A hydrometallurgical method of processing nickel containing raw material such is provided. The raw material is leached in chloride-based leaching media in a process integrated with chlorine-alkali electrolysis, solvent extraction and electrowinning process stages.
(57) Abrégé(suite)/Abstract(continued):

for producing metallic nickel. The solvent extraction stage comprises a nickel solvent extraction stage, where nickel is extracted from an aqueous solution containing high concentration of chloride. The electrolyte in the electrowinning stage is a sulphate containing aqueous liquid.
Title: METHOD OF PROCESSING NICKEL BEARING RAW MATERIAL

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METHOD OF PROCESSING NICKEL BEARING RAW MATERIAL

FIELD OF THE INVENTION
The invention relates to a hydrometallurgical method of processing nickel containing raw material such as sulphidic nickel concentrate or sulphidic nickel ore where the raw material is leached in chloride-based leaching media in a process integrated with solvent extraction and electrowinning process stages for obtaining metallic nickel. The solvent extraction stage comprises a nickel solvent extraction stage, where nickel is extracted from an aqueous solution containing high concentration of chloride.

BACKGROUND OF THE INVENTION
The world nickel resources are divided into two major categories, sulphide ore and oxidized ore (laterite ore). The conventional exploitation of nickel sulphide ore essentially comprises a pyrometallurgical process step followed by hydrometallurgical process steps, where the ore is first finely ground, and then the nickel sulphide minerals are concentrated by froth flotation into a nickel concentrate. The concentrate is treated further by smelting and reduction to produce a nickel bearing matte, which also contains 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.

Lean ores set challenges in the concentration process. Poor quality concentrates are difficult and expensive to refine in pyrometallurgical
processes. Pyrometallurgical treatment of such concentrates is especially difficult, when the magnesium content in the concentrate is high and respectively the iron content is low. In such a case, the iron/magnesium ratio of the concentrate becomes low causing further difficulties. For example when the MgO content of the slag created in the smelting process is over 11%, the viscosity of the slag rises so high that it disturbs the removal of the slag from the furnace. As the viscosity rises part of the nickel matte remain in the slag. In arid areas, saline water must be used for wet concentration, in which case the concentrate contains halides that are hazardous in pyrometallurgical processes.

A large number of hydrometallurgical routes for processing nickel sulphide concentrates are disclosed in literature. In general the prior art processes include grinding or fine grinding of the concentrate, where after the sulphide is treated in oxidative pressure leaching for processing sulphuric acid for the leach process.

The Activox process that is described for example in the EP patent 1 303 641 comprises the grinding of nickel concentrate into a very fine ground material, where after it is subjected to oxidative leaching at a high pressure for separating nickel into the sulphate solution, and subsequently impurities are removed by known methods, and metallic nickel is recovered.

A drawback of the above described hydrometallurgical processes is that a large part of the sulphur contained in the sulphide is oxidized into sulphuric acid, which results in high expenses caused by neutralization reagents, and the creation of large waste quantities that must be removed, such as ammonium sulphate and gypsum. It can be estimated that the high expenses resulting from these two factors when combined make said processes commercially less attractive.
The WO patent application 96/41029, "Chloride assisted hydrometallurgical extraction of nickel and cobalt from sulphide ores", describes oxidative pressure leaching of nickel and cobalt sulphide ores in the presence of oxygen and likewise an acidic leaching containing halide, copper and sulphate ions. The obtained solution is subjected to solids separation and solution purification, precipitation of the mixed nickel and cobalt hydroxide, re-leaching of the precipitate in an ammoniacal solution, where after the metals are separated by solvent extraction and recovered by electrowinning. The process suffers similar limitations as the sulphate-based hydrometallurgical processes described above.

