. This may for example comprise acidification of the aqueous extract (as described above for the anode slime) and extraction of the gold into an organic extractant. The organic extractant should be one that is selective for gold. A suitable organic extractant for this purpose is the alcohol used as an extractant for the original acidic liquor. The resultant organic extract can then be reextracted into an aqueous extractant (optionally the same as described earlier for extracting the alcoholic extract of the acid digest), and gold recovered from the resultant aqueous gold solution.

The method described herein may provide a shorter lock-up period for the gold than for conventional methods. Lock-up period is defined by the time it takes for the gold-containing feed introduced into the method to come out as the product. A continuous extraction method, such as described herein, in which the gold is dissolved early in the method and then is continuously fed into an extraction circuit has a much lower lock-up time for gold than other methods. Lock-up times for gold in the present method may be between about 1 and about 10 days, but may be more or less than this range. The gold lock-up time may be about 1 to 7, 1 to 5, 1 to 3, 3 to 10, 5 to 10 or 5 to 8 days, e.g. about 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 days.


A suitable overall process for recovering gold is shown in Fig. 3. The method of the present invention primarily relates to the right hand portion of Fig. 3. Advantages of recovery processes using oxidative chlorination of decopperised slime, such as that described in Fig. 3, over conventional recovery processes include:
simple, compact and efficient;
reduction in labour cost;
generally less expensive and more productive as compared to the conventional refiner method;
recover metals with a high yield;
achieve better separations of the elements extracted from the anode slimes and, hence,

✓ produce metals with significantly reduced level of the impurities;
✓ avoid the undesirable circulation of the residues from the process;

avoid high temperature processes (e.g. smelting) resulting in the emission of toxic substances (for example, selenium and lead) into atmosphere and, hence

✓ avoid expensive recycle of secondary slags and reverts,
✓ provide considerably enhanced occupational safety and working conditions,
✓ better for the environment;

considerably reduced gold and silver (lock-up) period;
considerably reduced in-process inventory.

Examples
Following are specific examples demonstrating the application of the gold solvent extraction process for the recovery and purification of gold from copper anode slimes. The SX process is incorporated into a flowsheet using oxidative chloride leaching of decopperised slimes. A simplified flowsheet is shown in Figure 1.

Pre-treatment of anode slime
Copper anode slimes contain as the main constituents Cu, Au, Ag, Pb, Se, Te, Sb, Ni, As and Bi. The copper anode slimes composition can vary substantially for different plant operations but is typically in the range shown in Table 2. Note the Au concentration in copper anode slimes is at a maximum of 2%. There are also many other impurities present in lower concentrations including the presence of radionuclides such as Po-210. In producing solutions for the tests outlined below, copper anode slimes of composition falling within the typical copper anode slimes, but with lower Sb concentrations, were used.
Table 2

<table>
<thead>
<tr>
<th>element</th>
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<tbody>
<tr>
<td>Ag</td>
<td>0.02-40</td>
</tr>
<tr>
<td>As</td>
<td>1-3</td>
</tr>
<tr>
<td>Au</td>
<td>0.1-2</td>
</tr>
<tr>
<td>Bi</td>
<td>1</td>
</tr>
<tr>
<td>Cu</td>
<td>6-50</td>
</tr>
<tr>
<td>Ni</td>
<td>0.5-2</td>
</tr>
<tr>
<td>Pb</td>
<td>7-12</td>
</tr>
<tr>
<td>Se</td>
<td>4-25</td>
</tr>
<tr>
<td>Sb</td>
<td>2-4</td>
</tr>
<tr>
<td>Te</td>
<td>0.5-6</td>
</tr>
</tbody>
</table>

The decopperised anode slimes were treated with an oxidative chloride leach. Typically this was carried out by the addition of concentrated HCl (12 M) and H₂O₂ (12.6 M) to the decopperised slimes. A temperature of 96°C was maintained for 4 hours under reflux conditions. Very high dissolution of Au (>98%) was achieved. Ag and Pb were rejected to the residue with only <0.05% of Ag and 6.7% of Pb going into solution. The dissolution of Se and Te was very high (> 98%). Significant dissolution of As, Bi and remaining Cu also occurred. The resultant liquor contained 5-10 g/L Au.

