(54) Title: SEPARATION OF COBALT FROM MANGANESE USING ORGANOPHOSPHORIC ACID SOLVENT EXTRACTION

(57) Abstract: A method of separating cobalt from impurity elements including manganese in an aqueous leach solution, the process including an organophosphoric acid solvent extraction stage including the steps of: (a) contacting the aqueous leach solution with an organic solution comprising an organophosphoric acid in an organic solvent to produce a loaded organic solution containing manganese and, to the extent that they are present, calcium, zinc and copper, and a some cobalt; and an aqueous raffinate solution containing most of the cobalt; (b) scrubbing the loaded organic solution with an aqueous scrub solution containing manganese and copper to produce a scrubbed organic solution containing less cobalt and a spent aqueous scrub solution containing some cobalt, as well as manganese; (c) recycling the spent aqueous scrub solution to step (a); (d) selectively stripping the scrubbed organic solution to remove a portion of the manganese and copper to form the aqueous scrub solution for use in step (b); and (e) recovering cobalt from the aqueous raffinate produced in step (a).
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
SEPARATION OF COBALT FROM MANGANESE USING ORGANOPHOSPHORIC
ACID SOLVENT EXTRACTION

The present invention relates to a method of
5 separating cobalt from other elements contained in an
aqueous leach solution.

The world mineral industry is experiencing an
unprecedented interest in nickel-cobalt extraction from
10 laterite ores through high pressure acid leach (HPAL) and
solvent extraction - electrowinning (SX-EW) processes. In
WA, three nickel laterite projects have been commissioned.
These are the Cawse project of Centaur Mining Ltd, the
Bulong project of Preston Resources and the Murrin Murrin
project of Anaconda Nickel Ltd. The HPAL process for the
three projects is very similar, however the down stream
processes (including SX) differ substantially.

In the Murrin Murrin process (Motteram et al.,
1996), a sulfide precipitation is used to separate the
nickel, cobalt, copper and zinc from impurities such as
calculator, magnesium and manganese which remain in the leach
solution. After solids/liquid separation, the nickel,
cobalt, copper and zinc are re-leached under pressure with
acid. Further solution purification is needed to separate
nickel and cobalt from copper and zinc. The cobalt is then
separated from nickel by solvent extraction with Cyanex
272. The nickel and cobalt are recovered by reduction with
hydrogen. The drawbacks of the Murrin Murrin process are:
30 • the separation of manganese from cobalt by sulphide
precipitation is incomplete and causes problems in the
downstream processes,
• the leaching of sulphides needs high pressure and high
temperature, indicating high capital and operating
35 costs, and
• the separation of other impurities such as copper and
zinc from nickel and cobalt needs separate processes.
In the Cawse process (Manson et al., 1997), a hydroxide precipitation is used to separate the impurities such as calcium, magnesium and manganese (partly). After solids/liquid separation, the nickel, cobalt, copper and zinc are re-leached with an ammoniacal solution. Nickel and copper are separated from cobalt and zinc by solvent extraction with LIX84I. Further solution purification is needed to separate nickel from copper and cobalt from zinc. The nickel is recovered by electrowinning while cobalt is precipitated as sulphide. The drawbacks of the Cawse process are:

- the use of ammoniacal leaching to separate manganese from cobalt results in complexity of the flowsheet and causes serious problems in the downstream processes,
- the reductive stripping of cobalt from organic extractant and the re-oxidation of the organic extractant causes organic degradation (Kindred, 2000), which in turn results in crude formation,
- ammonia is expensive and the scrubbing and recovery of ammonia are difficult, and
- cobalt product containing zinc is a semi-product, indicating revenue loss.

The Bulong process (Taylor and Cairns, 1997), uses a direct solvent extraction approach. Cobalt, copper, zinc and manganese are separated from nickel, calcium and magnesium by solvent extraction with Cyanex 272. The nickel in the raffinate is separated from calcium and magnesium by solvent extraction with Versatic 10 and then electrowon. The solution containing cobalt, copper, zinc and manganese is subjected to sulphide precipitation, solids/liquid separation and acid pressure re-leach to separate cobalt, copper and zinc from manganese. The copper is eliminated from the solution by ion exchange and zinc by solvent extraction with D2EHPA. The cobalt is then recovered from the purified solution by electrowinning. The drawbacks of
the Bulong process are that:

- manganese is separated from cobalt by sulphide precipitation and other impurities are separated by different further processes (ion exchange and further SX),
- gypsum precipitation occurs in both Cyanex 272 and Versatic 10 circuits, and
- aqueous feed solution with its original volume is treated twice - in both the Cyanex and Versatic 10 SX circuits. This requires larger circuits (higher capital expenditure) than if the valuable metal (nickel) were concentrated by extraction into the organic phase in the first circuit.

An object of the present invention is to provide a practical process for separating cobalt (and nickel if it is present) from impurities (particularly manganese) contained in leach solutions. An object of a preferred embodiment of the invention is to provide process that also provides steps for the recovery of cobalt from such solutions.

Accordingly, the present invention provides a method of separating cobalt from impurity elements including manganese contained in an aqueous leach solution, the process including the steps of:

(a) contacting the aqueous leach solution with an organic solution comprising an organophosphoric acid (and optionally a modifier) in an organic solvent to produce a loaded organic solution containing manganese and, to the extent that they are present, calcium, zinc and copper, and a some cobalt and, if present in the aqueous leach solution, some nickel and magnesium, and an aqueous raffinate solution containing most of the cobalt and, if they were present in the leach solution, nickel and magnesium;
(b) scrubbing the loaded organic solution with an aqueous scrub solution containing (mainly) manganese and copper to produce a scrubbed organic solution containing less cobalt (and nickel if nickel was present in the aqueous leach solution) and a spent aqueous scrub solution containing some cobalt (and nickel if nickel was present in the aqueous leach solution), as well as manganese;

10 (c) recycling the spent aqueous scrub solution to step (a);

(d) selectively stripping the scrubbed organic solution to remove a portion of the manganese and copper to form the aqueous scrub solution for use in step (b); and

15 (e) recovering cobalt from the aqueous raffinate produced in step (a).

As will be understood to persons skilled in the art of the invention, the aqueous leach solution may be the leach solution obtained from acid digestion of an ore or ore concentrate, or may be a leach solution that has been subjected to other procedures to remove undesired elements therefrom. For instance, the leach solution may be one that has been subjected to a preliminary iron precipitation step.

In most commercial situations, the method would involve the further step (f) of bulk stripping the selectively stripped organic solution from step (d) to remove a large proportion or almost all of the elements therein to regenerate the organic solution for recycling to step (a).

35 In a preferred embodiment of the invention, nickel is present in the aqueous leach solution, and in step (e) nickel could also recovered from the aqueous
raffinate produced in step (a).

In the most preferred embodiment of the invention, the organophosphoric acid is di-2-ethylhexyl phosphoric acid (D2EHPA), however it will be appreciated by persons skilled in the art that an organophosphoric acid having extraction characteristics similar to D2EHPA could be used. Organophosphoric acids have the formula \((R'O)\_2PO\_2H\), in which \(R\) represents an organic group. The two organic groups \(R\), which may be the same or different, can be selected from optionally substituted branched, straight chained or cyclic alkyl, alkenyl or alkynyl groups. Preferably the organic groups are fairly bulky, and have a minimum of 4 carbon atoms, more preferably from 6 to 18 carbon atoms. The organic groups may suitably be n-octyl, cyclooctyl or 2-ethylhexyl.

