A hydrometallurgical method for precipitating iron in the form of hematite from leach solutions containing nickel, cobalt and iron, characterised by the steps of: i) pre-neutralising (12) the leach solution by the addition of a neutralising agent (14); ii) oxidising ferrous sulphate to ferric sulphate (16) by sparging air or oxygen into the solution resulting from step (i) at an elevated temperature; iii) adjusting the free acid and pH of the solution resulting from step (ii) to levels suitable for hematite precipitation; iv) adding hematite seed (22) to the solution resulting from step (iii) and maintaining the solution in these conditions for a residence time such that substantially complete conversion of ferric sulphate to hematite precipitate is achieved; v) filtering or thickening (24) the solution from step (iv) to remove the hematite precipitate; vi) recycling a portion of the hematite precipitate of step (v) to step (iv) as the hematite seed; and vii) recovering nickel and cobalt (26) from the filtrate solution.
Published:
— with international search report

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.
"Hematite Precipitation"

Field of the Invention

The present invention relates to hematite precipitation. In particular, the present invention relates to a hydrometallurgical method for precipitating iron in the form of hematite from solutions containing nickel and cobalt, under atmospheric conditions. More particularly, the method of the present invention is intended to allow the precipitation of iron as hematite from solutions recovered from the processing of either nickel laterites and/or nickel sulphides.

Background Art

In hydrometallurgical nickel processing methods, iron is typically precipitated as a ferric oxyhydroxide (commonly a goethite) and as a hematite product from the high pressure acid leaching process for nickel laterites. In some situations iron is also rejected as a jarosite product.

Unfortunately the rejection of iron as a ferric oxyhydroxide also results in significant co-precipitation of the valuable nickel and cobalt products. This either results in metallurgical losses or necessitates the reprocessing of the iron residue in order to recover the valuable nickel and cobalt.

The rejection of iron as a hematite product in the high pressure acid leaching processes used for nickel laterites necessitates the use of temperatures in the order of 250°C and pressures in the order of 45 Bar. This process by its very nature involves the use of capital intensive equipment. This equipment is also expensive to maintain and has associated high operating costs.

The jarosite process, whilst having lower losses of nickel and cobalt due to cleaner separation coefficients, can be an expensive process. The jarosite process typically requires the use of a suitable cation (such as Na⁺, K⁺ or NH₄⁺) together with elevated temperature and/or pressure.
In addition to the losses of nickel and cobalt associated with the ferric oxyhydroxide and ferric hydroxide formation, the major problems with this process are poor filtration rates, thickener settling characteristics and thickener underflow densities which are achievable. The ferric hydroxide in particular, and to a lesser extent the ferric oxyhydroxide, tends to have an open structure, which incorporates large amounts of base metals. Also, the solids have a low density. The low thickener underflow densities impact on both downstream processing equipment plus the volume of tailings which need to be disposed of.

Hematite is one of the most acceptable iron products for intermediate storage or disposal. This is due to its high thermodynamic stability, its high density (4.9 to 5.3 g/cm³), its high iron content (60% - 70%) and its low adsorption of water and base metals.


The method of the present invention has as one object thereof to overcome substantially the problems of the prior art, or to at least provide a useful alternative thereto.

The preceding discussion of the background art is intended to facilitate an understanding of the present invention only. It should be appreciated that the discussion is not an acknowledgement or admission that any of the material referred to was part of the common general knowledge in Australia as at the priority date of the application.

Throughout the specification, unless the context requires otherwise, the word "comprise" or variations such as "comprises" or "comprising", will be understood to
imply the inclusion of a stated integer or group of integers but not to the exclusion of any other integer or group of integers.