**EXAMPLE 1 Selectivity of reagent for Au over Po-210**

The leach liquor produced from the oxidative chlorination of decopperised slimes as described above was used for the following tests. The leach liquor was diluted to ~ 160 mg/L Au in a series of solutions with varying hydrochloric acid concentrations (1 ~ 8 M HCl). The solutions were then contacted in separate tests with the same volume of organic solution. Two types of organic solutions were tested:

i) 50% by volume of isodecanol (Exxal®10) in Escaid 500 (a low aromatic content hydrocarbon diluent)

ii) 50% by volume of 2-ethyl hexanol in Escaid 500

The percentage extraction of Au and Po-210 as a function of HCl concentration is presented in Table 3 and it can be seen that provided the HCl concentration is controlled between 3-5 M, high Au extraction is achieved with high rejection of Po-210 to the residue.
Table 3

<table>
<thead>
<tr>
<th>2-ethyl Hexanol</th>
<th>isodecanol</th>
</tr>
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<tbody>
<tr>
<td>% Extraction</td>
<td>% Extraction</td>
</tr>
<tr>
<td>HCl (M)</td>
<td>Au</td>
</tr>
<tr>
<td>1.0</td>
<td>16</td>
</tr>
<tr>
<td>2.0</td>
<td>57</td>
</tr>
<tr>
<td>3.0</td>
<td>73</td>
</tr>
<tr>
<td>4.0</td>
<td>86</td>
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<tr>
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<td>6.0</td>
<td>95</td>
</tr>
<tr>
<td>7.0</td>
<td>96</td>
</tr>
<tr>
<td>8.0</td>
<td>96</td>
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</table>

EXAMPLE 2 Au recovery and purification with solvent extraction

Leach liquor obtained from oxidative chlorination of decopperised anode slimes containing 4.1% Au to cation ratio in solution was treated as follows. The leach liquor was contacted in a batch counter-current mode with an organic solution containing 50 vol.% isodecanol in Escaid 300 diluent in 4 extraction stages. Five cycles were carried out in order to ensure that that equilibrium had been reached. An A:O ratio (i.e. leach liquor to organic solution) of 4.5 was used. The feed to the solvent extraction process contained 6.5 g/L Au and the loaded organic obtained contained 30.3 g/L Au. Gold extraction of >96% was obtained. The loaded organic analysis is presented in Table 4, and indicates an upgrade of Au relative to the major impurities, Se, Te, As and Sb from 4.1% to 82%. The loaded solvent was submitted to a further 7 stages of counter-current scrubbing with an hydrochloric acid solution, resulting in a further upgrade of Au to 93%. The scrubbed solvent was then stripped with a dilute hydrochloric acid solution (0.05N) to produced a loaded strip solution. Direct precipitation of Au by addition of sodium oxalate to the loaded strip solution resulted in an Au product of 99.9% purity.
Table 4

Purification of Au using Solvent Extraction

<table>
<thead>
<tr>
<th>% Au (wrt Se,Te,As,Sb)</th>
<th>Loaded Org</th>
<th>Scrubbed Org</th>
<th>Loaded Strip</th>
<th>Au Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>82</td>
<td>93</td>
<td>99.1</td>
<td></td>
<td>99.99</td>
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<table>
<thead>
<tr>
<th>Solution (mg/L)</th>
<th>Au</th>
<th>Se</th>
<th>Te</th>
<th>As</th>
<th>Sb</th>
<th>Au Product</th>
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<td></td>
<td>30300</td>
<td>6030</td>
<td>12</td>
<td>540</td>
<td>27</td>
<td>99.95</td>
</tr>
<tr>
<td></td>
<td>29760</td>
<td>1950</td>
<td>6</td>
<td>165</td>
<td>11</td>
<td>0.0065</td>
</tr>
<tr>
<td></td>
<td>18700</td>
<td>150</td>
<td>6</td>
<td>10</td>
<td>11</td>
<td>0.0002</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>11</td>
<td>0.0003</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>0.000001</td>
</tr>
</tbody>
</table>
Claims:

1. A method for recovering gold from an acid digest of a gold-containing copper anode slime, said method comprising the steps of:
   a) selectively extracting the acid digest with an alcohol to form an alcoholic extract comprising the gold, said alcohol having low miscibility with water; and
   b) recovering the gold from the alcoholic extract;

wherein the gold in the acid digest is in a form that is extractable into said alcohol.

2. The method of claim 1 wherein the alcohol has a solubility in water of less than about 0.2% w/w, v/v or w/v at 20°C.

3. The method of claim 1 or claim 2 wherein the alcohol is a primary alcohol.

4. The method of claim 3 wherein the primary alcohol is a branched chain alcohol.

5. The method of claim 4 wherein the branched chain alcohol is selected from the group consisting of 2-ethyl-1-hexanol, 8-methyl-1-nonanol and mixtures thereof.

