
Declarations under Rule 4.17:
— as to applicant’s entitlement to apply for and be granted a patent (Rule 4.17(U))
— as to the applicant’s entitlement to claim the priority of the earlier application (Rule 4.17(Hi))
— if inventorship (Rule 4.17(iv))

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.

Title: PROCESSING OF NICKEL SULPHIDE ORE OR CONCENTRATES WITH SODIUM CHLORIDE

Abstract: The present invention relates to a new hydrometallurgical process for recovering nickel from nickel bearing raw materials, such as sulphide flotation concentrates. In general, the process involves the oxidative atmospheric pressure leaching of nickel sulphide concentrates using a sodium chloride/hydrochloric acid based leach media.
PROCESSING OF NICKEL SULPHIDE ORE OR CONCENTRATES WITH SODIUM CHLORIDE

FIELD OF THE INVENTION

The present invention relates to a new hydrometallurgical process for recovering nickel from nickel bearing raw materials, such as sulphide flotation concentrates. In general, the process involves the oxidative atmospheric pressure leaching of nickel sulphide concentrates using a sodium chloride/hydrochloric acid based leach media.

BACKGROUND OF THE INVENTION

The world nickel resources are divided into two major categories, sulphide ore and oxidised ore (laterite ore). The conventional exploitation of nickel sulphide ore is essentially a pyrometallurgical process, where the mined ore is then finely ground, and the nickel sulphide minerals concentrated by froth flotation to produce a nickel concentrate. The concentrate is then treated further by smelting and reduction to produce a nickel bearing matte, which contains also copper, cobalt, and iron. The matte is then refined by known hydrometallurgical processes, which might include oxidative leaching or pressure leaching, followed by impurity removal and hydrogen reduction or electrowinning.

A drawback of the smelting process is the generation of sulphur dioxide, which has to be treated in an acid plant to produce sulphuric acid, a product that is not always easy to dispose of from the smelter location. Losses of nickel and cobalt into smelter slag are significant, and there can be problems in dealing with some of the minor elements in concentrates, such as magnesium and arsenic.

A number of other hydrometallurgical routes for processing nickel sulphide concentrates have been discussed in the literature, generally relying
on grinding, or fine grinding of the concentrate, followed by oxidative pressure leaching of the sulphide to produce sulphuric acid for the leach process.

Biological treatment of nickel sulphides has also been described, where bacterially assisted leaching is followed by solution purification, metal separation, and electrowinning of nickel. The long residence times required for this type of process has resulted in extremely large reactors for the leach stage, and the process has therefore not achieved commercial success to date due to the large capital requirements.

The proprietary "Activox" process relies on an extremely fine grind of the nickel concentrate followed by high pressure oxidative leaching to extract the nickel into a sulphate solution, followed by known impurity removal steps and recovery of the metallic nickel.

The hydrometallurgical processes described above generally have the disadvantage that much of the sulphur content of the sulphide is oxidised to sulphuric acid, with high costs of reagents for neutralisation, and generation of large amounts of waste, such as ammonium sulphate, to dispose of. As would be appreciated these two factors combine to make these processes commercially unattractive due to the high costs involved.

Patent WO 96/41029, "Chloride assisted hydrometallurgical extraction of nickel and cobalt from sulphide ores", teaches the pressure oxidation leaching of nickel and cobalt from sulphide ores in the presence of oxygen, and an acid solution containing halide, copper, and sulphate ions. The leach slurry is treated by solids separation and solution purification, precipitation of mixed nickel and cobalt hydroxide, re-leaching of the precipitate in ammoniacal solution, followed by solvent extraction for metal separation and electrowinning of the metals. The process suffers from similar limitations to the other sulphate based hydrometallurgical processes described above.
This invention aims to overcome some of the limitations of the existing processes by providing a low cost chlorine/chloride based process for nickel sulphide concentrate treatment.

The discussion of documents, acts, materials, devices, articles and the like is included in this specification solely for the purpose of providing a context for the present invention. It is not suggested or represented that any or all of these matters formed part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed before the priority date of each claim of this application.