US patent 3,880,653 describes the recovery of metallic nickel from a nickel matte containing copper and precious metals. The leaching of the nickel matte is realized as a concurrent process, where the nickel matte is first suspended to a chloride solution obtained from nickel electrowinning and containing monovalent copper. The chloride solution is conducted to a leaching step, where also chlorine created in electrolysis is fed. Chlorine oxidizes the monovalent copper, which in turn dissolves the nickel and is at the same time reduced back to monovalent form and precipitated as copper sulphide. The sulphur contained in the dissolving sulphides is precipitated as element sulphur. The precious metals remain undissolved in the leaching. After the first leaching step, the whole batch of slurry is conducted to a second step, where the dissolved divalent copper is precipitated by means of nickel matte. The solution and the solid material are separated, and the solution is conducted to nickel electrowinning.

JP patent application 10-140257 describes the recovery of nickel by means of chlorine leaching and electrolysis from materials, such as nickel matte, containing nickel, cobalt, copper and sulphur. Nickel matte is leached in concurrent leaching into a chloride solution that contains monovalent copper, and chlorine is supplied into the solution for leaching nickel and other metals. When chlorine is supplied into the first steps of the leaching process, the
sulphur contained in the nickel matte also is partly dissolved and forms sulphuric acid in the solution. In the final step of the leaching process, there is no more supplied chlorine but air, which means that in the final step, the leaching is carried out by means of the oxygen contained in the air and sulphuric acid. The nickel chloride bearing solution is conducted to electrolysis for recovering the metallic nickel, and the chlorine created in the electrolysis is used for leaching the raw material. Also the recycled solution obtained from electrolysis is used for leaching the raw material.

Among the methods described above, the latter two deal with nickel mattes that are produced by first processing the nickel concentrate pyrometallurgically. The large quantity of sulphur dioxide created in the process, which sulphur dioxide is generally processed further into sulphuric acid, can be regarded as a drawback in the pyrometallurgical treatment. The use and commercial marketing of sulphuric acid is difficult, particularly when the smelter location is far from the location where sulphuric acid should be used.

WO publication WO2007/039665 discloses a method of producing a nickel product from nickel-bearing sulphide raw materials, such as nickel sulphide concentrate or ore or scrap. In the method, the raw material is leached in atmospheric conditions to an aqueous solution of sodium chloride and copper (II) chloride. Chlorine, hydrogen and sodium hydroxide needed in the process are produced in a chlorine-alkali electrolysis cell that is integrated as a process stage in the overall process. The nickel-enriched pregnant leach solution is subjected to a precipitation of dissolved iron and sulphates, and the precipitate is fed into the final step of the leaching process. Nickel is precipitated as nickel hydroxide Ni(OH)₂ from the pregnant leach solution by means of sodium hydroxide.

WO publication WO2007/039664 discloses a method of recovering nickel from a nickel sulphide containing material including the steps of: providing a
nickel sulphide containing material; oxidative leaching of the nickel sulphide containing material with a sodium chloride leach solution containing cupric chloride and hydrochloric acid in an oxidising atmosphere at atmospheric pressure and temperature to form a pregnant leach solution containing dissolved nickel; treating the pregnant leach solution containing dissolved nickel to separate copper and recycle it at least partly back to the leaching stage (b); purification of the nickel pregnant leach solution by the use of solvent extraction to remove cobalt, zinc and residual copper; recovering nickel from the pregnant leach solution to form a nickel depleted leach solution; and electrolytically treating the depleted leach solution in chlorine alkali electrolysis to recover chlorine, hydrogen, and sodium hydroxide. WO2007/039664 does not refer to a possibility of recovering nickel from a sulphate solution in electrowinning after nickel solvent extraction stage.

A cobalt solvent extraction from chloride environment is known where cobalt is extracted from very high chloride environment using an anionic extractant to extract a cobalt-chloride complex. Also a cationic extractant for cobalt extraction from chloride containing sulphate solutions is known. In the known applications the chloride concentrations relatively low.

OBJECT OF THE INVENTION
The object of the present invention is to overcome disadvantages of the prior art processes and to provide a new and advantageous hydrometallurgical process for producing nickel metal.