If a modifier is required to assist phase separation, the modifier can any suitable modifier that improves separation of the organic and aqueous phases. Suitable modifiers include 2-ethylhexanol, isodecanol, isotridecanol and tri n-butyl phosphate (TBP). TBP is the preferred modifier.

The organic solvent may be any suitable organic solvent for the organophosphoric acid that achieves good phase separation from the aqueous phase with the modifier, and accordingly the organic solvent could be considered to be a diluent for the organophosphoric acid. Kerosene is the most common solvent/diluent used for this purpose due to its low cost and availability.

The scrubbed organic solution may be selectively stripped of manganese and copper by contacting it with an acid. Sulphuric acid is preferred due to its low cost, however other acids such as HCl and HNO\(_3\) could be used. The partially stripped scrubbed organic solution may be
fully stripped of impurity elements by contacting the partially stripped scrubbed organic solution with a second (stronger) acid. Accordingly, when sulphuric acid is used as the first acid, a more concentrated sulphuric acid or hydrochloric acid may be used as the second acid to fully strip the partially stripped scrubbed organic solution of the impurity elements to avoid gypsum formation if the aqueous solution is saturated with calcium. The fully stripped organic solution may then be recycled to step (a).

The range of the Mn and Cu in the aqueous scrub solution will depend on how much Co (and Ni) is to be scrubbed and the aqueous to organic (A/O) ratio. Preferably, the mole ratio of \((\text{Mn+Cu})/\text{(Co+Ni)}\) is at least 1.5 for complete scrubbing.

The amount of organophosphoric acid in the organic solution used in step (a) will depend on the concentration of the elements to be extracted and the A/O ratio, however the amount would typically be in the range of from 3% to 35% v/v, with a preferred range of 5% to 25%. At levels above 35% the organic solution will be too viscous resulting in lower extraction kinetics.

The amount of modifier in the organic solution used in step (a) will also vary. The range of modifier will typically be in the range of 3% to 15% v/v, with a preferred range of 5% to 10%.

Preferably, the pH of the aqueous phase is maintained in a range from 3.0 to 4.5 and more preferably 3.5 to 4.0 in step (a). The temperature is preferably maintained in the range of from 10°C to 60°C, more preferably from 20 to 40°C. Whilst temperatures as low as 10°C are achievable, a temperature lower than 15°C results in high viscosity. At temperatures higher than 60°C there is a risk of evaporation and degradation of the organic
phase.

The aqueous to organic ratio (A/O) in step (a) is most preferably 1:1, but may lie in the range from 10:1 to 1:10, and preferably 1:2 to 5:1. The aqueous to organic ratio maintained in step (b) may lie within the range of from 1:5 to 1:20, but preferably it is in the range of 1:5 to 1:20.

The cobalt may be recovered from the solution by any suitable means. For example, cobalt could be recovered by electrowinning or precipitation.

In the situation where nickel is present, the method may be combined with an organophosphinic acid solvent extraction step as described in further detail below, to effect separation of cobalt from nickel.

As a consequence, the present invention also provides a method of separating cobalt from other elements contained in an aqueous leach solution, the process including the steps of subjecting the aqueous leach solution to successive solvent extraction steps using an organophosphoric acid and an organophosphinic acid as extractants.

If the leach solution is one containing manganese, zinc, copper, cobalt, nickel, calcium and magnesium (as would be the case for a lateritic or bio-leach solution), and the organophosphinic acid is used as the first organic extractant, it transfers manganese, zinc, copper and cobalt into an organic strip liquor leaving an aqueous raffinate containing nickel, calcium and magnesium. Treatment of the organic strip liquor from the organophosphinic acid extraction stage with the organophosphoric acid results in a loaded organic solution containing manganese, zinc and copper and an aqueous
raffinate containing cobalt.

If the leach solution is one containing manganese, zinc, copper, cobalt, nickel, calcium and magnesium (as would be the case for a lateritic or bio-leach solution), and the organophosphoric acid is used as the first organic extractant, the loaded organic solution contains manganese, calcium, zinc and copper and the aqueous raffinate solution contains cobalt, nickel and magnesium. Subsequent solvent extraction of the aqueous raffinate with organophosphinic acid results in an organic phase containing cobalt and an aqueous raffinate containing nickel and magnesium.

In the most preferred embodiment involving successive organophosphoric and organophosphinic acid extraction stages, the organophosphinic acid is di-2,4,4-trimethylpentyl phosphinic acid (eg Cyanex 272). However it will be appreciated by persons skilled in the art that any organophosphinic acid having extraction characteristics similar to di-2,4,4-trimethylpentyl phosphinic acid could be used. Organophosphinic acids have the formula R₂PO₂H, in which R represents an organic group. The two organic groups R, which may be the same or different, can be selected from optionally substituted branched, straight chained or cyclic alkyl, alkenyl or alkynyl groups. Preferably the organic groups are fairly bulky, and have a minimum of 4 carbon atoms, more preferably from 6 to 18 carbon atoms. The organic groups are preferably unsubstituted branched, straight chained or cyclic alkyl groups, and may suitably be n-octyl, cyclooctyl, 2-ethylhexyl or 2,4,4-trimethylpentyl.

The term "alkyl" used either alone or in a compound word such as "optionally substituted alkyl" or "optionally substituted cycloalkyl" denotes straight chain, branched or mono- or poly- cyclic alkyl, preferably C₁-30
alkyl or cycloalkyl. Examples of straight chain and branched alkyl include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, amyl, isoamyl, sec-amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, heptyl, 5-methylhexyl, 1-methylheptyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, nonyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-methyloctyl, 1-, 2-, 3-, 4- or 5-ethylheptyl, 1-2- or 3-propylhexyl, decyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- and 8-methylnonyl, 1-, 2-, 3-, 4-, 5- or 6-ethyloctyl, 1-, 2-, 3- or 4-propylheptyl, undecyl 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-methyldecan, 1-, 2-, 3-, 4-, 5-, 6- or 7-ethylnonyl, 1-, 2-, 3-, 4- or 5-propyldecal, 1-, 2- or 3-butylheptyl, 1-pentylhexyl, dodecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 10-methylundecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- or 8-ethyldodecal, 1-, 2-, 3-, 4-, 5- or 6-propylundecyl, 1-, 2-, 3- or 4-butyldecal, 1-2-pentylheptyl and the like. Examples of cyclic alkyl include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl and cyclooctyl and the like. The alkyl may optionally be substituted by any non-deleterious substituent.

In this specification "optionally substituted" means that a group may or may not be further substituted with one or more groups selected from alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenoxy, aryloxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, amino, alkylamino, dialkylamino, alkenylamino, alkynylamino, arylamino, diarylamino, benzylamino,
dibenzylamino, acyl, alkenylacetyl, alkynylacetyl, arylacetyl, acylamino, diacylamino, acyloxy, alkylsulphonyloxy, arylsulphonyloxy, heterocyclyl, heterocycloxy, heterocyclamino, haloheterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, benzylthio, acylthio and the like.

Suitable optional substituents will be chosen on the basis that the organophosphinic or organophosphoric acid have the desired extraction characteristics, and the substituents do not react with any other component of the mixture under the given extraction conditions.