SUMMARY OF THE INVENTION

In general, the present invention provides a hydrometallurgical process to recover nickel from nickel bearing raw materials, such as nickel sulphide flotation concentrates. The process is based on oxidative leaching of the sulphides with air or oxygen, sodium chloride solution, gaseous chlorine, and hydrochloric acid at atmospheric pressure. The process is applicable to all nickel sulphide concentrates, but is particularly suitable where the concentrate is difficult to treat by the conventional smelting methods.

In general, the process is aimed at recovery of nickel from sulphidic nickel concentrates, but it also encompasses recovery of the cobalt and copper, which are frequently found in nickel sulphide flotation concentrates.

Accordingly, in a first aspect of the present invention there is provided a process for the recovery of nickel from a nickel sulphide containing material including the steps of:
(a) providing a nickel sulphide containing material;
(b) oxidative leaching of the nickel sulphide containing material with a sodium chloride leach solution containing hydrochloric acid in an
oxidising atmosphere to form a pregnant leach solution containing dissolved nickel;
(c) subjecting the pregnant leaching solution to solid/liquid separation to produce a solid tailings residue and a pregnant leach solution containing dissolved nickel;
(d) treating the pregnant leach solution containing dissolved nickel with limestone to remove Cu(II) and sulphate;
(e) purification of the nickel pregnant leach solution by the use of solvent extraction to remove cobalt, zinc and residual copper (II);
(f) recovering nickel from the pregnant leach solution to form a depleted leach solution; and
(g) electrolytically treating the depleted leach solution to recover chlorine, hydrogen, and sodium hydroxide.

The nickel sulphide containing material may be provided in any suitable form. It is preferred however that the nickel sulphide containing material is provided as fine particles. As such the process of providing a nickel sulphide containing material preferably includes the step of reducing the particle size of the nickel sulphide containing material to produce fine particles. In the preferred embodiment the fine particles have a particle size of less than 0.08mm.

The oxidative leach is carried out at atmospheric pressure. In the preferred embodiment the oxidising atmosphere is air, oxygen, oxygen enriched air or a mixture thereof.

The leaching may be carried out at any suitable temperature but it is preferred that the leaching is carried out at a temperature of from 80°C to 120°C. The elevated leach temperature may be achieved in any of a number of ways but is preferably achieved by addition of steam to the leach vessel.
Following completion of the leaching the pregnant leaching solution is subjected to solid/liquid separation to produce a solid tailings residue and a pregnant leach solution containing dissolved nickel.

The pregnant leach solution containing dissolved nickel is treated to remove Cu(II) by precipitation. The precipitation is achieved by addition of limestone to precipitate the Cu(II) as copper hydroxy chloride. The material thus recovered is then re-subjected to the leaching stage to facilitate the efficient recovery of copper in the process.

In a further preferred embodiment the pregnant leach solution containing dissolved nickel is treated to remove zinc and cobalt. The zinc and cobalt may be removed by any technique well known in the art but are preferably removed by solvent extraction.

The nickel may be recovered from the pregnant leach solution using any of a number of techniques well known in the art. It is preferably recovered by treatment of the pregnant leach solution containing dissolved nickel to precipitate nickel and to form a depleted leach solution. In a particularly preferred embodiment the treatment involves addition of sodium hydroxide and the nickel is precipitated as nickel hydroxide.

Following recovery of the nickel in the form of nickel hydroxide it is preferred that the process includes the step of reducing the nickel hydroxide to metallic nickel. The reducing may be carried out in any way well known in the art but preferably includes contacting the nickel hydroxide with hydrogen gas.

In a preferred embodiment of the invention the process further includes removal of divalent metal ions from the depleted leach solution. The removal of divalent metal ions of this type may be carried out by any method well known in the art but are preferably removed by ion exchange.
It is also preferred that the process includes a step of treating the depleted leach solution to remove copper (I). The step of removal of copper (I) preferably includes treatment of the depleted leach solution to precipitate copper (I). In a preferred embodiment the treatment involves addition of sodium hydroxide to the depleted leach solution such that the copper is precipitated as copper hydroxide. If copper is removed it is preferably recovered by reducing the copper hydroxide to metallic copper. The reducing preferably includes contacting the copper hydroxide with hydrogen gas.

The depleted leach solution is subjected to electrolytic treatment to recover chlorine, hydrogen, and sodium hydroxide. These may be re-used in the process of the invention thus providing significant cost savings.

In a particularly preferred embodiment of the invention a portion of the pregnant leach solution is re-subjected to the leaching step. In a particularly preferred form of this embodiment prior to being re-subjected to the leaching step the pregnant leach solution is treated with chlorine gas to oxidise the copper contained in the portion of pregnant leach solution.

In a particularly preferred embodiment the invention provides a process for the recovery of nickel from a nickel sulphide containing material including the steps of:
(a) providing a nickel sulphide containing material,
(b) grinding the nickel sulphide containing material to less than 0.08 mm in size,
(c) oxidative leaching of the nickel sulphide containing material at atmospheric pressure with sodium chloride leach solution containing hydrochloric acid in an oxidising atmosphere to form a pregnant leach solution containing dissolved nickel;
subjecting the pregnant leach solution to solid/liquid separation to produce a solid residue tailings and a pregnant leach solution containing dissolved nickel,

treating the pregnant leach solution containing dissolved nickel to remove Cu(II).

subjecting the pregnant leach solution to solvent extraction to remove zinc and cobalt,

treating the pregnant leach solution with sodium hydroxide to precipitate nickel from the pregnant leach solution as nickel hydroxide and to form a depleted leach solution,

subjecting the depleted leach solution to ion exchange to remove divalent metal ions,

treating the depleted leach solution with sodium hydroxide to precipitate copper(I) from the pregnant leach solution as copper(I) hydroxide,

subjecting the depleted leach solution to electrolytic treatment to recover chlorine, hydrogen, and sodium hydroxide,

wherein at least a portion of the pregnant leach solution obtained in step (c) is treated with chlorine gas to oxidise at least a portion of the copper contained in the pregnant leach solution and then resubjected to the leaching step.

LIST OF DRAWINGS

Figure 1 presents a flow chart of one embodiment of the invention, Figure 2 shows a flow chart of another embodiment of the invention, and Figure 3 shows still another embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the recovery of nickel from a nickel sulphide containing material. Examples of suitable nickel sulphide containing material include a primary sulphide ore material, an ore concentrate obtained
by froth flotation or from another extraction process, a tailings material containing residual nickel sulphide containing material.

Once the desired nickel sulphide containing material has been chosen it is then subjected to the further steps of the process of the invention. The nickel sulphide containing material may be in any suitable form for processing, but is required to be finely ground, preferably to a particle size less than 0.08mm. Such a process may be carried out in any of a number of ways well known in the art but preferably involves grinding or comminution of the nickel sulphide containing material.

A preferred embodiment of process is summarised in figure 1 and a discussion of this figure will serve to illustrate the invention. In the preferred embodiment, the nickel sulphide concentrate is provided (1) and then initially finely ground (2) to less than 0.08mm in size before addition to the leach stage.

The leach is preferably carried out at atmospheric pressure in a multistage counter current leach (3), with preferably at least three stages and with preferably a solids/liquid separation between each stage. Each leach stage might typically be carried out in agitated tanks for example. The leach liquor is preferably made up of sodium chloride solution (such as sodium chloride solution or hypersaline water), spent liquor from a chlorine alkali cell (4), and recycled pregnant leach liquor. A portion of the pregnant leach solution after the removal of copper (II) is then removed prior to further processing and resubjected to the leach process as make up leach solution. The pregnant leach solution to be used in this way is subjected to a chlorine oxidation step (5) and thus contains divalent copper (produced in the chlorine oxidation step) to assist in the nickel leach process. The sodium chloride solution may be of any suitable type and may be provided by producing a sodium chloride solution from commercially obtained sodium chloride admixed with water, naturally occurring brines, or underground saline or
hypersaline water. Steam is preferably added to the leach stage (3) to maintain a temperature close to the boiling point at between 95°C and 110°C. Air, oxygen, or oxygen enriched air, are also preferably added to the leach to maintain the required oxidising conditions, and hydrochloric acid is added to maintain the required pH. It is expected that approximately 99% of the sulphide sulphur will be precipitated in the leach in elemental sulphur form, and will be disposed of in tailings, minimising sulphate take up in the leach solution.

After the leach stage (3) the tailings solids are separated in a solids/liquid separation stage (6) and disposed of. Iron in the tailings is in the form of haematite, which results in minimum acid consumption, and is a preferred form for disposal.

In the preferred embodiment, after tailings solids removal, a portion of the pregnant leach liquor is recycled to the chlorine oxidation stage (5).

The bulk of the pregnant leach liquor is treated in step (7) to remove all the cupric ions from the liquor by the addition of limestone or sodium hydroxide to precipitate copper hydroxy chloride (\(\text{Cu}_2(\text{OH})_3\text{Cl}\)). This is separated and recycled to the leach stage as discussed above. This ensures that only copper in the monovalent form remains in the pregnant liquor.

The pregnant leach liquor is then preferably treated in a solvent extraction step (9) for further purification, where cobalt and zinc are extracted onto an organic solvent containing tri iso-octyl amine, or a similar suitable organic extractant. Cobalt and zinc are then water stripped from the organic solvent, and the cobalt recovered as either cobalt carbonate or cobalt sulphide by precipitation with either sodium carbonate or sodium sulphide respectively. Nickel, and other impurities such as copper (I) and magnesium remain in the pregnant leach liquor.
Nickel is recovered from the pregnant leach liquor as nickel hydroxide in a nickel recovery step (10), which is precipitated out of solution by the addition of sodium hydroxide.

The nickel hydroxide can then be converted to nickel metal by known methods in a metallic nickel recovery step (11), but the preferred method is hydrogen reduction, as hydrogen is a by product of the chlor-alkali electrolysis stage (4) of this process.

The nickel depleted leach liquor still typically contains undesirable divalent metal impurities such as magnesium, lead, and traces of zinc, cobalt and nickel, and any monovalent copper that was present in the leach discharge, which is a valuable by product of the process. After pH adjustment, the divalent metal species are typically removed by absorption on an ion exchange resin in divalent impurities removal step (12), followed by stripping of the resin with a hydrochloric acid solution to produce a predominantly magnesium chloride solution. The magnesium chloride solution may then be sent to evaporation ponds for recovery of the solid material if required.

The depleted leach liquor is by now almost pure cuprous chloride solution, which is recovered in a cuprous recovery stage (13). In this stage sodium hydroxide is added to the liquor to precipitate cuprous hydroxide as a solid, which may then be reduced with hydrogen in a kiln or reduction furnace (14) to produce metallic copper as a valuable by product. It is important to note that both the sodium hydroxide and hydrogen required for this step are products of the process itself.

At this stage the depleted liquor, which is sodium chloride solution, passes to the chlorine alkali electrolysis stage (4), where the sodium chloride is converted to sodium hydroxide at the cathode, releasing hydrogen gas,
and releasing chlorine gas on the anode. A portion of both the hydrogen and the chlorine gas produced are then typically sent to a hydrochloric acid production plant (15) to produce the hydrochloric acid requirements for the concentrate leach stage.

This process step produces the sodium hydroxide required for the nickel hydroxide precipitation and cuprous oxide precipitation. In addition, the excess gaseous chlorine left after hydrochloric acid production is used in the copper oxidation stage (5) and the concentrate leach stage, and the excess hydrogen is used for the reduction of nickel hydroxide to nickel metal, and cuprous oxide to copper metal. Any imbalances, which should be small, in the production of these three raw materials from the chlor-alkali electrolysis stage, can be made up by direct purchase of the materials.

In the preferred embodiment, the depleted sodium chloride solution from the electrolysis stage (4) is mixed with a recycled pregnant leach liquor stream, and any make up brine or hypersaline water required for makeup, and treated in a stirred reactor with gaseous chlorine gas injection, in a chlorine oxidation stage (5). In this stage the cuprous copper in the recycled liquor is oxidised to cupric copper, which assists in the leaching of nickel in the leach stage (3). This avoids the need to add chlorine gas directly to the leach stage, simplifying construction of the leach stage (3). The liquor from the chlorine oxidation stage typically passes directly to the concentrate leach stage.

In another embodiment of the process, where the composition of the nickel bearing raw material require that economically no copper recycle stream is required to assist nickel extraction in the concentrate leach stage, the depleted sodium chloride solution from the electrolysis stage (4), make up brine, and chlorine gas may be added directly to the leach stage (3) as illustrated in Fig. 2.
In yet another embodiment, where the concentrate contains significant amounts of gold, silver, and/or platinum group elements, a step (8) to recover these may be introduced by treatment of the pregnant leach liquor following tailings removal, as indicated in Fig. 3.

The process described for recovery of nickel from a nickel sulphide bearing raw material or concentrate by employing a sodium chloride, hydrochloric acid leach has the following advantages over existing processes.

The process can be used on nickel sulphide concentrates, which are unsuitable for processing by the conventional smelting process.

The high solubility of metal chlorides allows high recovery of the target metals. In addition the rapid kinetics of the process allows use of smaller reaction vessels.

The process does not produce jarosite phases which would result in excess acid consumption, and the discharge of iron residue is as environmentally acceptable haematite.

The use of the chlorine-alkali electrolysis step to treat the spent brine produces within the process the majority of the raw materials required by the process.

Copper is separated as the monovalent cuprous hydroxide, which has a lower hydrogen requirement for the reduction step to copper metal than if copper was precipitated in the divalent form.

The sodium chloride leach media allows the use of saline or hypersaline waters, which may allow processing of the nickel sulphide
concentrate in arid areas of the world where pure water might be unavailable.

The above description is intended to be illustrative of the preferred embodiments of the present invention. Variations to the invention without departing from the spirit or ambit described herein should also be considered to form part of the invention.
1. A process for the recovery of nickel from a nickel sulphide containing material including the steps of:
   (a) providing a nickel sulphide containing material;
   (b) oxidative leaching of the nickel sulphide containing material with a sodium chloride leach solution containing hydrochloric acid in an oxidising atmosphere at atmospheric pressure to form a pregnant leach solution containing dissolved nickel;
   (c) subjecting the pregnant leaching solution to solid/liquid separation to produce a solid residue tailings and a pregnant leach solution containing dissolved nickel;
   (d) treating the pregnant leach solution containing dissolved nickel with limestone or sodium hydroxide to remove Cu(II);
   (e) purification of the nickel pregnant leach solution by the use of solvent extraction to remove cobalt, zinc and residual copper (II);
   (f) recovering nickel from the pregnant leach solution to form a depleted leach solution; and
   (g) electrolytically treating the depleted leach solution to recover chlorine, hydrogen, and sodium hydroxide.

2. A process for the recovery of nickel from a nickel sulphide containing material including the steps of:
   (a) providing a nickel sulphide containing material,
   (b) grinding the nickel sulphide containing material to less than 0.08 mm in size,
   (c) oxidative leaching of the nickel sulphide containing material at atmospheric pressure with sodium chloride leach solution containing hydrochloric acid in an oxidising atmosphere to form a pregnant leach solution containing dissolved nickel;
(d) subjecting the pregnant leach solution to solid/liquid separation to produce a solid residue tailings and a pregnant leach solution containing dissolved nickel,
(e) treating the pregnant leach solution containing dissolved nickel to remove Cu(II);
(f) subjecting the pregnant leach solution to solvent extraction to remove zinc and cobalt,
(g) treating the pregnant leach solution with sodium hydroxide to precipitate nickel from the pregnant leach solution as nickel hydroxide and to form a depleted leach solution,
(h) subjecting the depleted leach solution to ion exchange to remove divalent metal ions,
(i) treating the depleted leach solution with sodium hydroxide to precipitate copper(I) from the pregnant leach solution as copper(II) hydroxide,
(j) subjecting the depleted leach solution to electrolytic treatment to recover chlorine, hydrogen, and sodium hydroxide, wherein at least a portion of the pregnant leach solution obtained in step (c) is treated with chlorine gas to oxidise at least a portion of the copper contained in the pregnant leach solution and then resubjected to the leaching step.

3. A process according to claims 1 or 2, characterizing in that oxidising conditions are maintained by feeding air, oxygen or oxygen enriched air to the oxidative leaching.

4. A process according to any one of claims 1 - 3, characterizing in that the temperature in the oxidative leaching is between 80 - 120 °C.

5. A process according to claim 4, characterizing in that the temperature in the oxidative leaching is between 95 and 110 °C.
6. A process according to any one of claims 1 - 5, **characterizing** in that the oxidative leaching of the nickel sulphide containing material takes place preferably at least in three stages.

7. A process according to any one of claims 1 - 6, **characterizing** in that iron in the tailings is in the form of haematite.

8. A process according to any one of claims 1 - 6, **characterizing** in that copper (II) is removed as copper hydroxy chloride and recycled to the oxidative leaching.

9. A process according to any one of claims 1 - 8, **characterizing** in that an organic solvent containing tri iso-octyl amine or similar is used to extract cobalt and zinc.

10. A process according to claim 2, **characterizing** in that nickel hydroxide is converted to metallic nickel.

11. A process according to claim 10, **characterizing** in that nickel hydroxide is converted to metallic nickel by hydrogen reduction.

12. A process according to any one of claims 1 - 11, **characterizing** in that at least a part of the sodium chloride solution is saline or hypersaline water.

13. A process according to any one of claims 1 - 12, **characterizing** in that at least a part of the sodium chloride solution is formed from sodium chloride admixed with water or naturally occurring brines.
Fig. 3

Nickel Sulphide Concentrate 1

Grind 2

Air/O₂ Steam HCl

Atmospheric 3 stage counter current leach 3

Tailings Solids/liquid separation 6

Precious Metals recovery 8

Limestone Cu(II)hydroxy Chloride precipitation 7

Zn and Co SX 9

Cobalt Product Nickel hydroxide Precipitation 10

H₂ Nickel hydroxide Reduction 11

Nickel Metal

NaCl solution or Hypersaline water

Chlorine Copper Oxidation 5

Recycle Pregnant liquor

Cl₂

Chlorine Alkali Electrolysis 4

HCl Production 15

Hydrogen

Sodium hydroxide

NaOH HCL

Ion Exchange Divalent impurities removal 12

MgCl₂ to evaporation

Cuprous Hydroxide Precipitation 13

Cuprous hydroxide Reduction 14

H₂ Copper metal
INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2006/000321

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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)

IPC8: C22B, C01G, C25C

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

FI, SE, DK, NO

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

EPO-Internal, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CN 1206747 A (CHEMICAL METALLURG CHINESE) 02 February 1999 (02.02.1999), whole document</td>
<td>1-13</td>
</tr>
</tbody>
</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
  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  "&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing the international search report
23 January 2007 (23.01.2007)

Name and mailing address of the ISA/FT
National Board of Patents and Registration of Finland
P O Box 1160, FI-00101 HELSINKI, Finland
Facsimile No. +358 9 6939 5328

Authorized officer
Matti Koskela
Telephone No +358 9 6939 500

Form PCT/ISA/210 (second sheet) (April 2005)
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family members(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO 96/41029 A</td>
<td>19/12/1996</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>CN 1206747 A</td>
<td>02/02/1999</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>US 4067952</td>
<td>10/01/1978</td>
<td>None</td>
<td></td>
</tr>
</tbody>
</table>
### INTERNATIONAL SEARCH REPORT

**International application No.**
PCT/FI2006/000321

**CLASSIFICATION OF SUBJECT MATTER**

<table>
<thead>
<tr>
<th>Int.Cl.</th>
<th>Classification</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>C22B 23/00</td>
<td></td>
<td>2006.01</td>
</tr>
<tr>
<td>C22B 75/00</td>
<td></td>
<td>2006.01</td>
</tr>
<tr>
<td>C22B 75/00</td>
<td></td>
<td>2006.01</td>
</tr>
</tbody>
</table>

Form PCMSA/210 (Extra sheet) (April 2005)