The invention provides method where the advantages of atmospheric leaching are utilized and recycling and regeneration of leaching chemicals are arranged through chlorine-alkali electrolysis. The method is particularly suitable for recovering metals from poor nickel concentrates and ores. The recycling of reagents within the process makes the method particularly advantageous.
A special advantage of the present invention is that it provides a hydrometallurgical method for recovering metallic nickel where the metallic nickel is won on a cathode of an electrowinning cell from a sulphate electrolyte.

Further, the present invention provides a method of handling and recovering impurities of the raw material. Such impurities are for example magnesium and halides which, when treated according to the present invention, can be treated without disturbing the recovery of nickel.

SUMMARY OF THE INVENTION
The invention relates to a method for producing nickel metal from nickel-bearing sulphide raw materials, such as nickel sulphide concentrate or ore or scrap.

Nickel bearing feed material such as nickel sulphide concentrate or ore or scrap, particularly poor nickel concentrates and ores can be successfully treated in according to the method of the present invention. Even low-grade nickel feed materials (Ni < 1-10%) can be processed and number of impurities, such as cobalt, iron, magnesium, zinc, copper and arsenic, can be treated without disturbing the recovery of nickel. Generally nickel sulphide bearing raw material always contains a certain amount of copper, iron, cobalt and magnesium.

A method according to the present invention comprises the steps of:
(a) providing a nickel sulphide containing material;
(b) leaching the nickel sulphide containing material with a chloride leach solution at atmospheric pressure in a leaching stage to form a pregnant leach solution containing dissolved nickel and a concentration of chloride;
(c) extracting the dissolved nickel from the leach solution with solvent extraction to produce a nickel sulphate containing electrolyte;
(d) recovering nickel from the electrolyte at a nickel electrowinning stage;
(e) regenerating depleted chloride containing process solutions from process steps c) to d) in chlorine-alkali electrolysis stage to recover chlorine, hydrogen and sodium hydroxide back to the process.

The leaching of the nickel raw material is carried out in chloride-based aqueous solution. The leaching step preformed in the leaching stage produces a process liquid containing very high amount of chlorides. In a minor metal removal stage cobalt and other minor metals are separated from the very high chloride content solution in a solvent extraction process using cationic extractant. The raffinate from the minor metal removal stage (MM SX) is fed to a nickel solvent extraction stage (Ni SX) where nickel is selectively extracted from a very high chloride solution and stripped to a sulphate liquid to form a nickel sulphate electrolyte. The nickel electrolyte is conducted to a nickel electrowinning stage. The reagents, such as chlorine, hydrogen and sodium hydroxide, needed in the leaching stage and in other processing steps, are obtained from chlorine-alkali electrolysis that is integrated as a step in the process.

According to the method, the raw material is preferably leached in atmospheric conditions to an aqueous solution containing sodium chloride and copper (II) chloride. The pregnant leach solution (PLS) from the leaching stage is lead to solvent extraction stages. The chloride content of the PLS is over 100 g/l.

According to one embodiment of the invention the production method of a nickel product contains the following steps:
a) nickel bearing raw material is leached in two or more steps by a solution containing sodium chloride and copper (II) chloride as a countercurrent leach in atmospheric conditions, so that the first leaching step when observed in the proceeding direction of the concentrate is non-oxidative, and the next steps are oxidative with respect to forming a nickel enriched nickel chloride - sodium chloride pregnant leach solution (PLS) and leach residue,

b) the nickel-enriched pregnant leach solution is subjected to a liquid purification for a precipitation of dissolved iron and sulphates, and the precipitate is fed into the final step of the leaching process,

c) cobalt and other minor metals (such as zinc and copper) are separated from the very high chloride containing liquid with cationic extractants in a cobalt solvent extraction unit. The cobalt depleted raffinate is conducted to a nickel solvent extraction (Ni SX) unit,

d) cobalt is recovered from cobalt solvent extraction unit in an aqueous solution and precipitated,