**Disclosure of the Invention**

In accordance with the present invention there is provided a hydrometallurgical method for precipitating iron in the form of hematite from leach solutions containing nickel, cobalt and iron, the method comprising the steps of:

(i) pre-neutralising the leach solution by the addition of a neutralising agent;

(ii) oxidising ferrous sulphate to ferric sulphate by sparging air or oxygen into the solution resulting from step (i) at an elevated temperature;

(iii) adjusting the free acid and pH of the solution resulting from step (ii) to levels suitable for hematite precipitation;

(iv) adding hematite seed to the solution resulting from step (iii) and maintaining the solution in these conditions for a residence time such that substantially complete conversion of ferric sulphate to hematite precipitate is achieved;

(v) filtering or thickening the solution from step (iv) to remove the hematite precipitate;

(vi) recycling a portion of the hematite of step (v) to step (iv) as the hematite seed; and

(vii) recovering nickel and cobalt from the filtrate solution.

Preferably, the oxidation of ferrous sulphate to ferric sulphate in step (ii) occurs at a temperature within the range of about 60°C to 150°C.
SiII preferably, the oxidation of ferrous sulphate to ferric sulphate in step (ii) occurs at a temperature within the range of about 60°C to 100°C.

The free acid concentration is preferably lower than about 10g/L.

The pH of the solution resulting from step (ii) is preferably maintained below about 2.5 to avoid precipitation of ferric oxyhydroxide.

Still further preferably, the solution temperature of step (iv) is maintained between about 60°C and 150°C during hematite precipitation.

Yet still further preferably, the solution temperature of step (iv) is maintained between about 60°C and 100°C during hematite precipitation.

Seed concentration preferably ranges between about 5g/L and 100g/L.

Preferably, air or oxygen is sparged into the solution of step (iv) during hematite precipitation.

The neutralising agent preferably comprises any one or more of calcrete, limestone or lime.

Brief Description of the Drawings

The present invention will now be described, by way of example only, with reference to one embodiment thereof and the accompanying drawing, in which:-

Figure 1 is a diagrammatic representation of a flow sheet depicting a hydrometallurgical method for the precipitation of iron in the form of hematite from a leach solution containing nickel and cobalt in accordance with the present invention.

Best Mode(s) for Carrying Out the Invention
In Figure 1 there is shown a hydrometallurgical method 10 for precipitating iron in the form of hematite from a leach solution containing nickel and cobalt. In this example the leach solution is the pregnant leach solution containing nickel, cobalt and iron resulting from the leaching of a nickel laterite or fraction thereof under atmospheric conditions.

As sulphuric acid is released when ferric sulphate is converted to hematite the free acid in the leach solution needs to be neutralised prior to hematite precipitation. The leach solution is subjected to a pre-neutralisation step 12 in which a neutralising agent 14, for example calcrete, limestone and/or lime, is added to lower the free acid concentration in solution to below about 10g/L whilst keeping the pH below about 2.5.

The solution resulting from pre-reduction is then heated to between about 60 and 150°C, for example between about 60 and 100°C, before undergoing an oxidation step 16 through exposure to an oxidising agent 18, for example air or oxygen. The majority of ferrous sulphate present is oxidised to ferric sulphate.

Whilst maintaining the solution temperature the solution proceeds to a precipitation stage 20 where hematite seed 22 is added in a concentration range of between about 5 and 100g/L. The quantity of seed added will not alter precipitation kinetics but the amount added can affect the final product composition. The addition of the hematite seed 22 promotes the formation of hematite over other forms of iron hydroxides. The amount of seed added is important in as much as too much seed is a waste from an installed capital and operating cost perspective. If too little seed is added the likelihood of iron precipitating as something other than hematite increases.

A residence time of between about 0.5 and 200 hours, for example between about 0.5 and 20 hours, is employed to effect complete conversion of ferric sulphate to hematite, and this residence time will vary depending on the operating conditions adopted. The product solution is then filtered or thickened 24 to remove the hematite from solution. A recycle stream 26 is then employed to return a portion of the hematite residue back to the precipitation circuit 20 as the hematite seed.
The filtrate or thickener overflow is then advanced to a nickel and cobalt recovery stage 26, in which the nickel and cobalt can be recovered using various known hydrometallurgical techniques including precipitation, solvent extraction or ion exchange.