The term "halogen" denotes fluorine, chlorine, bromine or iodine.

The amount of organophosphinic acid in the organic solution used in the organophosphinic acid solvent extraction step will depend on the concentration of the elements to be extracted and the A/O ratio, however the amount would typically be in the range of from 3% to 35% v/v, with a preferred range of 5% to 25%. At levels above 35% the organic solution will be too viscous resulting in lower extraction kinetics.

It is also advantageous to use a modifier in the organophosphinic acid extraction stage as for the organophosphoric acid extraction stage. Again, TBP is preferred.

Preferably, the pH of the aqueous phase is maintained in a range from 5.0 to 6.0 in the organophosphinic acid solvent extraction circuit. The temperature is preferably maintained in the range of from 10°C to 60°C, more preferably from 20 to 40°C. Whilst temperatures as low as 10°C are achievable, a temperature lower than 15°C results in high viscosity. At temperatures
higher than 60°C there is a risk of evaporation and degradation of the organic phase.

The aqueous to organic ratio (A/O) in the organophosphinic acid solvent extraction circuit is most preferably 1:1, but may lie in the range from 3:1 to 1:3.

The cobalt extracted into the loaded organic phase in the organophosphinic acid extraction circuit is stripped therefrom and either recovered (when following the organophosphoric acid extraction stage) or directed to the organophosphoric acid extraction stage. In the stripping stage, the A/O ratio may be from 1:2 up to 1:200, and the pH from 2.0 to 4.0. Other details concerning the organophosphinic acid extraction stage are well within the knowledge and experience of persons in the art of the invention.

The steps outlined above can be conducted in combination with other solvent extraction steps and optionally one or more precipitation steps to separate certain elements from each other. For instance, it is common in the art of the invention for a preliminary iron precipitation step to be conducted to precipitate out iron to leave an aqueous leach solution containing the target elements. However, it is a major advantage of the process of the present invention that precipitation steps involving precipitation out of the target elements (such as cobalt and nickel) and re-leaching of the precipitate can be avoided. Even when such a precipitation step is required, it is to be noted that no precipitation steps for the purpose of separating manganese from cobalt are required. Therefore, in a preferred embodiment of the invention the process does not include a sulphide precipitation stage for separating cobalt from manganese. In a more preferred embodiment of the invention, the process does not include a precipitation step involving precipitation out of the
target elements and re-leaching of the precipitate.

It will be well understood to persons skilled in the art of the invention that scrubbing stages of the type well known in the art may be used for recovering elements even if the scrubbing stages are not specifically mentioned. The design of the optimum arrangement of scrubbing stages will depend on the specific aqueous leach solution and the elements desired to be recovered therefrom (and target percentage recovery levels).

The present invention also provides a plant for conducting the methods and processes described above, the plant including:

- a solvent extraction contactor in which the aqueous leach solution is contacted with the organophosphoric acid-containing organic solution;
- a scrubbing contactor for scrubbing the loaded organic solution generated in solvent extraction contactor;
- a loaded organic solution conduit for conducting the loaded organic solution generated in the solvent extraction contactor to the scrubbing contactor;
- a stripping contactor in which the scrubbed organic solution generated in the scrubbing contactor is subjected to selective stripping to generate the aqueous scrub solution for use in the scrubbing contactor;
- a scrubbed organic solution conduit for conducting the scrubbed organic solution to the stripping contactor;
- an aqueous scrub solution conduit for conducting the aqueous scrub solution to the scrubbing contactor; and
- a spent aqueous scrub solution conduit for conducting the spent aqueous scrub solution from the scrubbing contactor to the solvent extraction contactor.

Preferably the plant further includes an organic solution recycle conduit for conducting the partially
stripped scrubbed solution from the stripping contactor to the solvent extraction contactor. More preferably, a bulk stripping contactor is located in this recycle conduit, in which the partially stripped scrubbed solution is stripped of remaining impurities before being conducted to the solvent extraction contactor.

As will be understood to persons skilled in the art of the invention, the solvent extraction contactor is preferably a countercurrent solvent extraction contactor. Similarly, further scrubbing stages and vessels may be included in the plant.

If the process of the invention also includes the organophosphinic acid solvent extraction stage, the plant will also include an organophosphinic acid solvent extraction contactorextraction circuit. This circuit will include an organophosphinic acid solvent extraction contactor (preferably countercurrent), and one or more scrubbing contactors, together with the appropriate conduits for passing the various streams between the vessels in the plant. The plant will also include a cobalt recovery stage, for instance a cobalt precipitation vessel or an electrolytic cell in which a cobalt electrowinning process can be conducted. The arrangement of an appropriate plant including all of these elements is well within the skill of a person in the art of the invention now that the direction has been made to conduct the process for recovering cobalt as described above.

Some preferred embodiments of the invention are described in the accompanying examples and figures, in which:

Figure 1 illustrates a flow chart for the di-2-ethylhexyl phosphoric acid solvent extraction step of the process of one preferred embodiment of the invention, and represents schematically a plant of one
preferred embodiment of the invention;
Figure 2 illustrates a schematic flow chart for one
embodiment of the successive organophosphoric and
organophosphinic acid solvent extraction process of
the invention, and represents schematically a plant
for this embodiment of the invention; and
Figure 3 illustrates a schematic flow chart for a
second embodiment of the successive organophosphinic
and organophosphoric acid solvent extraction process
of the invention, and represents schematically a plant
for this embodiment of the invention.

The first aspect of the invention is described in
detail with reference to Figure 1. An aqueous leach
solution 1 (which may be the input aqueous leach solution -
the "cobalt solution" in Figure 3 - or the strip liquor in
Figure 2, or any other leach solution) is fed into a
countercurrent solvent extraction contactor 2 in which the
aqueous leach solution 1 is contacted with an organic
extractant solution 3 comprising a solution of an
organophosphoric acid (preferably D2EHPA) and a modifier
(preferably TBP) in an organic solvent (preferably
kerosene). The aqueous raffinate 4 from the solvent
extraction contains most of the cobalt, nickel and a large
proportion of the magnesium from which the cobalt and
nickel may be recovered. However, it is noted that if
preliminary solvent extraction and/or precipitation stages
have been conducted on the leach solution, as in the case
of the Figure 2 process, in which magnesium, calcium and
nickel have already been separated from the aqueous leach
solution, the aqueous raffinate 4 from the organophosphoric
extraction stage contains cobalt.

The loaded organic liquor 5 from the solvent
extraction contactor 2 is scrubbed in a scrubbing contactor
6 with a scrub solution 7 containing manganese and copper.
Scrubbed loaded organic solution 8 is selectively stripped
with a first acid, a dilute sulphuric acid 9, in a stripping contactor 10 to form scrub solution 7, part of which is recycled to scrubbing contactor 6. Partially stripped organic extractant 11 is then stripped of all impurities with a second acid, dilute hydrochloric acid 12, in a bulk stripping contactor 13. Stripped organic solution 3 is recycled to extraction contactor 2.

Flow sheets for alternative embodiments of the invention involving successive organophosphoric and organophosphinic acid solvent extraction stages are illustrated in Figures 2 and 3. In these two figures, the boxes referring to "D2EHPA SX" (di-2-ethylhexyl phosphoric acid solvent extraction) should be understood to be a short-hand reference to all of the steps outlined in Figure 1.

Figure 2 shows the aqueous leach solution being subjected to a first solvent extraction with an organophosphinic acid, followed by a second solvent extraction step with di-2-ethylhexyl phosphoric acid. Figure 3 shows the aqueous leach solution being subjected to a first solvent extraction using di-2-ethylhexyl phosphoric acid dissolved in kerosene, followed by solvent extraction of the aqueous raffinate with an organophosphinic acid.

**EXAMPLE 1 - Figure 1 process**
Separation of nickel and cobalt from manganese and other impurities, using a synthetic nickel laterite acid leach solution.

1. Extraction

The aqueous solution was a synthetic iron-free laterite leach solution containing 2.60 g/L Ni, 0.24 g/L
Co, 0.27 g/L Zn, 0.52 g/L Ca, 0.09 g/L Cu, 1.87 g/L Mn and 2.89 g/L Mg. The organic solution consisted of 12% di-2-ethylhexyl phosphoric acid (D2EHPA), 2.5% tri-n-butyl phosphate (TBP) and 85.5% kerosene (Shell sol 2046), all by volume. Four counter-current extraction stages were used at an A/O flowrate ratio of 1:1. The pH in the four mixers was controlled at 3.7 using three pH controllers with the addition of ammonia solution (Fig 1). The results are shown in Table 1. All the zinc, calcium, manganese and copper were extracted in four stages. Some 12.6% cobalt, 20% magnesium and no nickel were co-extracted. The raffinate contained only cobalt, nickel and magnesium.

Table 1 Summary of semi-continuous extraction test results

<table>
<thead>
<tr>
<th>Metal name</th>
<th>Concentration (g/L)</th>
<th>Total extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In feed</td>
<td>In loaded organic</td>
</tr>
<tr>
<td>Zn</td>
<td>0.265</td>
<td>0.255</td>
</tr>
<tr>
<td>Ca</td>
<td>0.516</td>
<td>0.605</td>
</tr>
<tr>
<td>Mn</td>
<td>1.865</td>
<td>1.775</td>
</tr>
<tr>
<td>Cu</td>
<td>0.094</td>
<td>0.089</td>
</tr>
<tr>
<td>Co</td>
<td>0.240</td>
<td>0.031</td>
</tr>
<tr>
<td>Ni</td>
<td>2.597</td>
<td>0.000</td>
</tr>
<tr>
<td>Mg</td>
<td>2.893</td>
<td>0.590</td>
</tr>
</tbody>
</table>

2. Scrubbing

Two scrubbing stages were used with a combined solution of manganese (6.78 g/L) and copper (0.35 g/L) at an A/O flowrate ratio of 1:5. Scrubbing results are listed in Table 2. The cobalt and nickel scrubbing efficiencies were 100% with no cobalt and nickel being left in the organic solution. This scrub raffinate containing 0.142 g/L cobalt would be recycled back to the feed. By doing this,
the cobalt and nickel recovery would approach 100%.

Table 2 Summary of scrubbing test results using a combined Mn and Cu scrub solution

<table>
<thead>
<tr>
<th>Metal name</th>
<th>Concentration (g/L)</th>
<th>Total</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Scrub solution</td>
<td>loaded organic</td>
<td>scrubbed organic</td>
</tr>
<tr>
<td>Zn</td>
<td>0.000</td>
<td>0.255</td>
<td>0.256</td>
</tr>
<tr>
<td>Ca</td>
<td>0.035</td>
<td>0.605</td>
<td>0.610</td>
</tr>
<tr>
<td>Mn</td>
<td>6.781</td>
<td>1.775</td>
<td>3.095</td>
</tr>
<tr>
<td>Cu</td>
<td>0.349</td>
<td>0.089</td>
<td>0.146</td>
</tr>
<tr>
<td>Co</td>
<td>0.000</td>
<td>0.031</td>
<td>0.000</td>
</tr>
<tr>
<td>Ni</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Mg</td>
<td>0.019</td>
<td>0.590</td>
<td>0.000</td>
</tr>
</tbody>
</table>

3. Selective stripping

One selective strip stage was used at an A/O flowrate ratio of 1:5 with 14.9 g/L sulphuric acid. The results are shown in Table 3. The strip raffinate contained 7.3 g/L manganese and 0.54 g/L copper, which was just slightly higher than the scrubbing solution used in the previous stage (6.78 g/L manganese and 0.35 g/L copper). However this could be easily corrected by using slightly more dilute sulphuric acid for stripping, say 12 g/L.

4. Bulk stripping

Two bulk strip stages were used at an A/O flowrate ratio of 1:5 with 37 g/L hydrochloric acid. The results are also shown in Table 3. All the zinc, calcium, copper and manganese were stripped. If no calcium is present in the feed, sulphuric acid can be used for bulk
stripping.

Table 3  Summary of semi-continuous stripping test results with an A/O ratio of 1:5

<table>
<thead>
<tr>
<th>Metal name</th>
<th>Concentration (g/L)</th>
<th>Strip raffinate 1</th>
<th>Total strip efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Scrubbed organic</td>
<td>Stripped organic 1</td>
<td></td>
</tr>
<tr>
<td>(Selective strip, 14.9 g/L H₂SO₄)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.256</td>
<td>0.255</td>
<td>0.022</td>
</tr>
<tr>
<td>Ca</td>
<td>0.610</td>
<td>0.405</td>
<td>0.280</td>
</tr>
<tr>
<td>Mn</td>
<td>3.095</td>
<td>1.570</td>
<td>7.319</td>
</tr>
<tr>
<td>Cu</td>
<td>0.146</td>
<td>0.030</td>
<td>0.540</td>
</tr>
<tr>
<td>(Bulk strip, 36.6 g/L HCl)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.255</td>
<td>0.000</td>
<td>1.494</td>
</tr>
<tr>
<td>Ca</td>
<td>0.405</td>
<td>0.000</td>
<td>2.401</td>
</tr>
<tr>
<td>Mn</td>
<td>1.570</td>
<td>0.000</td>
<td>8.679</td>
</tr>
<tr>
<td>Cu</td>
<td>0.030</td>
<td>0.000</td>
<td>0.159</td>
</tr>
</tbody>
</table>

EXAMPLE 2 – Figure 1 process
Separation of nickel and cobalt from manganese and other impurities, using a synthetic nickel laterite acid leach solution with high chloride and magnesium concentrations.

1. Extraction

The chloride and magnesium concentration in the leach solution could be very high if saline water is used as process water in the plant. The aqueous solution was a synthetic laterite leach solution containing 2.67 g/L Ni, 0.20 g/L Co, 0.29 g/L Zn, 0.50 g/L Ca, 0.08 g/L Cu, 1.80 g/L Mn, 13.3 g/L Mg and 17.7 g/L Cl. The organic solution
consisted of 12% di-2-ethylhexyl phosphoric acid (D2EHPA), 2.5% tri-n-butyl phosphate (TBP) and 85.5% kerosene (Shellsol 2046), all by volume. Four counter-current extraction stages were used at an A/O flowrate ratio of 1:1. The pH in the four mixers was controlled at 3.70 using three pH controllers with the addition of ammonia solution. The results are shown in Table 4.

All the zinc, calcium, manganese and copper were extracted in four stages. Some 15.81% cobalt, 8.76% magnesium, 0.46% nickel and 2.84% chloride were co-extracted. The raffinate contained only cobalt, nickel, magnesium and chloride, which would go to the next solvent extraction process.

Table 4 Semi-continuous extraction test results

<table>
<thead>
<tr>
<th>Metal name</th>
<th>Concentration (g/L)</th>
<th>Total extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In feed</td>
<td>In loaded organic</td>
<td>In raffinate</td>
</tr>
<tr>
<td>Zn</td>
<td>0.288</td>
<td>0.273</td>
</tr>
<tr>
<td>Ca</td>
<td>0.495</td>
<td>0.545</td>
</tr>
<tr>
<td>Mn</td>
<td>1.814</td>
<td>1.730</td>
</tr>
<tr>
<td>Cu</td>
<td>0.076</td>
<td>0.070</td>
</tr>
<tr>
<td>Co</td>
<td>0.198</td>
<td>0.029</td>
</tr>
<tr>
<td>Ni</td>
<td>2.668</td>
<td>0.010</td>
</tr>
<tr>
<td>Mg</td>
<td>13.33</td>
<td>0.995</td>
</tr>
<tr>
<td>Cl</td>
<td>17.96</td>
<td>0.330</td>
</tr>
</tbody>
</table>

2. Scrubbing

Two scrubbing stages were used with a combined solution of manganese (8.88 g/L) and copper (0.37 g/L) at an A/O flowrate ratio of 1:5. The scrubbing results are listed in Table 5. The cobalt and nickel scrubbing efficiencies were 100% with no cobalt and nickel being left in the organic solution. The scrub raffinate containing 0.124 g/L cobalt and 0.064 g/L nickel would be recycled back to the feed. By
doing this, the cobalt and nickel recovery would approach 100%.

Table 5 Semi-continuous scrubbing test results

<table>
<thead>
<tr>
<th>Metal name</th>
<th>Concentration (g/L)</th>
<th>Scrub efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Scrub solution</td>
<td>loaded organic</td>
</tr>
<tr>
<td>Zn</td>
<td>0.000</td>
<td>0.273</td>
</tr>
<tr>
<td>Ca</td>
<td>0.032</td>
<td>0.545</td>
</tr>
<tr>
<td>Mn</td>
<td>8.883</td>
<td>1.730</td>
</tr>
<tr>
<td>Cu</td>
<td>0.365</td>
<td>0.070</td>
</tr>
<tr>
<td>Co</td>
<td>0.000</td>
<td>0.029</td>
</tr>
<tr>
<td>Ni</td>
<td>0.000</td>
<td>0.010</td>
</tr>
<tr>
<td>Mg</td>
<td>0.007</td>
<td>0.995</td>
</tr>
<tr>
<td>Cl</td>
<td>0.112</td>
<td>0.330</td>
</tr>
</tbody>
</table>

The scrubbed organic solution would be selectively stripped with dilute sulphuric acid (part of which would be used as scrubbing solution) and then bulk-stripped with hydrochloric acid. The stripped organic would returned for extraction.

EXAMPLE 3 - Processes of Figures 1, 2 and 3

Separation of cobalt from manganese and other impurities from a cobalt plant bio-leach solution.

1. Extraction

The aim of the extraction is to extract all the zinc, calcium, copper and manganese from the aqueous leach solution (PLS – "plant leach solution") into the organic D2EHPA solution and to minimise the extraction of cobalt, nickel and magnesium.

After a preliminary iron precipitation step, the cobalt bio-leach solution contained 0.04 g/L Zn, 0.53 g/L Ca, 0.08 g/L Mn, 0.19 g/L Cu, 0.37 g/L Co, 0.01 g/L Ni and
0.32 g/L Mg. The organic extraction solution consisted of
6% di-2-ethylhexyl phosphoric acid (D2EHPA), 10% tri-n-
butyl phosphate (TBP) and 84% kerosene (Shellsol 2046), all
by volume. Three counter-current extraction stages were
used at an aqueous:organic (A/O) flowrate ratio of 1.2:1.
The pH in the three mixers was controlled at 3.7 using
three pH controllers with the addition of ammonia solution
(Fig 1). The results are shown in Table 6. All the zinc,
calcium, manganese and copper were extracted in three
stages. Some 16% cobalt, 1% nickel and 62% magnesium were
coa-extracted. The raffinate contained only cobalt, nickel
and magnesium.

In accordance with the embodiment of the
invention illustrated in Figure 3, the above raffinate
containing Co, Ni and Mg is subjected to a subsequent
solvent extraction step where cobalt is extracted from the
aqueous solution by di-2, 4, 4-trimethylpentyl phosphinic
acid (Cyanex 272), using a well proven commercial process.
The cobalt is then recovered by electrowinning (as
illustrated in the process of Figure 3 - this is the
preferred method of recovery according to this embodiment
of the invention) or hydroxide precipitation.

If the D2EHPA extraction described above had been
preceded by a Cyanex 272 extraction (as per the process
illustrated in Figure 2), Ni and Mg (and Ca) would already
have been removed, leaving only Co in the raffinate, which
could be recovered by a known hydroxide precipitation
process. In the following description of the scrubbing and
stripping stages, it is to be noted that the results relate
to the embodiment as represented in Figure 3.

Table 6 Summary of results of semi-continuous extraction at
A/O ratio 1.2:1

<table>
<thead>
<tr>
<th>Metal name</th>
<th>Concentration (g/L)</th>
<th>Extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. Scrubbing

The aim of scrubbing is to scrub all of the co-extracted cobalt (and nickel, to the extent that it is in the organic extraction solution, and likewise magnesium) from the organic D2EHPA extraction solution to the aqueous scrub raffinate and to minimise the scrubbing of manganese, copper, calcium and zinc. Two scrubbing stages were used with a combined solution of sulphuric acid (4.4 g/L) manganese (0.01 g/L) and copper (0.02 g/L) at A/O flowrate ratio of 1:4. Scrubbing results are listed in Table 7. The cobalt and nickel scrubbing efficiencies were 100% with no cobalt and nickel being left in the organic solution. This scrub raffinate containing 0.30 g/L cobalt would be recycled back to the feed (PLS). By doing this, the cobalt and nickel recovery would approach 100%.