e) nickel is extracted from the cobalt solvent extraction raffinate in a nickel solvent extraction unit with cationic extractants,

f) nickel sulphate electrolyte from the nickel solvent extraction stage is conducted to a nickel electrowinning plant, where nickel is won to cathodes,

g) the sodium chloride solution, depleted in nickel, is conducted to magnesium precipitation, where magnesium is precipitated from the solution, by means of sodium hydroxide, as magnesium hydroxide Mg(OH)₂,

h) other divalent dissolved impurity residues are removed from the NaCl solution by means of ion exchange,

i) the NaCl solution is subjected to concentration,

j) the concentrated NaCl solution is conducted to chlorine-alkali electrolysis, where part of the solution is by electrolysis processed into chlorine, hydrogen and sodium hydroxide that are used as reagents in the method,
k) the NaCl solution that was depleted in the electrolysis is fed to the final leaching step of the concentrate and/or ore.

Preferably the leaching of nickel sulphide bearing concentrate and/or ore is carried out in two steps.

In the first leaching step, raw material is leached in non-oxidative conditions by means of copper (II) chloride, so that part of the sulphides contained in the concentrate are dissolved, and copper is precipitated as copper sulphide.

In the non-oxidative leaching step of raw material, the pH is within the range 0.5 – 3.0.

In the oxidative leaching steps of raw material, the raw material is advantageously leached by means of copper (II) chloride for dissolving sulphides, and in the first leaching step the precipitated copper sulphide is made to be dissolved into copper (II) chloride. In the oxidative leaching steps, the pH is adjusted within the range 1.7 – 2.8, preferably within the range 2.0 – 2.5.

According to one embodiment of the method, the oxidative reagent employed in the oxidative leaching steps of concentrate and/or ore is oxygen-bearing gas, which is oxygen, oxygen-enriched air or air, and hydrochloric acid is fed into the leaching process.

According to another embodiment of the method, the oxidative reagent employed in the oxidative leaching steps of concentrate and/or ore is chlorine formed in chlorine-alkali electrolysis.

According to one embodiment of the method, into a nickel-enriched pregnant leach solution there is fed a calcium compound and sodium hydroxide for removing the dissolved sulphates and iron. The created iron/gypsum precipitate is conducted to the final leaching step.
According to a preferred embodiment of the method, cobalt is removed from the pregnant leach solution by a cationic solvent extraction reagent, the raffinate from the cobalt extraction is fed to a nickel solvent extraction, where nickel is extracted by a cationic organic extractant and sulphate based nickel solution suitable as an electrolyte for nickel electrowinning stage is produced. The nickel electrolyte from the nickel solvent extraction plant is advanced to a nickel electrowinning plant, where nickel is won to cathodes in a conventional manner.

Depending on the impurity levels in the nickel electrolyte and Ni EW electrolyte quality requirements further purification of the nickel electrolyte can be done for example with an ionic exchange process, where small amounts for example copper, cadmium, iron and zinc can be removed from the produced advance electrolyte.

According to a preferred embodiment of the method, the nickel depleted NaCl solution, the raffinate from the nickel solvent extraction, which has become poor in nickel, is subjected to Mg precipitation in order to remove dissolved magnesium prior to the electrowinning stage. The magnesium precipitation is advantageously carried out at the pH value 9-10.

The hydrochloric acid that is used as the leach reagent of raw material is advantageously made of the hydrogen and chlorine created in the chlorine-alkali electrolysis.

A nickel bearing raw material may contain gold and/or other precious metals (PGM). In that case the gold is dissolved in the final leaching step and recovered from the solution of the final leaching step; the gold-free solution is conducted to the preceding leach step, when observed in the proceeding direction of the concentrate. Other precious metals are recovered from the leach residue.
According to one embodiment of the method, part of the depleted solution created in the concentration of sodium chloride is conducted to a concentrate leaching process.