The free acid is maintained in the range of about 0 to 10 g/L during the hematite precipitation stage 20. This can be achieved by adding a neutralising agent comprising calcrete, lime or limestone. Other neutralising agents including ammonia and caustic will also be suitable.

It is envisaged that it may also be beneficial to also sparge oxygen through the solution during the precipitation stage 20, thereby ensuring that ferrous iron is fully oxidised to ferric and enhancing the precipitation of hematite.

It is further envisaged that this method can be applied to leach solutions resulting from the leaching of nickel sulphide concentrates and nickel laterite ores.

As can be seen from the above description, the method of the present invention facilitates the precipitation of iron in the form of hematite from nickel containing hydrometallurgical process solutions ranging from atmospheric to medium pressure conditions, thereby constituting a very useful alternative to the methods of the prior art.
The Claims Defining the Invention are as Follows:

1. A hydrometallurgical method for precipitating iron in the form of hematite from leach solutions containing nickel, cobalt and iron, characterised by the steps of:

   i) pre-neutralising the leach solution by the addition of a neutralising agent;

   ii) oxidising ferrous sulphate to ferric sulphate by sparging air or oxygen into the solution resulting from step (i) at an elevated temperature;

   iii) adjusting the free acid and pH of the solution resulting from step (ii) to levels suitable for hematite precipitation;

   iv) adding hematite seed to the solution resulting from step (iii) and maintaining the solution in these conditions for a residence time such that substantially complete conversion of ferric sulphate to hematite precipitate is achieved;

   v) filtering or thickening the solution from step (iv) to remove the hematite precipitate;

   vi) recycling a portion of the hematite of step (v) to step (iv) as the hematite seed; and

   vii) recovering nickel and cobalt from the filtrate solution.

2. A method according to claim 1, wherein the oxidation of ferrous sulphate to ferric sulphate in step (ii) occurs at a temperature within the range of about 60°C to 150°C.
3. A method according to claims 1 or 2, wherein the free acid concentration is below 10 g/L.

4. A method according to any one of claims 1 to 3, wherein the pH of the solution resulting from step (ii) is maintained below about 2.5.

5. A method according to any one of the preceding claims, wherein the solution of step (iv) is maintained between about 60°C and 150°C.

6. A method according to any one of the preceding claims, wherein the seed concentration is preferably within the range of about 5g/L and 100g/L.

7. A method according to any one of the preceding claims, wherein oxygen is sparged into the solution of step (iv) during hematite precipitation.

8. A method according to any one of the preceding claims, wherein the neutralising agent comprises any one or more of calcrete, limestone or lime.

9. A hydrometallurgical method for the for precipitating iron in the form of hematite from leach solutions containing nickel, cobalt and iron, substantially as hereinbefore described with reference to Figure 1.
INTERNATIONAL SEARCH REPORT

A: CLASSIFICATION OF SUBJECT MATTER

Int Cl.
C22B3/20 (2006.01) C22B 3/44 (2006.01)
C22B 3/06 (2006.01) C22B 23/00 (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

REfer ELECTRONIC DATA BASE CONSULTED

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)

DWPI-IPC: C22B 3/IC, C22B 23/00 and hematite, hematite, "ferric oxide", Fe2O3, ferric+

C. DOCUMENTS CONsidered TO BE RELEVANT

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* Special categories of cited documents:
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  "E" earlier application or patent but published on or after the international filing date
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  "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search
23 February 2007

Date of mailing of the international search report
O p r m 2007

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Form PCT/ISA/210 (second sheet) (April 2005)
**INTERNATIONAL SEARCH REPORT**

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Form PCT/ISA/2 10 (continuation of second sheet) (April 2005)
This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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

END OF ANNEX