<table>
<thead>
<tr>
<th>Metal</th>
<th>In feed</th>
<th>In loaded organic</th>
<th>In raffinate</th>
<th>Scrubbing efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.040</td>
<td>0.042</td>
<td>0.000</td>
<td>100.00</td>
</tr>
<tr>
<td>Ca</td>
<td>0.529</td>
<td>0.595</td>
<td>0.000</td>
<td>100.00</td>
</tr>
<tr>
<td>Mn</td>
<td>0.075</td>
<td>0.082</td>
<td>0.000</td>
<td>100.00</td>
</tr>
<tr>
<td>Cu</td>
<td>0.185</td>
<td>0.184</td>
<td>0.000</td>
<td>99.74</td>
</tr>
<tr>
<td>Co</td>
<td>0.366</td>
<td>0.068</td>
<td>0.290</td>
<td>16.10</td>
</tr>
<tr>
<td>Ni</td>
<td>0.009</td>
<td>0.000</td>
<td>0.008</td>
<td>0.97</td>
</tr>
<tr>
<td>Mg</td>
<td>0.319</td>
<td>0.180</td>
<td>0.092</td>
<td>61.59</td>
</tr>
</tbody>
</table>

Table 7 Summary of results of scrubbing at A/O ratio 1:4 with combined scrub solution

<table>
<thead>
<tr>
<th>Metal name</th>
<th>Concentration (g/L)</th>
<th>Scrubbing efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In loaded organic</td>
<td>In scrubbed organic</td>
</tr>
<tr>
<td>Zn</td>
<td>0.042</td>
<td>0.042</td>
</tr>
<tr>
<td>Ca</td>
<td>0.565</td>
<td>0.555</td>
</tr>
<tr>
<td>Mn</td>
<td>0.068</td>
<td>0.083</td>
</tr>
</tbody>
</table>
3. Selective stripping

The aim of selective stripping is to generate a solution containing mainly manganese and copper for using as scrubbing solution in the previous stage. One selective strip stage was used at an A/O flowrate ratio of 1:5 using 5 g/L sulphuric acid. The results are shown in Table 8. The strip raffinate generated by this procedure was too strong (too much Zn, Ca, Mn and Cu present) to use as a scrubbing solution. However this would be corrected by using a more dilute acid for stripping, say 2 g/L sulphuric acid.

4. Bulk stripping

The aim of bulk stripping is to re-generate the D2EHPA organic solution by stripping all elements from the organic extractant. Two bulk strip stages were used at an A/O flowrate ratio of 1:5 with 10 g/L hydrochloric acid. The results are also shown in Table 8. Some zinc and calcium were left in the organic solution. However this could be corrected by using a slightly stronger hydrochloric acid, say 15 g/L. If no calcium is present in the feed, sulphuric acid can be used for bulk stripping.

Table 8 Summary of results of stripping at A/O ratio 1:5

<table>
<thead>
<tr>
<th>Metal name</th>
<th>Concentration (g/L)</th>
<th>Strip efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Scrubbed organic 1</td>
<td>Stripped organic 1</td>
</tr>
<tr>
<td>(Selective strip, 5.0 g/L H₂SO₄)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.042</td>
<td>0.033</td>
</tr>
<tr>
<td>Ca</td>
<td>0.600</td>
<td>0.444</td>
</tr>
<tr>
<td>Mn</td>
<td>0.069</td>
<td>0.026</td>
</tr>
</tbody>
</table>
EXAMPLE 4 - Process of figures 1 and 2

The recovery of cobalt from a bio-leach solution.

A. Cyanex 272 circuit

1. Extraction

The aqueous solution was a bio-leach solution containing 0.010 g/L Ni, 0.387 g/L Co, 0.041 g/L Zn, 0.565 g/L Ca, 0.352 g/L Cu, 0.072 g/L Mn and 0.300 g/L Mg. The organic solution consisted of 4% di-2,4,4-trimethylpentyl phosphinic acid (eg Cyanex 272), 5% tri-n-butyl phosphate (TBP) and 91% kerosene (Shellisol 2046), all by volume.

Three counter-current extraction stages were used at an A/O flowrate ratio of 1.5:1. The pH in the three mixers was controlled at 5.5 using three pH controllers with the addition of ammonia solution. The results are shown in Table 9. All zinc, and almost all cobalt, manganese and copper were extracted. Small amounts of calcium, nickel and magnesium was co-extracted. Since the concentration of calcium, nickel and magnesium in the organic solution was low, scrubbing was not necessary.

Table 9 Semi-continuous extraction test results

<table>
<thead>
<tr>
<th>Metal name</th>
<th>Concentration (g/L)</th>
<th>Total extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In feed</td>
<td>In loaded organic</td>
</tr>
<tr>
<td>Cu</td>
<td>0.131</td>
<td>0.025</td>
</tr>
</tbody>
</table>

(Bulk strip, 10.0 g/L HCl)

<table>
<thead>
<tr>
<th></th>
<th>Stripped organic 1</th>
<th>Stripped organic 2</th>
<th>Strip raffinate 2</th>
<th>Total efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.033</td>
<td>0.012</td>
<td>0.105</td>
<td>70.65</td>
</tr>
<tr>
<td>Ca</td>
<td>0.444</td>
<td>0.099</td>
<td>1.654</td>
<td>83.58</td>
</tr>
<tr>
<td>Mn</td>
<td>0.026</td>
<td>0.000</td>
<td>0.063</td>
<td>100.00</td>
</tr>
<tr>
<td>Cu</td>
<td>0.025</td>
<td>0.000</td>
<td>0.043</td>
<td>100.00</td>
</tr>
</tbody>
</table>
2. Stripping
The loaded organic was stripped in three stages with dilute sulphuric solution (8 g/L) at an A/O ratio of 1:3. The results are shown in Table 10. Almost all manganese, cobalt, zinc and copper were stripped.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration (g/L)</th>
<th>Strip efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Loaded organic</td>
<td>stripped organic</td>
</tr>
<tr>
<td>Zn</td>
<td>0.086</td>
<td>0.003</td>
</tr>
<tr>
<td>Mn</td>
<td>0.140</td>
<td>0.001</td>
</tr>
<tr>
<td>Cu</td>
<td>0.744</td>
<td>0.001</td>
</tr>
<tr>
<td>Co</td>
<td>0.394</td>
<td>0.002</td>
</tr>
</tbody>
</table>

10 B. D2EHPA circuit

1. Extraction
A synthetic aqueous solution mimicking the strip liquor from the previous circuit (Cyanex 272 circuit) containing 0.093 g/L Zn, 0.330 g/L Mn, 1.518 g/L Cu and 1.041 g/L Co was used as the feed for the D2EHPA circuit. The organic solution consisted of 5% di-2-ethylhexyl phosphoric acid (D2EHPA), 5% tri-n-butyl phosphate (TBP) and 90% kerosene (Shell sol 2046), all by volume. Three counter-current extraction stages were used at an A/O flowrate ratio of 1.1:1. The pH in the three mixers was controlled at 3.70 using three pH controllers with the addition of sodium
hydroxide solution. The results are shown in Table 11. Almost all the zinc, manganese and copper were extracted. Some 8% of cobalt was co-extracted, which would be scrubbed in the next stage.

<table>
<thead>
<tr>
<th>Metal name</th>
<th>Concentration (g/L)</th>
<th>Extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Loaded organic</td>
</tr>
<tr>
<td>Mn</td>
<td>0.330</td>
<td>0.351</td>
</tr>
<tr>
<td>Zn</td>
<td>0.093</td>
<td>0.096</td>
</tr>
<tr>
<td>Co</td>
<td>1.041</td>
<td>0.080</td>
</tr>
<tr>
<td>Cu</td>
<td>1.518</td>
<td>1.691</td>
</tr>
</tbody>
</table>

2. Scrubbing

Two scrubbing stages were used with a combined solution of sulphuric acid (2.0 g/L), manganese (0.070 g/L) and copper (0.35 g/L) at an A/O flowrate ratio of 1:5. The scrubbing results are listed in Table 12. The cobalt and nickel scrubbing efficiencies were 100% with no cobalt and nickel being left in the organic solution. The scrub raffinate containing 0.254 g/L cobalt would be recycled back to the feed. By doing this, the cobalt recovery would approach 100%.

<table>
<thead>
<tr>
<th>Metal name</th>
<th>Concentration (g/L)</th>
<th>Scrub efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Scrub solution</td>
<td>loaded organic</td>
</tr>
<tr>
<td>Mn</td>
<td>0.067</td>
<td>0.404</td>
</tr>
<tr>
<td>Zn</td>
<td>0.000</td>
<td>0.109</td>
</tr>
<tr>
<td>Co</td>
<td>0.000</td>
<td>0.062</td>
</tr>
<tr>
<td>Cu</td>
<td>0.353</td>
<td>1.806</td>
</tr>
</tbody>
</table>

The scrubbed organic solution was bulk-stripped with sulphuric acid. The stripped organic would be returned for
extraction.

It will be understood to persons skilled in the art of the invention that various modifications could be made to the preferred embodiment illustrated without departing from the spirit and scope of the invention.
CLAIMS:

1. A method of separating cobalt from impurity elements including manganese in an aqueous leach solution, the process including an organophosphoric acid solvent extraction stage including the steps of:
   (a) contacting the aqueous leach solution with an organic solution comprising an organophosphoric acid in an organic solvent to produce a loaded organic solution containing manganese and, to the extent that they are present, calcium, zinc and copper, and a some cobalt; and an aqueous raffinate solution containing most of the cobalt;
   (b) scrubbing the loaded organic solution with an aqueous scrub solution containing manganese and copper to produce a scrubbed organic solution containing less cobalt and a spent aqueous scrub solution containing some cobalt, as well as manganese;
   (c) recycling the spent aqueous scrub solution to step (a);
   (d) selectively stripping the scrubbed organic solution to remove a portion of the manganese and copper to form the aqueous scrub solution for use in step (b); and
   (e) recovering cobalt from the aqueous raffinate produced in step (a).

2. The method as claimed in claim 1, wherein, to the extent that the aqueous leach solution fed into step (a) contains nickel and magnesium:
   (i) in step (a), a large proportion of the nickel and magnesium report to the aqueous raffinate, and a small proportion of the nickel and magnesium report to the loaded organic solution; and
   (ii) in scrubbing step (b), the spent aqueous scrub solution contains nickel recovered from the scrubbing step.
3. The method as claimed in claim 1 or claim 2, wherein the organophosphoric acid is of the formula (RO)₂PO₄H, in which each R group, which may be the same or different, is an optionally substituted branched, straight chained or cyclic alkyl, alkenyl or alkynyl group.

4. The method as claimed in claim 3, wherein each R group has a minimum of 4 carbon atoms.

5. The method as claimed in claim 4, wherein each R group has between 6 to 18 carbon atoms.

6. The method as claimed in claim 5, wherein R is n-octyl, cyclooctyl or 2-ethylhexyl.

7. The method as claimed in claim 1 or claim 2, wherein the organophosphoric acid is di-2-ethylhexyl phosphoric acid, or an organophosphoric acid having extraction characteristics similar to or the same as di-2-ethylhexyl phosphoric acid.

8. The method as claimed in any one of the preceding claims, wherein the organic solution includes a modifier selected from the group consisting of 2-ethylhexanol, isodecanol, isotridecanol and tri n-butyl phosphate (TBP).

9. The method as claimed in claim 8, wherein the modifier is TBP.

10. The method as claimed in any one of the preceding claims, wherein the organic solvent is kerosene.

11. The method as claimed in any one of the preceding claims, wherein the process includes the further step (f) of bulk stripping the selectively stripped organic solution from step (d) to remove a large proportion or almost all of
the elements therein to regenerate the organic solution for recycling to step (a).

12. The method as claimed in any one of the preceding claims, wherein the scrubbed organic solution is selectively stripped of manganese and copper by contacting the scrubbed organic solution with an acid.

13. The method as claimed in claim 12, wherein the acid is sulphuric acid.

14. The method as claimed in any one of claims 11 to 13, wherein the selective stripping stage yields a selectively stripped organic solution, and the selectively stripped organic solution is bulk stripped of impurity elements by contacting the selectively stripped organic solution with a second acid.

15. The method as claimed in any one of the preceding claims, wherein the mole ratio of (Mn+Cu)/(Co+Ni) in the aqueous scrub solution is at least 1.5.

16. The method as claimed in any one of the preceding claims, wherein the amount of organophosphoric acid in the organic solution used in step (a) is in the range of from 3% to 35% v/v.

17. The method as claimed in claim 16, wherein the amount of organophosphoric acid in the organic solution is 5% to 25% v/v.

18. The method as claimed in any one of the preceding claims, wherein the amount of modifier in the organic solution used in step (a) is in the range of 3% to 15% v/v.

19. The method as claimed in claim 18, wherein the
amount of modifier in the organic solution used in step (a) is in the range of 5% to 10% v/v.

20. The method as claimed in any one of the preceding claims, wherein the pH of the aqueous phase in step (a) is maintained in a range from 3.0 to 4.5.

21. The method as claimed in any one of the preceding claims, wherein the temperature of all stages of the process is maintained in the range of from 10°C to 60°C.

22. The method as claimed in claim 21, wherein the temperature is maintained in the range of from 20 to 40°C.

23. The method as claimed in any one of the preceding claims, wherein the aqueous to organic ratio (A/O) in step (a) is maintained in the range from 10:1 to 1:10.

24. The method as claimed in claim 23, wherein the A/O ratio in step (a) is maintained in the range of 1:2 to 5:1.

25. The method as claimed in any one of the preceding claims, wherein the aqueous to organic ratio (A/O) in step (b) is maintained within the range of from 1:5 to 1:200.

26. The method as claimed in claim 25, wherein the A/O ratio in step (b) is maintained in the range of 1:5 to 1:20.

27. The method as claimed in any one of the preceding claims, wherein the method does not include a sulphide precipitation stage for separating cobalt from manganese.

28. The method as claimed in any one of the preceding claims, wherein the method does not include a precipitation step involving precipitation of the target elements and re-
leaching of the precipitate.

29. The method as claimed in any one of the preceding claims, wherein the process further includes an organophosphinonic acid extraction stage.

30. The method as claimed in claim 29, wherein the organophosphinonic acid extraction stage is conducted prior to the organophosphoric acid extraction stage.

31. The method as claimed in claim 30, wherein the aqueous leach solution contains manganese, zinc, copper, cobalt, nickel, calcium and magnesium; the organophosphinonic acid extracts manganese, zinc, copper and cobalt into an organic phase leaving an aqueous raffinate containing nickel, calcium and magnesium; the aqueous raffinate thus formed in the organophosphinonic acid extraction stage is used as the aqueous leach solution in step (a) of the organophosphoric acid extraction stage of steps (a) to (e); the loaded organic solution obtained in step (a) contains manganese, zinc and copper; and the aqueous raffinate obtained in step (a) of the organophosphoric acid extraction stage contains cobalt.

32. The method as claimed in claim 29, wherein the organophosphinonic acid extraction stage is conducted after the organophosphoric acid extraction stage.

33. The method as claimed in claim 32, wherein the aqueous leach solution used in step (a) of the organophosphoric acid extraction stage contains manganese, zinc, copper, cobalt, nickel, calcium and magnesium; the loaded organic solution obtained in step (a) contains manganese, calcium, zinc and copper and the aqueous raffinate solution in step (a) contains cobalt, nickel and magnesium; and in the subsequent organophosphinonic solvent extraction of said aqueous raffinate, an organic phase
containing cobalt, and an aqueous raffinate containing nickel and magnesium are obtained.

34. The method as claimed in any one of claims 29 to 33, wherein the organophosphinic acid is of the formula R₂PO₃H, in which the two R groups, which may be the same or different, are selected from optionally substituted branched, straight chained or cyclic alkyl, alkenyl or alkynyl groups.

35. The method as claimed in claim 34, wherein the two R groups each contain a minimum of 4 carbon atoms.

36. The method as claimed in claim 35, wherein the two R groups each contain from 6 to 18 carbon atoms.

37. The method as claimed in any one of claims 29 to 33, wherein the organophosphinic acid is di-2,4,4-trimethylpentyl phosphinic acid or an organophosphinic acid having extraction characteristics similar to or the same as di-2,4,4-trimethylpentyl phosphinic acid.

38. The method as claimed in any one of claims 29 to 37, wherein the amount of organophosphinic acid in the organic solution used in the organophosphinic acid solvent extraction stage is in the range of from 3% to 35% v/v.

39. The method as claimed in claim 38, wherein the amount of organophosphinic acid in the organic solution used in the organophosphinic acid solvent extraction stage is in the range of 5% to 25%.

40. The method as claimed in any one of claims 29 to 39, wherein a modifier is used in the organophosphinic acid extraction stage.

41. The method as claimed in any one of claims 29 to
40, wherein the pH of the aqueous phase is maintained in a range from 5.0 to 6.0 in the organophosphinic acid solvent extraction stage.

42. The method as claimed in any one of claims 29 to 41, wherein the aqueous to organic ratio (A/O) in the organophosphinic acid solvent extraction stage is in the range from 3:1 to 1:3.

43. A process of separating cobalt from other elements contained in an aqueous leach solution, the process including the steps of subjecting the aqueous leach solution to successive solvent extraction steps using an organophosphoric acid and an organophosphinic acid as extractants.

44. The process as claimed in claim 43, wherein the organophosphoric acid extraction step is conducted in accordance with the method as defined in any one of claims 1 to 28.

45. A plant for conducting the method as claimed in any one of claims 1 to 44, the plant including:
- a solvent extraction contactor in which the aqueous leach solution is contacted with the organophosphoric acid-containing organic solution;
- a scrubbing contactor for scrubbing the loaded organic solution generated in solvent extraction contactor;
- a loaded organic solution conduit for conducting the loaded organic solution generated in the solvent extraction contactor to the scrubbing contactor;
- a stripping contactor in which the scrubbed organic solution generated in the scrubbing contactor is subjected to selective stripping to generate the aqueous scrub solution for use in the scrubbing contactor;
- a scrubbed organic solution conduit for conducting the scrubbed organic solution to the stripping contactor;
an aqueous scrub solution conduit for conducting the aqueous scrub solution to the scrubbing contactor; and
- a spent aqueous scrub solution conduit for conducting the spent aqueous scrub solution from the scrubbing contactor to the solvent extraction contactor.

46. The plant as claimed in claim 45, the plant further including an organic solution recycle conduit for conducting the partially stripped scrubbed solution from the stripping contactor to the solvent extraction contactor.

47. The plant as claimed in claim 46, the plant further including bulk stripping contactor located in the organic solution recycle conduit, in which the partially stripped scrubbed solution is stripped of remaining impurities before being conducted to the solvent extraction contactor.

48. The plant as claimed in any one of claims 45 to 49, wherein the solvent extraction contactor is a countercurrent solvent extraction contactor.

49. The plant as claimed in any one of claims 45 to 48, wherein the plant also includes an organophosphinic acid solvent extraction contactor circuit.
FIGURE 2
Cobalt solution

D2EHPA SX

Raffinate

Strip liquor

Mn, Zn, Cu, Ca disposal

Cyanex 272 SX

Raffinate

Strip liquor

Mg, Ni disposal

Cobalt Electrowinning

Cobalt cathodes

FIGURE 3
### INTERNATIONAL SEARCH REPORT

**International application No.**

PCT/AU01/01163

<table>
<thead>
<tr>
<th>A.</th>
<th>CLASSIFICATION OF SUBJECT MATTER</th>
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<td>Int. Cl.</td>
<td>C22B 3/26, 3/38, 23/00</td>
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According to International Patent Classification (IPC) or to both national classification and IPC

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<th>FIELDS SEARCHED</th>
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<td>IPC7 AS ABOVE AND IPC4 C22B 3/00, 23/04</td>
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</table>

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

NIL

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

DWPI: IPC as above with key words cobalt, nickel, solvent, extraction

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<tr>
<th>C.</th>
<th>DOCUMENTS CONSIDERED TO BE RELEVANT</th>
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<tr>
<td>Category*</td>
<td>Citation of document, with indication, where appropriate, of the relevant passages</td>
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<tr>
<td>X</td>
<td>Derwent abstract accession No. 96-219924/22, Class J01, M25, KR 9407372 B1, (Kim B), 16 August 1994</td>
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<td>A</td>
<td>Abstract</td>
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<td>A</td>
<td>AU 40890/96 A (Resolute Resources Ltd.), 18 July 1996 Whole Document</td>
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<tr>
<td>A</td>
<td>DE 3411885 A (Starck H C Berlin), 10 October 1985 Whole Document</td>
</tr>
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</table>

☐ Further documents are listed in the continuation of Box C ☐ See patent family annex

* Special categories of cited documents:
  * "A" document defining the general state of the art which is not considered to be of particular relevance
  * "E" earlier application or patent but published on or after the international filing date
  * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  * "O" document referring to an oral disclosure, use, exhibition or other means
  * "P" document published prior to the international filing date but later than the priority date claimed
  * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  * "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family

Date of the actual completion of the international search

22 October 2001

Date of mailing of the international search report

25 Oct 2001

Name and mailing address of the ISA/AU

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Form PCT/ISA/210 (second sheet) (July 1998)
INTERNATIONAL SEARCH REPORT

Box I  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:

2. [ ] Claims Nos: 
   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:

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 II  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:

Claims 1-42 and 44, 45. See attachment.

Claim 43. See attachment.

1. [ ] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims

2. [X] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

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.

[ ] No protest accompanied the payment of additional search fees.
Supplemental Box
(To be used when the space in any of Boxes I to VIII is not sufficient)

Continuation of Box No: II

The claims do not relate to one invention only (or to a group of inventions so linked as to form a single general inventive concept). In assessing whether there is more than one invention claimed, I have given consideration to those features, which can be considered to be “special technical features”. These are features, which potentially distinguish the claimed combination of features from the prior art. Where different claims have different special technical features they define different inventions. I have found that there are different inventions as follows:

(1) Claims 1-42, 44, 45 are directed at a specific sequence of steps comprising extraction and aqueous scrubs used in the solvent extraction of cobalt. It is considered that the specific sequence of steps comprises a first “special technical feature”.

(2) Claim 43 is directed at the solvent extraction of cobalt using an organophosphoric acid and subsequently an organophosphinic acid. It is considered that the successive steps of solvent extraction using an organophosphoric and an organophosphinic acid respectively comprise a second “special technical feature”.

Form PCT/ISA/210 (extra sheet)(July 1998)