6. The method of any one of claims 1 to 5 comprising the step of digesting a gold-containing copper anode slime using acid to provide the acid digest.

7. The method of claim 6 wherein the step of digesting comprises combining the anode slime with concentrated hydrochloric acid.

8. The method of claim 6 or claim 7 wherein an oxidant is used with the acid in digesting the gold-containing copper anode slime.

9. The method of any one of claims 1 to 8 wherein the acid digest comprises a radioactive element and the acidity of the acid digest is such that at least about 90% of the gold present in the digest is extracted into the alcohol and less than about 10% of the amount of the radioactive element present in the acid digest is extracted into the alcohol.

10. The method of claim 9 wherein the radioactive element is polonium.

11. The method of any one of claims 1 to 10 wherein the proportion of gold to total metals in the acid digest prior to step a) is about 4% or less by weight or by moles.

12. The method of any one of claims 1 to 11 wherein step a) comprises continuous countercurrent extraction.

13. The method of any one of claims 1 to 12 additionally comprising the step of scrubbing the alcoholic extract to remove impurities from said extract, said step being conducted between steps a) and b).

14. The method of claim 13 wherein said scrubbing comprises scrubbing with a dilute mineral acid.
15. The method of any one of claims 1 to 14 wherein step b) comprises extracting the alcoholic extract with an aqueous extractant to provide a gold-containing aqueous extract.

16. The method of claim 15 wherein the aqueous extractant has a pH greater than about 5.

17. The method of claim 16 wherein the aqueous extractant is at approximately neutral pH.

18. The method of any one of claims 15 to 17 comprising the step of reducing the gold in the aqueous extract to Au(0).

19. The method of claim 18 comprising further refining the Au(0).

20. The method of any one of claims 1 to 19 wherein the gold in the acid digest is present as Au(III).

21. The method of claim 20 wherein the gold in the acid digest is present as AuCl₄⁻.

22. The method of any one of claims 1 to 21 comprising the step of recovering the alcohol from the alcoholic extract.

23. The method of claim 22 wherein the recovered alcohol is reused in step a).

24. Gold recovered by the method of any one of claims 1 to 23.

25. The gold of claim 24, said gold having a purity of greater than about 99.9% by weight.

26. Use of a primary alcohol for extracting gold from an acid digest of copper anode slime.

27. Use according to claim 26 wherein the primary alcohol is a branched chain alcohol.

28. Use according to claim 27 wherein the branched chain alcohol is selected from the group consisting of 2-ethyl-1-hexanol, 8-methyl-1-nonanol and mixtures thereof.

29. The method of claim 8 wherein the oxidant is hydrogen peroxide or chlorine.
Fig. 1

Fig. 2
Fig. 3
**INTERNATIONAL SEARCH REPORT**

A. **CLASSIFICATION OF SUBJECT MATTER**

Int. Cl.
- C22B 3/20 (2006.01)
- C22B 3/26 (2006.01)
- C22B 3/44 (2006.01)
- C25C 1/00 (2006.01)
- C22B 7/00 (2006)
- C22B 11/00 (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 database and, where practicable, search terms used)
- EPODOC and WPI: IPC C22B3/+-, C22B11/+-, C22B7/+-, C25C1/+- and key words - noble or precious metal or gold or aurum, anode slime, alcohol or +anol.

C. **DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>X</td>
<td>US 4390366 A (LEA ET AL.) 28 June, 1983. (Abstract, column 1, line 10 – 16; column 2, line 49 – 61; example – gold extraction)</td>
<td>1-21 and 24-29</td>
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<td>Y</td>
<td>US 2004/009095 A1 (MINTER) 27 May, 2004. (Abstract; paragraph 0057 and 0060; figure 4)</td>
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<td>US 4687559 A (COBURN ET AL.) 18 August, 1987. (Figure 1)</td>
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[X] Further documents are listed in the continuation of Box C  
[X] 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

**"I"** later document published after the international filing date of 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

**"G"** document member of the same patent family

Date of the actual completion of the international search: **21 April 2009**

Date of mailing of the international search report: **05 MAY 2009**

Name and mailing address of the ISA/AU

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Telephone No: +61 2 6283 7965

Form PCT/ISA/210 (second sheet) (July 2008)
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This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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Due to date integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX