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(54) Title: LEACHING COPPER-CONTAINING ORES

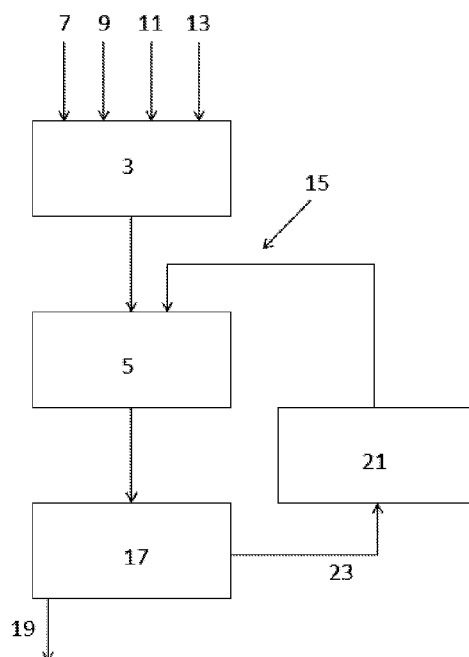


Figure 1.

(57) Abstract: A method of leaching copper-containing ores includes leaching copper-containing ores or concentrates or tailings of the ores or concentrates with a leach liquor in the presence of an additive that enhances the dissolution of copper from copper minerals in the ores and concentrates by forming a complex between (a) sulfur, that has originated from copper minerals in the ores, and (b) the additive. A method of leaching copper-containing ores or concentrates or tailings of the ores or concentrates with a leach liquor includes leaching copper-containing ores or concentrates or tailings of the ores or concentrates with a leach liquor in the presence of a nitrogen-containing organic complexing additive that forms a complex between sulfur, that has originated from copper minerals in the ores, and the additive.



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Leaching Copper-Containing Ores

Technical Field

The present invention relates to leaching copper-containing ores.

5 The present invention relates particularly, although not exclusively, to leaching any one or more of (a) copper-containing ores (which may be in the form of agglomerates of ore fragments), (b) concentrates of the ores, and (c) tailings of the ores or concentrates produced for example by flotation or other downstream processing of ores or concentrates.

10 The present invention relates particularly, although not exclusively, to leaching copper-containing sulfidic ores, such as sulfidic ores that contain copper minerals such as chalcopyrite (CuFeS_2) and/or enargite (Cu_3AsS_4). The sulfidic ores may contain other copper minerals.

15 The present invention relates particularly, although not exclusively, to a method of leaching copper-containing ores, particularly copper-containing sulfidic ores, using an additive to enhance dissolution of copper in the ores.

Background Art

20 In the leaching of copper-containing ores (including copper-containing sulfidic ores such as chalcopyrite and/or enargite or other copper-containing sulfide minerals), the particle size of the ores is typically reduced from run-of-mine size, for example by crushing and grinding operations, to allow processing via heap leaching, vat leaching or reactor leaching options.

25 These leaching processes involve the application of an acid and an oxidant to dissolve copper into solution. Copper is subsequently recovered from the acidic solution by a range of recovery options including solvent extraction and electrowinning (SX/EW), cementation onto more active metals such as iron, hydrogen reduction, and direct electrowinning. The acidic solution is regenerated and recycled to leach more copper from the ores. Leaching may be assisted by the use of microorganisms.

Generally, leaching may provide lower metal recoveries than other process options for recovering copper from sulfidic ores, such as milling and flotation, that produce copper-containing concentrates that are then smelted to produce copper metal.

- 5 It is known that it is difficult to leach more than 20-40 wt.% of the total copper from chalcopyrite by heap leaching. The low copper recovery is often thought to be associated with the formation of a passive film on the surface of the chalcopyrite that may be composed of degradation products from the dissolution reaction.

The present invention was made in research and development work by a Group company of the applicant.

- 10 The present invention makes it possible to achieve higher recoveries of copper from copper-containing minerals in ores via an enhanced leaching mechanism.

The above description is not to be taken as an admission of the common general knowledge in Australia or elsewhere.

Summary of the Disclosure

- 15 The present invention is based on a realisation that leaching copper-containing ores or concentrates of the ores or tailings of the ores or concentrates produced for example by flotation or other downstream processing of ores or concentrates can be enhanced via the formation of a complex comprising (a) sulfur, that has originated from copper minerals in the ores, and (b) an additive.
- 20 In particular, although not exclusively, the present invention is based on a realisation that leaching copper-containing ores or concentrates of the ores or tailings of the ores or concentrates can be enhanced via the formation of a complex between (a) sulfur, that has originated from copper minerals in the ores, and (b) an additive that results in an increase in dissolution rates.
- 25 By way of example, the sulfur may be in a passivating layer on copper minerals, and the complex may be a complex of the additive and sulfur in the passivating layer that breaks down the passivating layer or reduces the formation of the layer and therefore

allows greater access for leaching copper from copper minerals. This invention can be described as a “*mechanism invention*”.

The present invention is also based on a realisation that a particular group of nitrogen-containing complexing agents are effective additives for the above-described leaching method. This invention can be described as an “*additive-specific invention*”.

Mechanism invention - additive

- In general terms, the mechanism invention is a method of leaching copper-containing ores, such as copper-containing sulfidic ores that contain copper minerals such as chalcopyrite and/or enargite, or concentrates of the ores or tailings of the ores or concentrates, that includes leaching copper-containing ores or concentrates or tailings of the ores or concentrates with a leach liquor in the presence of an additive that enhances the dissolution of copper from copper minerals in the ores and concentrates by forming a complex between (a) sulfur, that has originated from copper minerals in the ores, and (b) the additive.
- The complex may comprise sulfur in a passivating layer on copper minerals and the additive, with the complex breaking down the passivating layer or reducing the formation of the layer and therefore allowing greater access for leaching copper from copper minerals.

The method may include any one of:

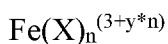
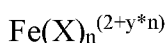
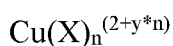
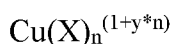
- (a) heap or vat or tank leaching ore fragments,
- (b) heap or vat or tank leaching agglomerates of ore fragments,
- (c) heap or vat or tank leaching ore concentrates,
- (d) heap or vat or tank leaching agglomerates of ore concentrates; and
- (e) heap or vat or tank leaching tailings of the ores or concentrates produced for example in flotation or other downstream processing of ores or concentrates.

The additive may comprise a nitrogen-containing complexing agent that includes at least two nitrogen atoms spaced by two carbon atoms to permit the additive to form

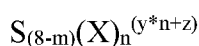
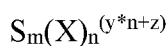
complexes between sulfur, that has originated from copper minerals in the ores, and the additive.

Each of the at least two nitrogen atoms in the additive may be present as a primary amine group, a secondary amine group or a tertiary amine group.

- 5 In addition to forming complexes with sulfur that has originated from copper minerals in the ores, including for example sulfur in the passivating layer on the copper minerals (including the complexes set out below), the additive may form complexes with copper(I), copper(II), iron(II), and iron(III) that has originated from the ores that enhance leaching of copper from copper minerals in the ores or concentrates, including
- 10 the complexes set out below:

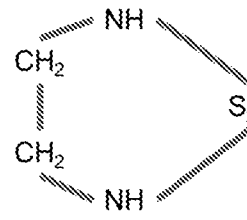
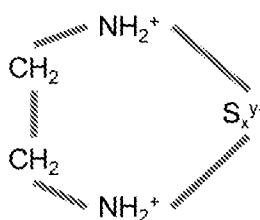
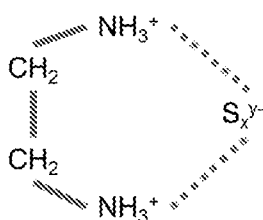


- 15 $\text{AsO}_4(\text{X})_n^{(-3+y*n)}$



where X = additive; n = number of additive molecules; y = electron charge of additive; m = number of sulfur atoms in the chain; z = electron charge of the sulfur chain.

- 20 The following structures show possible complexes that can form between sulfur that has originated from copper minerals in the ores and the additive, where the additive is, for example, ethylenediamine.



For each of the complexes, the metal ion or sulfur is derived from the dissolution of the copper minerals in the ores or concentrates or tailings of the ores or concentrates, such as chalcopyrite or enargite.

The complex may form a ring or chain structure.

- 5 The formation of these complexes may be controlled and/or enhanced by the addition of an acid, such as sulfuric acid, and an oxidant or reductant.

The applicant believes that these complexes are preferentially formed over existing intermediary phases and thereby break down or reduce the formation of passivating layers on the copper mineral surfaces and therefore allow greater access for leaching

- 10 copper from the minerals in the ores.

The applicant also believes that the additive may react directly with the sulfur from the mineral to enhance leaching via reducing the activation energy, i.e. have a catalytic effect.

Additive-specific invention

- 15 The additives described below have been found to be suitable additives for the mechanism invention.

In general terms, the additive-specific invention is a method of leaching copper-containing ores, such as copper-containing sulfidic ores that contain copper minerals such as chalcopyrite and/or enargite, or concentrates of the ores, that includes leaching
20 copper-containing ores or concentrates or tailings of the ores or concentrates with a leach liquor in the presence of a nitrogen-containing organic complexing additive that forms a complex between sulfur, that has originated from copper minerals in the ore, and the additive.

- 25 As noted above, the complex may comprise sulfur in a passivating layer on copper minerals and the additive, with the complex breaking down the passivating layer or reducing the formation of the layer and therefore allowing greater access for leaching copper from copper minerals during the method.

It is preferred that the additive be sufficiently water soluble to be able to enhance copper extraction into the leach solution.

The additive may be a degradation product that forms under the conditions of the leach and is an effective additive in the terms of the invention.

- 5 By way of example, the degradation product may be a degradation product of another said additive.

The nitrogen-containing complexing agent may include at least two nitrogen atoms.

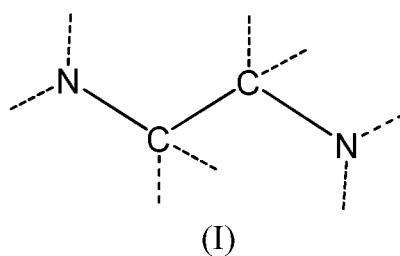
Each of the at least two nitrogen atoms in the additive may be present as a primary amine group, a secondary amine group or a tertiary amine group.

- 10 The possible interaction of sulfur that has originated from copper minerals in the ores with the at least two nitrogen atoms in the additive may be via the lone pair on each of the nitrogen atoms being involved in $p\pi-d\pi$ bonding with the adjacent sulfur atom. Alternatively, this may be via ionic interaction or a combination of both.

- 15 It is preferred that the nitrogen atoms of the additive are not significantly sterically hindered. Minimising steric hindrance assists the formation of a sufficiently strong interaction (e.g. $p\pi-d\pi$ bonding, ionic interaction or a combination of both) between the sulfur from the ore and the nitrogen atoms in the additive.

The nitrogen-containing complexing agent may include at least two nitrogen atoms spaced by two carbon atoms to permit the additive to form the complex.

- 20 The additive may be a compound that contains the following molecular scaffold or a polymer that contains the molecular scaffold repeated through the polymer:



wherein,

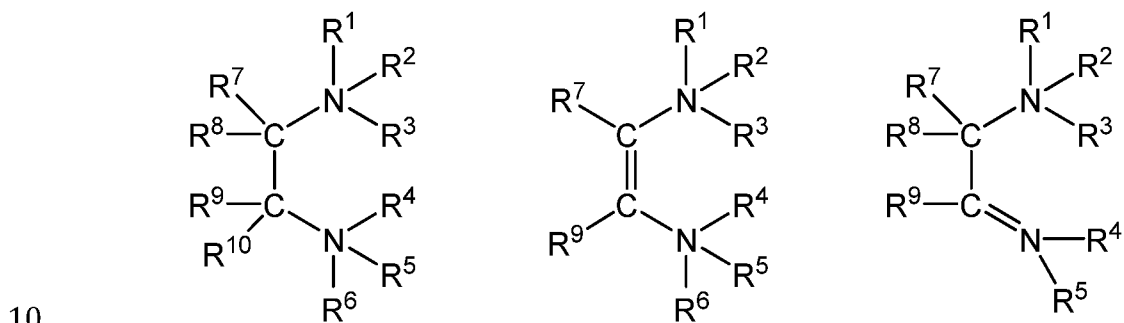
the two nitrogen atoms are each independently substituted or unsubstituted, each nitrogen atom is selected from the group consisting of a primary amine group, a secondary amine group, a tertiary amine group,

the carbon atoms may each be substituted or unsubstituted;

- 5 the bonds between the nitrogen atoms and carbon atoms in the scaffold may be single bonds or multiple bonds; and

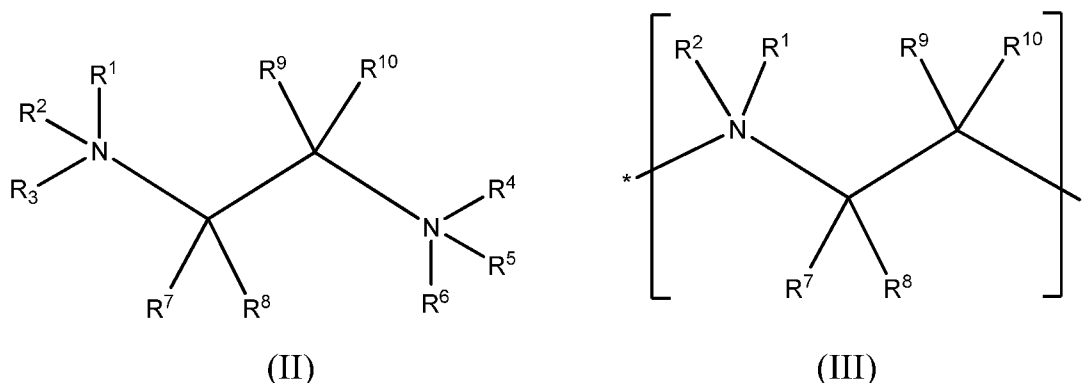
the bonds between the two carbon atoms in the scaffold may be single bonds or multiple bonds.

Examples of possible additive compound structures include the following:



- wherein, the groups R^1 to R^{10} may each be independently selected from the group including alkyl (such as C_1 to C_5 alkyl), alkenyl (such as C_2 to C_5 alkenyl), alkynyl (such as C_2 to C_5 alkynyl), OH, =O, alkyloxy groups (such as C_1 to C_5 alkyloxy groups), alkenyloxy groups (such as C_2 to C_5 alkenyloxy groups), alkynyloxy groups (such as C_2 to C_5 alkynyloxy groups), $C(=O)R$ (where R is alkyl, alkenyl or alkynyl), $C(O)OH$, $C(O)OR$ (where R is alkyl, alkenyl or alkynyl), $OC(=O)R$ (where R is alkyl, alkenyl or alkynyl), amino, alkylamino (such as C_1 to C_5 alkyl), alkenylamino (such as C_2 to C_5 alkenylamino), alkynylamino (such as C_2 to C_5 alkynylamino), $C(O)NH_2$, $C(O)NHR$ (where R is alkyl, alkenyl or alkynyl), $C(O)NR_2$ (where R is alkyl, alkenyl or alkynyl).
- 15
- 20

The additive may be a compound of the formula (II) or a polymer formed from two or more monomers of the formula (II):



wherein, in formula (II) and (III),

- R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may each be independently selected from a lone pair electron, H, alkyl groups (such as C_1 to C_5 alkyl groups), alkenyl groups (such as C_2 to C_5 alkenyl groups), alkynyl groups (such as C_2 to C_5 alkynyl groups), and alkylamino groups (such as C_1 to C_5 alkylamino groups), or the substituents on each of the two nitrogens together form an alkyl or alkynyl group that connect the two nitrogens to form a ring (e.g. the substituents together form a one or two carbon connecting the nitrogens to form a ring);
- R^7 , R^8 , R^9 and R^{10} may each be independently selected from H, alkyl (such as C_1 to C_5 alkyl), alkenyl (such as C_2 to C_5 alkenyl), alkynyl (such as C_2 to C_5 alkynyl), OH, alkyloxy groups (such as C_1 to C_5 alkyloxy groups), alkenyloxy groups (such as C_2 to C_5 alkenyloxy groups), alkynyloxy groups (such as C_2 to C_5 alkynyloxy groups), $C(=O)R$ (where R is alkyl, alkenyl or alkynyl), $C(O)OH$, $C(O)OR$ (where R is alkyl, alkenyl or alkynyl), $OC(=O)R$ (where R is alkyl, alkenyl or alkynyl), amino, alkylamino (such as C_1 to C_5 alkyl), alkenylamino (such as C_2 to C_5 alkenylamino), alkynylamino (such as C_2 to C_5 alkynylamino), $C(O)NH_2$, $C(O)NHR$ (where R is alkyl, alkenyl or alkynyl), $C(O)NR_2$ (where R is alkyl, alkenyl or alkynyl), or R^7 and R^8 together and/or R^9 and R^{10} together may be selected from $=O$, $=NH$ or $=NH$ (where R is alkyl, alkenyl or alkynyl);

and in formula (III),

R^1 or R^2 are each independently selected from the groups defined for R^1 and R^2 above or are connected to another monomer of formula (II).

Examples of suitable additives include ethylenediamine, polyethylenimine, imidazole, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, 1,2-diaminopropane, and 2,3-butanediamine. A large number of other additives exist that fulfil the criteria of formula (II) and formula (III).

5 Additive addition – mechanism/additive-specific

The concentration of the additive may be up to 10 g/L, typically up to 5 g/L, typically up to 2.5 g/L, typically up to 1.5 g/L, typically up to 1.25 g/L, and more typically up to 1 g/L, in the leach liquor.

10 The method may include adding the additive to the leach liquor continuously or periodically during the method to maintain a required concentration during the method.

The method of addition may be to the ores or concentrates of the ores or tailings of the ores or concentrates prior to leaching.

The method for addition may be to agglomerates of ore fragments prior to leaching.

15 For example, the additive may be added while forming agglomerates of ore fragments, as described further below.

In a situation where the method recycles leach solution, optionally after regenerating leach liquor from the leach step, the method may include adjusting the concentration of the additive in the regenerated leach liquor to maintain the concentration.

Leaching – generally – mechanism/additive-specific

20 Leaching may be any suitable option for leaching (a) ore fragments or ore concentrates or tailings of the ores or concentrates or (b) agglomerates of ore fragments or ore concentrates or tailings of the ores or concentrates.

For example, leaching may be vat or tank leaching.

25 By way of further example, which is of particular interest to the applicant, leaching may be heap leaching agglomerates of ore fragments or ore concentrates or tailings of the ores or concentrates.

Leaching may include supplying a leach liquor to a heap of agglomerates from an agglomeration step and allowing the leach liquor to flow through the heap and leach copper from agglomerates and collecting leach liquor from the heap, processing the leach liquor and recovering copper from the liquor.

- 5 The term “fragment” is understood herein to mean any suitable size of mined or treated (e.g. crushed) material having regard to materials handling and processing capabilities of the apparatus used to carry out the method. It is also noted that the term “fragment” as used herein may be understood by some persons skilled in the art to be better described as “particles”. The intention is to use both terms as synonyms.

- 10 The leach liquor may include microorganisms to assist leaching of copper.

The microorganisms may be one or more than one of psychrotolerant or mesophilic or thermophilic (moderate or extreme) bacteria or archaea. The microorganisms may be acidophilic bacteria or archaea. The microorganisms may be thermophilic acidophiles.

- The leach liquor may contain any suitable chemical oxidants, such as O_2/SO_2 ,
15 pyrolusite, permanganate ions, ferric ions, peroxide ions, and chlorate ions.

Leaching may include controlling the temperature to be less than 100 °C, typically less than 85 °C, typically less than 75 °C, typically less than 65 °C, typically less than 60 °C, typically less than 55 °C, and more typically less than 50 °C.

- 20 Leaching may include controlling the leach temperature to be at least 10 °C, typically at least 20 °C, typically at least 30 °C, typically at least 40 °C, and more typically at least 50 °C.

- Leaching may include controlling the oxidation potential of the leach liquor during an active leaching phase of the step to be less than 900 mV, typically less than 850 mV,
25 typically less than 800 mV, typically 500 to 750 mV, more typically in a range of 600 to 750 mV, all potentials being with respect to the standard hydrogen electrode.

Leaching and oxidation potential may be assisted by the addition of microorganisms capable of oxidizing ferrous ions, sulfides, polysulfides and sulfur.

It is noted that the oxidation potential will change during leaching and is likely to be higher when much of the copper has been leached and the reference to “active leaching phase” is intended to acknowledge this potential change.

- Leaching may include controlling the pH of the leach liquor to be less than 2.5,
5 typically less than 2.0, typically less than 1.8, and typically less than 1.5.

Leaching may include controlling the pH of the leach liquor to be greater than 0.5, typically greater than 1.

Leaching may include recovering copper from the leach liquor in downstream copper recovery steps.

- 10 The leach liquor may be regenerated and recycled to the leach.

Leaching may include adjusting the concentration of the additive in the regenerated leach liquor to maintain the concentration.

The concentration adjustment may include adding the additive to the regenerated leach liquor to maintain the concentration.

- 15 The concentration adjustment may include removing the additive from the regenerated leach liquor to maintain the concentration.

The method may also include recovering the leached metal as a metal product. Typically, this step includes recovering the leached metal from solution in pregnant leach liquor.

- 20 In general terms, the advantages of the invention include providing an opportunity for microorganism-assisted and/or chemically assisted leaching of copper minerals in copper-containing ores, particularly low grade ores (i.e. typically less than 2.0 wt.% copper, typically less than 1.5 % copper, typically less than 1.0 % copper), at relatively low temperatures and at comparatively low operating costs with high recoveries.
- 25 The following description focuses on particular embodiments of heap leaching, noting that the invention is not confined to heap leaching and extends to vat and tank leaching on copper ores and copper concentrates or tailings of the ores or concentrates.

The method may include an agglomeration step for forming agglomerates of ore fragments for heap leaching.

The agglomeration step may include adding the additive during the step.

5 The applicant has found that in situations where the additive is a polymer-like additive, such as longer chain organic substances, such as polyethylenimine (PEI), it may be preferred to include the additive in agglomerates of ore fragments rather than by adding the additive to the leach liquor.

The agglomeration step may include:

- 10 (a) forming a PEI solution having a pH greater than pH 4.5;
 - (b) optionally heating the solution to at least 50 °C to speed up the dissolution/dilution of the PEI; and
 - (c) adding the PEI solution to ore fragments at the start of the agglomeration step before other additions, such as acids/raffinate/etc, described below to the agglomeration step.
- 15 The agglomeration step may include forming the PEI solution while ensuring that the solution does not contain constituents that can cause precipitation and/or polymerization of PEI such as ferric ions.

20 The agglomeration step may include mixing together an acid, typically sulfuric acid but could also be dilute hydrochloric, with copper-containing ore fragments, such as fragments containing chalcopyrite. The added acid dose rate may be less than 100 kg H₂SO₄/dry t ore, typically less than 50 kg H₂SO₄/dry t ore, typically less than 30 kg H₂SO₄/dry t ore, and may be less than 10 kg H₂SO₄/dry t ore or less than 5 kg H₂SO₄/dry t ore. Typically, the acid dose rate is 0.5 – 10 kg H₂SO₄/dry t ore.

25 The agglomeration step may include mixing together pregnant leach solution or raffinate with copper-containing ore fragments, such as fragments containing chalcopyrite.

The agglomeration step may include mixing microorganisms that can assist leaching with copper-containing ore fragments, such as fragments containing chalcopyrite. The

microorganisms may be as described above. Specifically, the microorganisms may be one or more than one of mesophilic, thermophilic (moderate or extreme) or psychrotolerant bacteria or archaea. The microorganisms may be acidophilic bacteria or archaea. The microorganisms may be thermophilic acidophiles.

- 5 The agglomeration step may include simultaneously mixing and agglomerating fragments.

The agglomeration may include mixing fragments in one-step and then agglomerating the mixed fragments in a subsequent step. There may be overlap between the mixing and agglomeration steps.

- 10 The method may include reducing the size of the mined ore prior to agglomeration.

By way of example, the method may include crushing the mined ore prior to agglomeration. The mined ore may be crushed using any suitable means.

The method may include crushing mined ore in a primary crushing step prior to the agglomeration step.

- 15 The term “primary crushing” is understood herein to mean crushing ore to a top size of 250 to 150 mm in the case of copper-containing ores where the copper is in the form of sulfides. It is noted that the top size may be different for ores containing different valuable metals.

- 20 The method may include crushing mined ore in a primary crushing step and then a secondary and possibly tertiary and possibly quaternary crushing step prior to agglomeration.

The invention also provides a heap of material, with the material including the above-described agglomerates.

The invention also includes a method of heap leaching that includes:

- 25 (a) forming a heap of material, with the material including the above-described agglomerates; and
- (b) leaching valuable metal from the ore in the heap with a leach liquor.

Heap leaching may include recovering copper from the leach liquor in downstream copper recovery steps.

The leach liquor may be regenerated and recycled to the heap.

The leaching step may include adding the additive during the step.

- 5 The method may also include recovering the leached metal as a metal product. Typically, this step includes recovering the leached metal from solution in pregnant leach liquor.

The method may include forming heaps of the copper-containing ores or concentrates.

Brief Description of the Drawings

- 10 The present invention is described further with reference to the accompanying drawings of which:

Figure 1 illustrates the steps in one embodiment of a method of heap leaching agglomerates of fragments of copper-containing ore that contains chalcopyrite and/or enargite with a leach liquor containing an additive in accordance with the present

- 15 invention;

Figure 2 illustrates the enhancement of copper dissolution from relatively pure chalcopyrite mineral grains with the addition of examples of additives in accordance with the invention, with this improvement resulting in copper extraction being higher than the baseline conditions where no additive was added to the test;

- 20 Figure 3 illustrates cases where no enhancement of copper dissolution occurred from relatively pure chalcopyrite mineral grains with the addition of samples of additives that do not meet the requirements of the additives in accordance with the invention;

Figure 4 illustrates cases where a negative enhancement of copper dissolution occurred from relatively pure chalcopyrite mineral grains with the addition of samples of

- 25 additives that do not meet the requirements of the additives in accordance with the invention;

Figure 5 illustrates the enhancement of copper dissolution from a low copper grade (<1.5 wt.%) ore sample leached at 50 °C with the addition of examples of additives in accordance with the invention, with this improvement resulting in copper extraction being higher than the baseline conditions where no additive was added to the test;

- 5 Figure 6 illustrates the enhancement of arsenic dissolution from a low copper grade (<1.5 wt.%) ore sample leached at 50 °C with the addition of examples of additives in accordance with the invention, with this improvement resulting in arsenic extraction being higher than the baseline conditions where no additive was added to the test;

- 10 Figure 7 illustrates the enhancement of copper dissolution from a low copper grade (<1.5 wt.%) ore sample leached at 30 °C with the addition of examples of additives in accordance with the invention, with this improvement resulting in copper extraction being higher than the baseline conditions where no additive was added to the test;

- 15 Figure 8 illustrates the enhancement of arsenic dissolution from a low copper grade (<1.5 wt.%) ore sample leached at 30 °C with the addition of examples of additives in accordance with the invention, with this improvement resulting in arsenic extraction being higher than the baseline conditions where no additive was added to the test;

Figure 9 is a graph of copper extraction profiles for a chalcopyrite/enargite ore sample leached with and without the addition of the additive polyethylenimine at 50 °C; and

- 20 Figure 10 is a graph of arsenic extraction profiles for a chalcopyrite/enargite ore sample leached with and without the addition of the additive polyethylenimine at 50 °C.

Description of Embodiment

The following description is in the context of heap leaching agglomerates of copper-containing ore fragments.

- 25 It is noted that not all of the experimental work that has been carried out is reported in the specification and that the overall results of the work are positive and indicate invention is applicable to tank, vat and heap leaching.

Further to the preceding paragraph, it is noted that the invention extends to heap, vat and tank leaching copper-containing ores that are in the form of fragments or in the form of agglomerates of fragments.

It is also noted that the invention also extends to heap, vat, and tank leaching
5 concentrates of copper-containing ores, with the ore concentrates being in any suitable form, including unagglomerated and agglomerated forms.

It is also noted that the invention also extends to heap or vat or tank leaching tailings of the ores or concentrates produced for example in flotation or other downstream processing of ores or concentrates.

10 As noted above, the invention comprises leaching copper-containing ores or concentrates of the ores or tailings of the ores or concentrates with a leach liquor in the presence of an additive that enhances the dissolution of copper from copper minerals in the ores and concentrates by forming a complex between (a) sulfur, that has originated from copper minerals in the ore, and (b) the additive. Nitrogen-containing organic
15 complexing additives are specific examples of the additive.

The flow sheet of Figure 1 shows the steps in one embodiment of a method of heap leaching agglomerates of fragments of copper-containing ore that contains chalcopyrite and/or enargite with a leach liquor containing an additive in accordance with the invention.

20 The method includes the steps of forming agglomerates of copper containing ore in an agglomeration station 3, forming a heap 5 from the agglomerates, supplying a leach liquor 15 to the heap 5 and taking copper into solution, collecting leach liquor after it has passed through the heap, recovering copper from solution in the leach liquor from the heap in a copper recovery circuit 17, for example by solvent extraction, and
25 regenerating the leach liquor from the heap and recycling the regenerated leach liquor to the heap.

With reference to Figure 1, the following feed materials are transferred to the agglomeration station 3 and are mixed together and form agglomerates:

- (a) fragments of copper containing ore that includes chalcopyrite and/or enargite that have been crushed to a suitable particle size distribution, identified by the numeral 7 in the Figure;
- (b) optionally an activation agent, such as silver, in this embodiment as a silver solution (but could be in a solid form), typically having an added concentration of silver of less than 5 g silver per kg copper in the ore in the agglomerates, identified by the numeral 9 in the Figure;
- (c) an acid, typically sulfuric acid, identified by the numeral 11 in the Figure in any suitable concentration; and
- 10 (d) microorganisms, identified by the numeral 13 in the Figure, of any suitable type and in any suitable concentration.

The agglomerates produced in the agglomeration station 3 are subsequently used in the construction of the heap 5.

- For example, the agglomerates produced in the agglomeration station 3 may be
- 15 transferred directly to a heap construction site. Alternatively, the agglomerates may be stockpiled and used as required for a heap. The agglomeration station 3 and the heap 5 are typically in close proximity. However, this is not essential and may not be the case.

- By way of example only, the heap may be a heap of the type described in International publication WO2012/031317 in the name of the applicant and the disclosure of the heap
- 20 construction and leaching process for the heap in the International publication is incorporated herein by cross-reference.

- In a heap leaching operation, copper in the chalcopyrite and other copper-containing minerals in the agglomerates is leached from the agglomerates in the heap 5 via the supply of the leach liquor 15 and is taken into solution in the leach liquor as the leach
- 25 liquor passes through the heap 5.

The leached copper is recovered from the leach liquor in the downstream copper recovery circuit 17.

The recovered copper 19 is transferred for further processing and the leach liquor 23 is transferred to and regenerated in a regeneration circuit 21 and recycled to the heap 5 as leach liquor 15 to leach more copper from the chalcopyrite and other copper-containing minerals in the agglomerates in the heap 5.

- 5 The agglomeration station 3 may be any suitable construction that includes a drum, conveyor (or other device) for mixing the feed materials for the agglomerates and agglomerating the feed materials. The agglomeration conditions in the agglomeration station 3 are selected to form agglomerates of the required size and mechanical properties for the heap 5.
- 10 Mixing and agglomerating the feed materials for the agglomerates may occur simultaneously. Alternatively, mixing the feed materials may be carried out first and agglomerating (for example initiated by the addition of the acid) may be carried out after mixing has been completed to a required extent. Moreover, the timing of adding and then mixing and agglomerating feed materials may be selected to meet the end-use
- 15 requirements for the agglomerates. For example, it may be preferable in some situations to start mixing fragments containing chalcopyrite and then adding silver in a solution or in a solid form of silver, acid, and microorganisms progressively in that order at different start and finish times in the agglomeration step. By way of particular example, it may be preferable in some situations to start mixing fragments containing
- 20 chalcopyrite and then adding silver in a solution or in a solid form and acid together, and then adding microorganisms at different start and finish times in the agglomeration step.

The additives of the invention may be added to the leach liquor 15 in the required concentrations. Typically, the concentration of the additive is up to 10 g/L, up to 5 g/L,

25 up to 2.5 g/L, up to 1.5 g/L, up to 1.25 g/L, or up to 1 g/L, in the leach liquor.

Alternatively, or in addition, the additives of the invention may be added during forming agglomerates in the agglomeration station 3.

The applicant has found that in situations where the additive is a polymer-like additive, such as longer chain organic substances, such as polyethylenimine (PEI), it may be

preferred to add the additive while forming agglomerates in the agglomeration station 3 rather than adding the additive to leach liquor.

For example, one specific sequence of steps that has been found to be successful is as follows:

- 5
 - Form a PEI solution of pH greater than 4.5.
 - Ensure that the makeup solution does not contain constituents that can cause the precipitation/polymerization of the PEI.
 - Optionally heat the solution to at least 50 °C to speed up the dissolution/dilution of the PEI.
- 10
 - Add the PEI solution at the start of agglomerating ore fragments before any acids/raffinate/etc. are added.

As indicated above, a Group company of the applicant has carried out leach testing to investigate the impact of a number of additives in leach liquors on chalcopyrite mineral samples and chalcopyrite/enargite ores.

- 15 The leach tests are described in the Examples below.

Examples

- 20 As described above, test work conducted by a Group company of the applicant has shown that additives in the form of a nitrogen-containing organic complexing agent comprising two nitrogen atoms spaced by two carbon atoms can be used to enhance the dissolution of copper from copper-containing ores.

The additives tested include ethylenediamine, polyethylenimine, imidazole, bipyridyl, phenanthroline, 8-aminoquinoline, cysteine, glycine, arginine, picoline, putrescine, and spermidine.

- 25 The work has shown that additives ethylenediamine, polyethylenimine, and imidazole can be used to enhance the dissolution of copper from copper minerals in copper-containing ores.

Based on the test work and the experience of the inventors, it is expected that other compounds comprising at least two nitrogen atoms spaced by two carbon atoms, in particular compounds which are able to form a complex with sulfur that has originated from copper minerals in the ore, such as a complex with sulfur in a passivating layer on copper minerals in the ore, would have the same effect.

The test work using additive-containing liquor was conducted in small scale leaching reactors.

The following results were obtained with low grade chalcopyrite mineral samples containing greater than 90 % chalcopyrite. Low grade describes ores containing less than 2 wt.% copper, this material was a mixture of chalcopyrite and enargite, plus some background secondary copper sulfide minerals.

1 Reactor test work

1.1 Experimental procedure

Reactor leaching tests were all conducted at a pH less than 1.8, typically around 1.2.

The oxidation potential of the solution was maintained at approximately 700 mV determined with respect to the standard hydrogen electrode to simulate conditions that may be seen when leaching copper ores. The examples in Figures 2, 3 and 4 involved the leaching of a chalcopyrite mineral sample containing approximately 90 % chalcopyrite mineral, with the remainder being non-reactive gangue minerals. The copper grade in the sample was 29 %. The initial leach solution was an acidified iron solution at ~2 g/L Fe(III) added as a sulfate. These tests were maintained at 50 °C. In these methods, additives ethylenediamine, polyethylenimine, and imidazole were tested separately. Specifically, 1 g/L of one of each additive was added to the start of each test.

1.2 Impact of additives

Figure 2 is a graph that depicts copper extraction profiles (% extraction versus leach days) for chalcopyrite mineral samples leached with leach liquor containing additives ethylenediamine, polyethylenimine, and imidazole. The Figure also includes a copper extraction profile for a baseline test with the same leach liquor without an additive.

Figure 2 shows that there was an improvement observed for the leaching of chalcopyrite minerals with leach liquors in tests with the additives ethylenediamine, polyethylenimine, and imidazole compared to the results in the baseline test.

1.3 Comparative examples showing compounds that do not improve leaching

5 Figure 3 is a graph that depicts copper extraction profiles for chalcopyrite mineral samples leached with leach liquors in tests with the additives cysteine, glycine, arginine, picoline, putrescine, spermidine, proline and ethanolamine. The Figure also includes a copper extraction profile for a baseline test with the same leach liquor without an additive. The Figure shows that there was no improvement observed with
10 the leach liquors containing the additives.

Figure 4 is a graph that depicts copper extraction profiles for chalcopyrite mineral samples leached with leach liquors in tests with additives bipyridyl, phenanthroline, and 8-aminoquinoline. The Figure also includes a copper extraction profile for a baseline test with the same leach liquor without an additive. The Figure shows that there was a
15 negative impact on leaching with the leach liquors containing the additives.

2 Column test work

2.1 Experimental procedure

Column leaching tests were all conducted at a pH of less than 1.8, typically around 1.2. The examples in Figures 5, 6, 7 and 8 involved the leaching of a chalcopyrite and
20 enargite ore sample containing approximately 1.3 wt.% copper and 0.07 wt.% arsenic, with approximately 8 wt.% pyrite and the remainder being non-sulfide gangue minerals. The initial leach solution was an acidified 5 g/L ferric iron solution (in the sulfate form). Iron and sulfur oxidizing moderate thermophile bacteria were added to maintain the oxidation potential between 650 and 700 mV determined with respect to the
25 standard hydrogen electrode. In these methods, 1 g/L of the additive ethylenediamine was added at the start of each test.

2.2 Impact of additive

Figure 5 is a graph that depicts copper extraction profiles for a chalcopyrite/enargite ore sample leached with (red squares) and without (blue crosses) the addition of the additive ethylenediamine at 50 °C. The Figure also includes a copper extraction profile for the same leach liquor without an additive.

- 5 Figure 6 is a graph that depicts arsenic extraction profiles for a chalcopyrite/enargite ore sample leached with (red squares) and without (blue crosses) the addition of the additive ethylenediamine at 50 °C. The Figure also includes an arsenic extraction profile for the same leach liquor without an additive.

- 10 Figure 7 is a graph that depicts copper extraction profiles for a chalcopyrite/enargite ore sample leached with (green triangles) and without (blue crosses) the addition of the additive ethylenediamine at 30 °C. The Figure also includes a copper extraction profile for the same leach liquor without an additive.

- 15 Figure 8 is a graph that depicts arsenic extraction profiles for a chalcopyrite/enargite ore sample leached with (green triangles) and without (blue crosses) the addition of the additive ethylenediamine at 30 °C. The Figure also includes a copper extraction profile for the same leach liquor without an additive.

It is evident from each of Figures 5-8 that the additive ethylenediamine had a positive impact on leaching the chalcopyrite/enargite ore samples, with improvements observed in each Figure compared to the baseline results.

- 20 Figure 9 is a graph that depicts copper extraction profiles for a chalcopyrite/enargite ore sample leached with (orange circles) and without (blue crosses) the addition of the additive polyethylenimine at 50 °C. The Figure also includes a copper extraction profile for the same leach liquor without an additive.

- 25 Figure 10 is a graph that depicts arsenic extraction profiles for a chalcopyrite/enargite ore sample leached with (orange circles) and without (blue crosses) the addition of the additive polyethylenimine at 50 °C. The Figure also includes an arsenic extraction profile for the same leach liquor without an additive.

It is evident from each of Figures 9-10 that the additive polyethylenimine had a positive impact on leaching the chalcopyrite/enargite ore samples, with improvements observed in each Figure compared to the baseline results.

3 Summary

- 5 The above Examples, particularly the Figures presenting the results of the experimental work in the Examples, illustrate the effectiveness of the use of additives in accordance with the invention.

The Examples indicate that some additives were successful, and some additives were not successful. The successful additives reported above are ethylenediamine,
10 polyethylenimine, and imidazole. The unsuccessful additives reported above are bipyridyl, phenanthroline, 8-amineoquinoline, cysteine, glycine, arginine, picoline, putrescine, spermidine, proline and ethanolamine.

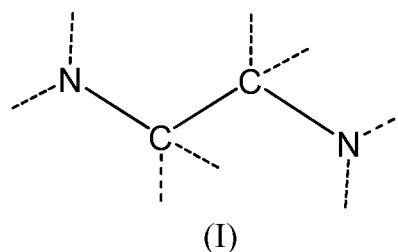
The applicant developed the above-described mechanism invention and additive-specific invention in the process of analysing the results of the above Examples and
15 experimental work on the above-mentioned and other additives.

Specifically, the applicant identified characteristics of additives that make it possible to form complexes comprising (a) sulfur, that has originated from copper minerals in the ore, and (b) additives that can enhance leaching of copper-containing ores or concentrates of the ores.

- 20 Many modifications may be made to the invention as described above without departing from the spirit and scope of the invention.

Claims

1. A method of leaching copper-containing ores, such as copper-containing sulfidic ores such as sulfidic ores that contain copper minerals such as chalcopyrite and/or enargite, or concentrates of the ores or tailings of the ores or concentrates, that includes leaching copper-containing ores or concentrates or tailings of the ores or concentrates with a leach liquor in the presence of an additive that enhances the dissolution of copper from copper minerals in the ores and concentrates by forming a complex between (a) sulfur, that has originated from copper minerals in the ores, and (b) the additive.
2. The method according to claim 1, wherein the complex comprises sulfur from the copper minerals and the additive, with the additive breaking down the passivating layer or reducing the formation of the layer and therefore allowing greater access for leaching copper from copper minerals during the method.
3. The method according to claim 1 or claim 2, wherein the additive comprises a nitrogen-containing complexing agent that includes at least two nitrogen atoms spaced by two carbon atoms to permit the additive to form complexes between sulfur, that has originated from copper minerals in the ores, and the additive.
4. The method according to any one of the preceding claims, wherein the additive is a compound that contains the following molecular scaffold or a polymer that contains the molecular scaffold repeated through the polymer:



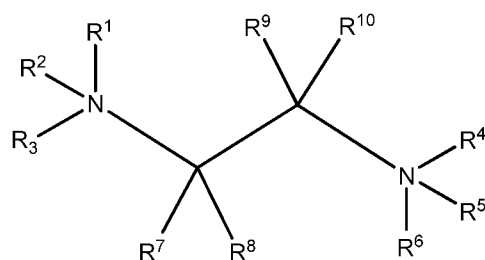
wherein, the two nitrogen atoms are each independently substituted or unsubstituted, each nitrogen atom is selected from the group consisting of a primary amine group, a secondary amine group, a tertiary amino group

the two carbon atoms may each be substituted or unsubstituted;

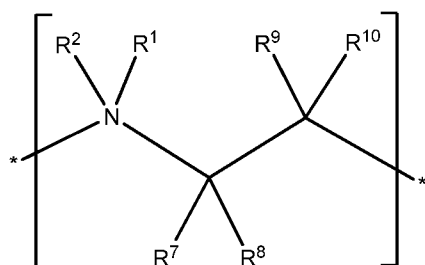
5 the bonds between the nitrogen atoms and carbon atoms in the scaffold may be single bonds or multiple bonds; and

the bonds between the two carbon atoms in the scaffold may be single bonds or multiple bonds.

10 5. The method according to any one of claims 1 to 3, wherein the additive is a compound of the formula (II) or a polymer formed from two or more monomers of the formula (II):



(II)



(III)

wherein, in formula (II) and (III),

15 R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are each independently selected from a lone pair electron, H, alkyl groups (such as C_1 to C_5 alkyl groups), alkenyl groups (such as C_2 to C_5 alkenyl groups), alkynyl groups (such as C_2 to C_5 alkynyl groups), and alkylamino groups (such as C_1 to C_5 alkylamino groups), or the

substituents on each of the two nitrogens together form an alkyl or alkynyl group that connect the two nitrogens to form a ring (e.g. the substituents together form a one or two carbon linker connecting the nitrogens to form a ring);

- 5 R^7 , R^8 , R^9 and R^{10} are each independently selected from H, alkyl (such as C_1 to C_5 alkyl), alkenyl (such as C_2 to C_5 alkenyl), alkynyl (such as C_2 to C_5 alkynyl), OH, alkyloxy groups (such as C_1 to C_5 alkyloxy groups), alkenyloxy groups (such as C_2 to C_5 alkenyloxy groups), alkynyloxy groups (such as C_2 to C_5 alkynyloxy groups), $C(=O)R$ (where R is alkyl, alkenyl or alkynyl), $C(O)OH$, $C(O)OR$ (where R is alkyl, alkenyl or alkynyl), $OC(=O)R$ (where R is alkyl, alkenyl or alkynyl), amino, alkylamino (such as C_1 to C_5 alkyl), alkenylamino (such as C_2 to C_5 alkenylamino), alkynylamino (such as C_2 to C_5 alkynylamino), $C(O)NH_2$, $C(O)NHR$ (where R is alkyl, alkenyl or alkynyl), $C(O)NR_2$ (where R is alkyl, alkenyl or alkynyl), or R^7 and R^8 together and/or R^9 and R^{10} together may be selected from =O, =NH or =NH (where R is alkyl, alkenyl or alkynyl);

and in formula (III),

R^1 or R^2 are each independently selected from the groups defined for R_1 and R_2 above or are connected to another monomer of formula (III).

- 20 6. The method according to any one of the preceding claims, wherein the concentration of the additive is up to 10 g/L, up to 5 g/L, up to 2.5 g/L, up to 1.5 g/L, up to 1.25 g/L, or up to 1 g/L, in the leach liquor.
- 25 7. The method according to any one of the preceding claims, wherein leaching includes controlling the temperature to be less than 100 °C, less than 65 °C, less than 60 °C, less than 55 °C, or less than 50 °C.
- 30 8. The method according to any one of the preceding claims, wherein leaching includes controlling the leach temperature to be at least 5 °C, at least 20 °C, at least 30 °C, or at least 50 °C.

- 5 9. The method according to any one of the preceding claims, wherein leaching includes controlling the oxidation potential of the leach liquor during an active leaching phase to be less than 900 mV, less than 800 mV, in a range of 500 to 800 mV, or in a range of 600 to 750 mV, wherein the oxidation potential is determined with respect to the standard hydrogen electrode.
- 10 10. The method according to any one of the preceding claims, wherein leaching includes controlling the pH of the leach liquor to be less than 2.5, less than 2.0, less than 1.8, or less than 1.5.
- 15 11. The method according to any one of the preceding claims, wherein leaching includes controlling the pH of the leach liquor to be greater than 0.5, or greater than 1.
12. The method according to any one of the preceding claims, wherein leaching includes bioleaching with microorganisms to assist leaching of copper.
- 20 13. The method according to any one of the preceding claims, wherein leaching includes adding chemical oxidants, such as O₂/SO₂, pyrolusite, permanganate ions, ferric ions, peroxide ions, and chlorate ions, to the leach liquor.
- 25 14. The method according to any one of the preceding claims, includes recovering copper from the leach liquor in downstream copper recovery steps.
- 30 15. The method according to any one of the preceding claims, includes adding the additive to the leach liquor continuously or periodically during the method to maintain a required concentration during the method.
16. The method according to any one of claims 1 to 14, includes adding the additive to ore fragments prior to the leaching step.

17. The method according to claim 16, includes forming agglomerates of ore fragments and adding the additive to agglomerates prior to the leaching step.
18. The method according to claim 16, includes forming agglomerates of ore fragments and adding the additive while forming agglomerates.
19. The method according to claim 16, wherein the additive is polyethylenimine (PEI) or another polymer-like additive, such as longer chain organic substances, the agglomeration step includes:
- (a) forming a PEI solution having a pH greater than pH 4.5;
 - (b) optionally heating the solution to at least 50 °C to speed up the dissolution/dilution of the PEI; and
 - (c) adding the PEI solution to ore fragments at the start of the agglomeration step, for example before other additions in the agglomeration step.
20. The method according to any one of the preceding claims, includes regenerating the leach liquor and recycling the regenerated leach liquor to the heap.
21. The method according to claim 20, includes adjusting the concentration of the additive in the regenerated leach liquor to maintain a concentration of up to 10 g/L, up to 5 g/L, up to 2.5 g/L, up to 1.5 g/L, up to 1.25 g/L, or up to 1 g/L, in the leach liquor.
22. The method according to claim 20 or claim 21, includes adding the additive to the regenerated leach liquor to maintain a concentration of up to 10 g/L, up to 5 g/L, up to 2.5 g/L, up to 1.5 g/L, up to 1.25 g/L, or up to 1 g/L, in the leach liquor.
23. The method according to claim 20 or claim 21, includes removing the additive from the regenerated leach liquor to maintain a concentration of up to 10 g/L, up to 5 g/L, up to 2.5 g/L, up to 1.5 g/L, up to 1.25 g/L, or up to 1 g/L, in the leach liquor.

24. A method of leaching copper-containing ores, such as copper-containing sulfidic ores such as sulfidic ores that contain copper minerals such as chalcopyrite and/or enargite, or concentrates of the ores or tailings of the ores or concentrates, that includes leaching copper-containing ores or concentrates or tailings of the ores or concentrates with a leach liquor in the presence of a nitrogen-containing organic complexing additive that forms a complex between sulfur, that has originated from copper minerals in the ores, and the additive.
25. The method defined in claim 24, wherein the complex comprises sulfur in a passivating layer on copper minerals and the additive, with the complex breaking down the passivating layer or reducing the formation of the layer and therefore allowing greater access for leaching copper from copper minerals during the method.
26. The method defined in claim 24 or claim 25, wherein the additive is a degradation product that forms under the conditions of the leach and is an effective additive in the terms of the invention.
27. The method defined in claim 26, wherein the degradation product is a degradation product of another said additive.
28. The method defined in any one of claims 24 to 27 wherein the nitrogen-containing complexing agent includes at least two nitrogen atoms.
29. The method defined in claim 28 wherein each of the at least two nitrogen atoms in the additive is present as a primary amine group, a secondary amine group or a tertiary amine group.

30. The method defined in any one of claims 24 to 29 wherein the nitrogen-containing complexing agent includes at least two nitrogen atoms spaced by two carbon atoms to permit the additive to form the complex.
- 5 31. The method defined in any one of claims 24 to 30 wherein the additive is as defined in claim 4 or claim 5.

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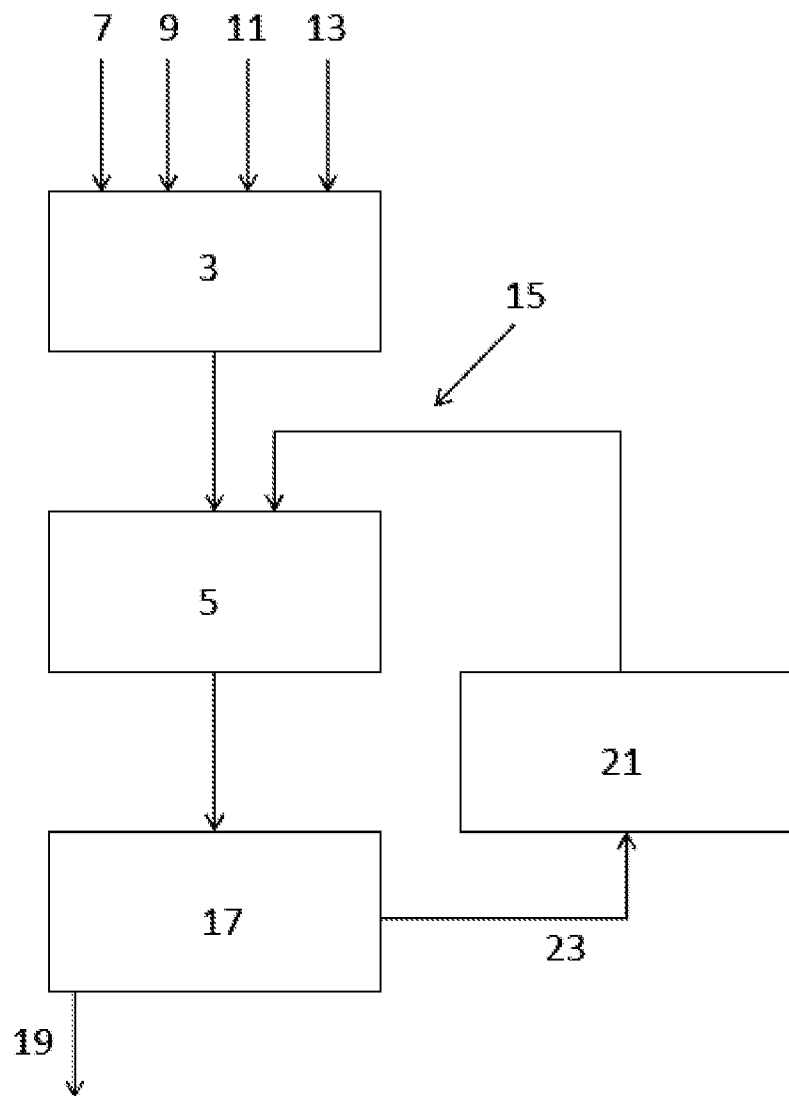


Figure 1.

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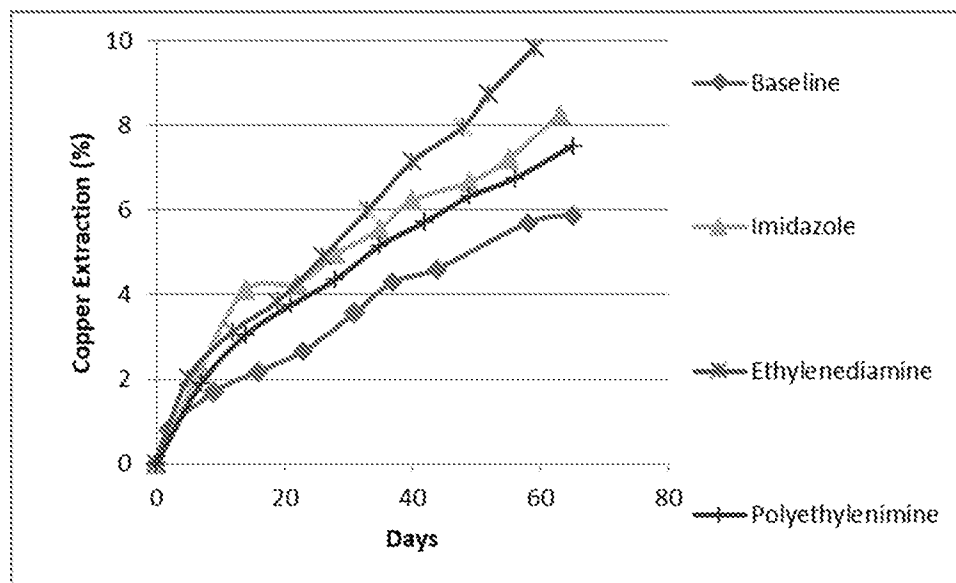


Figure 2.

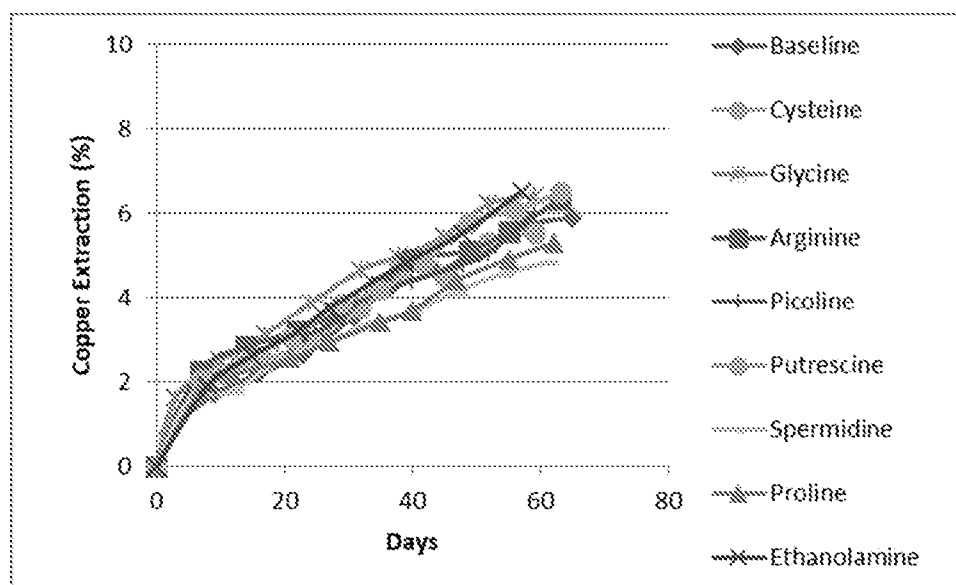


Figure 3.

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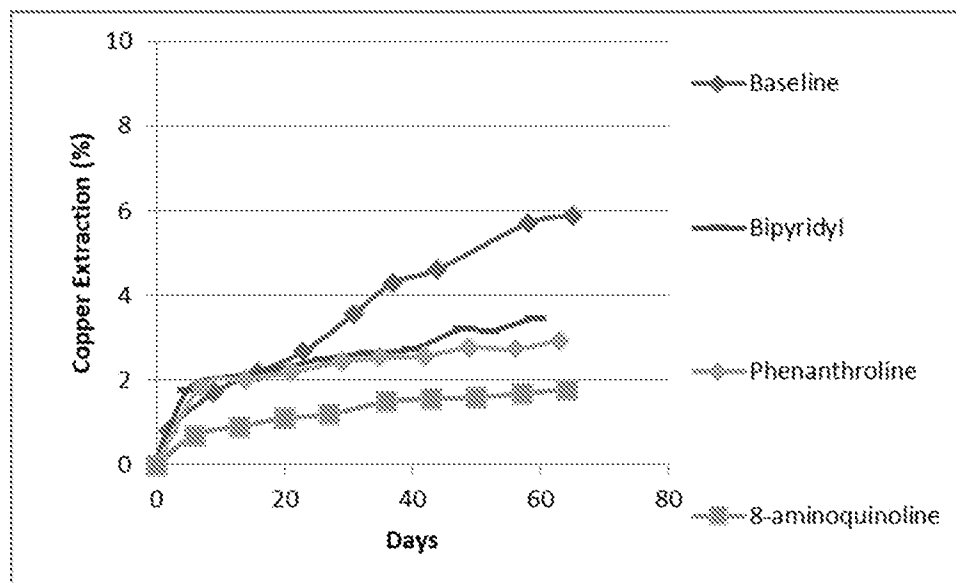


Figure 4.

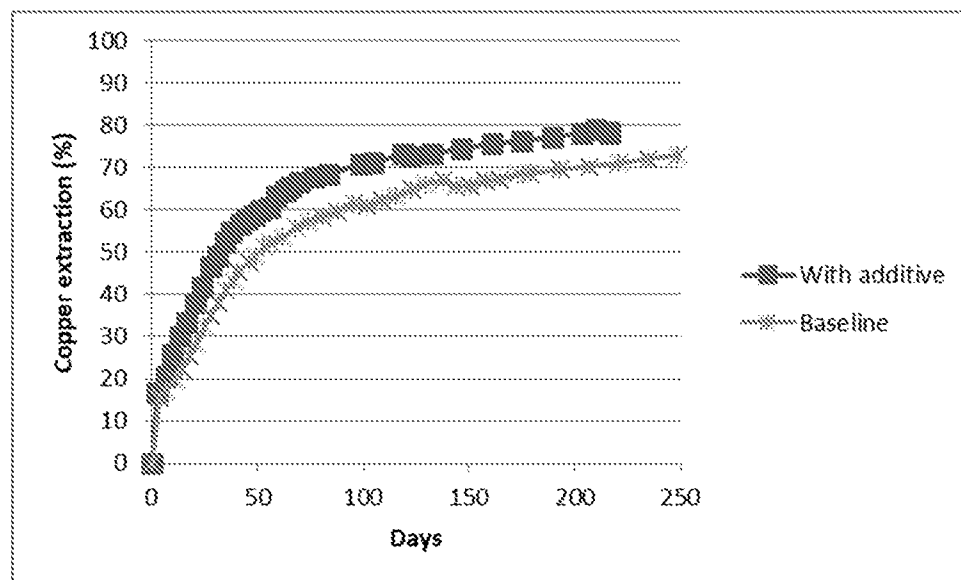


Figure 5.

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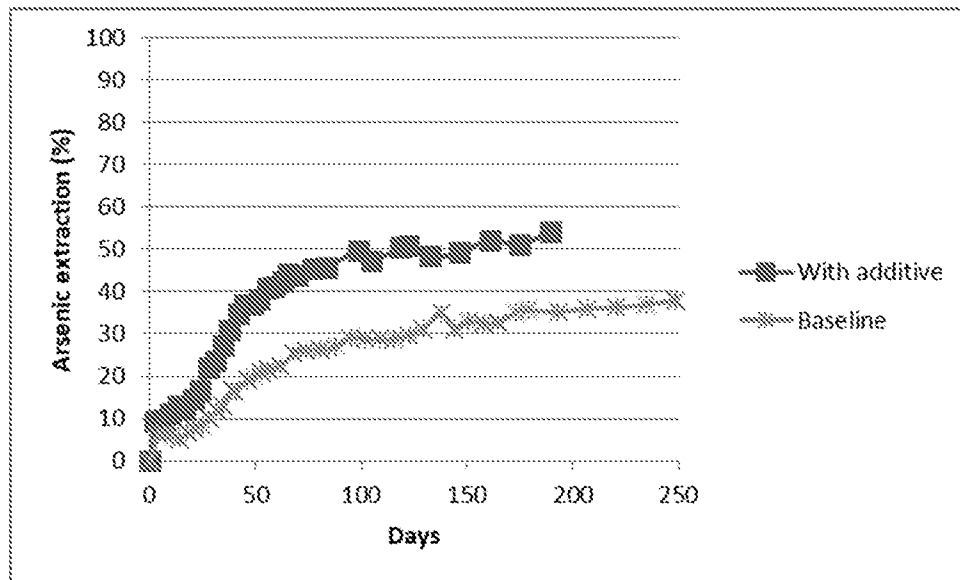


Figure 6.

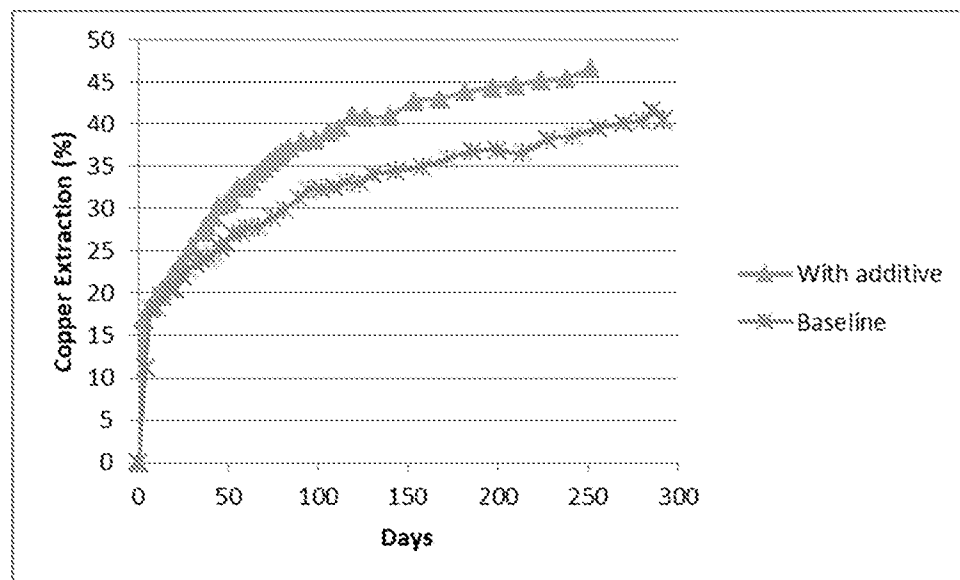


Figure 7.

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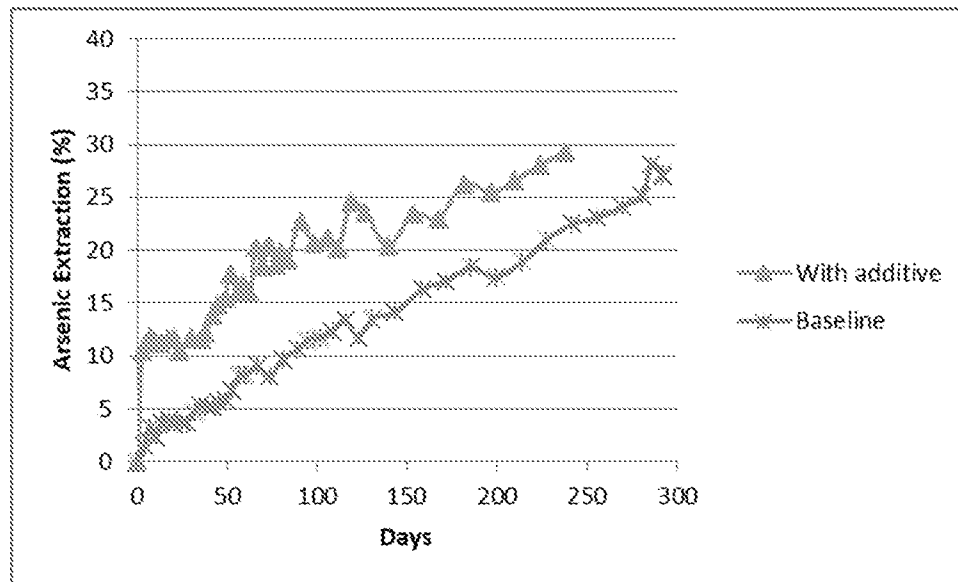


Figure 8.

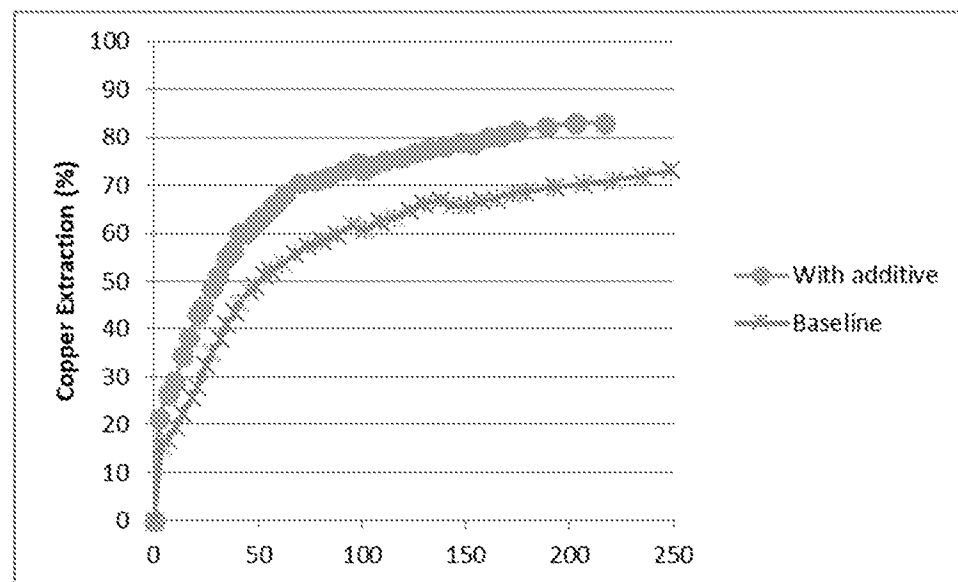


Figure 9.

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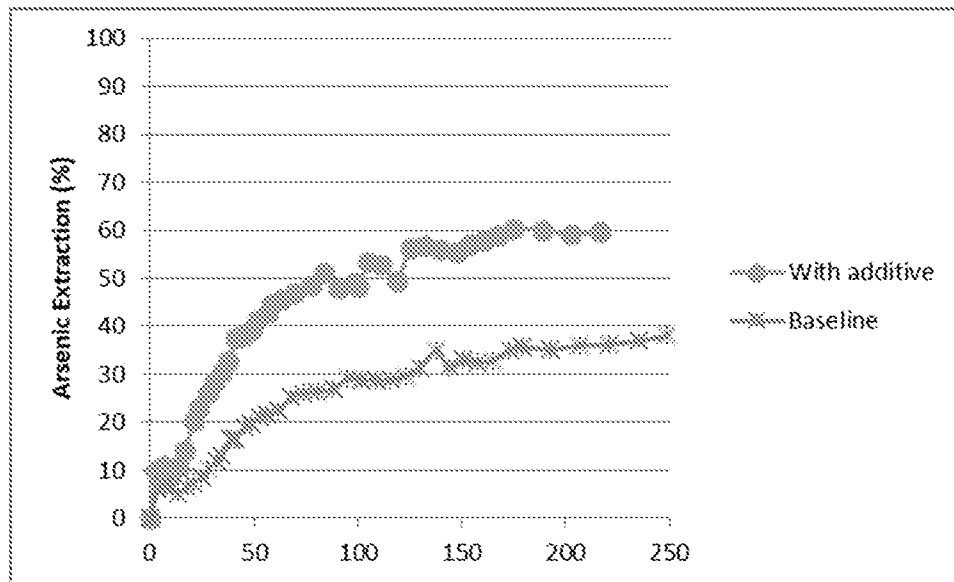


Figure 10.

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/AU2019/050383

A. CLASSIFICATION OF SUBJECT MATTER

C22B 15/00 (2006.01) C22B 3/16 (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)

PATENW, CAPLUS, REGISTRY, GOOGLE, GOOGLE SCHOLAR, ESPACENET, INSPEC: CPC/IPC marks C22B3/1625, C22B3/1666, C22B15, C22B15/0065 (in applicable databases); keywords (copper, sulfide, chalcopryrite, enargite, ethylenediamine, chelate, hydrometallurgy, leaching, ore, polyethyleneimine, ligand, complex) and like terms

CAPLUS, IP AUSTRALIA databases: Applicant/inventor name search

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	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 20 May 2019	Date of mailing of the international search report 20 May 2019
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au	Authorised officer Alan Criddle AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262832846

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including
2. ☒ Claims Nos.: **26–31**
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
See Supplemental Box
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

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

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

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

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

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2019/050383
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5411148 A (KELEBEK et al) 02 May 1995 Abstract; Col 1, ln 10–30; Examples; Claim 3	1–9, 11–25
X	US 5074993 A (KERR et al) 24 December 1991 Abstract; Examples; Claims 1 & 2	1–9, 11–25
X	US 7004326 B1 (DAI ZONGFU et al) 28 February 2006 Abstract; Col 5, ln 56–59; Col 6, ln 11–25; Claims 1, 5, 11 & 26	1–9, 11–25
X	WO 2002/099144 A1 (UNISEARCH LIMITED) 12 December 2002 Abstract; p 2, ln 9–21; p 6, ln 1–10; Claim 14	1–25
X	ZHIGANG YIN et al. Separation of Molybdenite from Chalcopyrite in the Presence of Novel Depressant 4-Amino-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)-one. Minerals. 2007, Vol. 7, 146. Abstract; Introduction; 3.2.1; Fig 2	1–25
X	WO 1998/008585 A1 (GEOCHEM TECHNOLOGIES INC) 05 March 1998 Abstract; p 3, ln 4–15; p 5, ln 21 – p 6, ln 3;p 15, ln 1–5; Examples 4 & 5	1–9, 11–25

Form PCT/ISA/210 (fifth sheet) (revised January 2019)

Supplemental Box**Continuation of Box II**

Claims 26–31 do not comply with Rule 6.2(a) because they rely on references to the description and/or drawings due to the use of the phrase: 'effective additive in the terms of the invention' in Claim 26. Since this phrase makes reference to 'the invention' generally and not to any subject matter defined in the claims, this can only be understood as a reference to the description and/or drawings. Claims 27–31 rely on the same reference due to their appendage to Claim 26.

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2019/050383	
This Annex lists known 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.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
US 5411148 A	02 May 1995	US 5411148 A	02 May 1995
		AU 5063393 A	02 Jun 1994
		AU 660858 B2	06 Jul 1995
		BR 9304723 A	17 May 1994
		CA 2082831 A1	14 May 1994
		FI 935008 A	14 May 1994
		FI 112921 B	13 Feb 2004
		ZA 9308461 B	23 Jun 1994
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		ZW 15293 A1	06 Jul 1994
US 5074993 A	24 December 1991	US 5074993 A	24 Dec 1991
		AU 4244489 A	26 Apr 1990
		AU 611059 B2	30 May 1991
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		BR PI0516117 A	26 Aug 2008
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		FI 121737 B	31 Mar 2011
		MX 2007003955 A	04 Mar 2008
		RU 2007116962 A	20 Nov 2008
		WO 2006037206 A1	13 Apr 2006
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		WO 02099144 A1	12 Dec 2002
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		US 2004213715 A1	28 Oct 2004
		ZA 200400052 B	17 Jan 2005
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		AU 4184297 A	19 Mar 1998
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.			

INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2019/050383	
This Annex lists known 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.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(revised January 2019)			