LIST OF DRAWINGS
Figure 1 represents a schematic flow sheet of one preferred embodiment of the invention, and figure 2 represents a schematic drawing of another embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

In this context, the concept of nickel sulphide bearing raw material means mainly nickel sulphide concentrate or ore but it can also be scrap type or matte. For the sake of simplicity, the text only mentions concentrate. Each leaching step typically consists of a series of several reactors, where the suspension of solution and solids is transferred as overflow from one reactor to the next. The reactors are provided with agitators. In between the process steps, there is performed thickening, so that the solution and the solids are transferred to different steps in the countercurrent leaching. The description of the invention describes a two-step leaching process, but it may turn out to be necessary to apply several steps. The notion of atmospheric conditions means that the operations are carried out at the pressure of the environment and at a temperature, which is within the range of 90° C – the boiling point of the solution – i.e. roughly 110° C. The alkaline chloride can be sodium or potassium chloride.

A method according to the present invention is described below with reference to figures.
The leaching of nickel sulphide bearing raw material (nickel concentrate in Figs. 1 and 2) is carried out in countercurrent leaching 11, 21 in two or more steps.

In one embodiment of the invention the raw material is fed into the first leaching step, and the chloride solutions and oxidative reagents used in the leaching process are fed into the second step. In the first leaching step, the conditions are adjusted such that part of the nickel and iron contained in the raw material are dissolved, owing to the influence of divalent copper, and the monovalent copper created in the leaching process is precipitated as copper sulphide. Neither oxygen nor other oxidant is fed into the first leaching step for dissolving copper, but the conditions in the first leaching step are non-oxidative. The leaching takes place in the pH range 0.5 – 3.0, depending on the raw material. The principal reaction that takes place in this step can be illustrated by the leaching reaction of pentlandite:

\[ 2(Ni,Fe)_9S_8 + 18 CuCl_2 \rightarrow 9 NiCl_2 + 9 FeCl_2 + 9 Cu_2S \downarrow + 7 S^0 \quad (1) \]

The reaction (1) can be described as an exchange reaction where divalent copper is reduced to monovalent and at the same time dissolves the iron and nickel contained in the concentrate. Other nickel and iron minerals, such as violarite, millerite and pyrrhotite, are also dissolved according to the same principle, and respectively copper sulphide and element sulphur are precipitated. The magnesium contained in the nickel raw material is dissolved, thus forming magnesium chloride.

The copper contained in the raw material does not dissolve in the first leaching step conditions, but only in the second step, or if there are several leaching steps, only in the last step. If the copper content of the raw material is not sufficient for efficient leaching, more copper is brought to the leaching process in some suitable way, for instance in the form of copper concentrate or copper sulphate. Advantageously the copper content in the solution is of
the order 5-50 g/l. By adjusting the conditions to be suitable in the way described above, nearly all of the copper is precipitated in the first step as sulphide and is conducted, along with the precipitate, to the next leaching step. It is an advantage of the method that there is not needed a separate precipitation step for separating copper from the nickel-enriched solution, but precipitation is carried out in connection with the leaching of nickel. If the quantity of the copper contained in the concentrate is more than what is needed in the leaching process, part of the copper can be removed in a way suitable for the purpose.

The nickel-enriched NiCl₂-NaCl solution, PLS, obtained from the leaching step 11, 21, contains an amount of dissolved iron and sulphates. The removal of iron and sulphates is carried out in a solution purification step 22. Sulphates are advantageously precipitated by means of a calcium compound, such as limestone, or other calcium compound, so that when calculated as sulphur, their content left in the solution is at the most 2 g/l. In order to oxidize iron into trivalent form, it is advantageous to feed lye (NaOH) in the solution, in which case iron is precipitated from the solution. The precipitate can be fed back to the final step of the concentrate leaching process, from where iron precipitate and gypsum are removed along with the leach residue.

In case the copper content of the nickel concentrate is higher than what is needed in the leaching process, the nickel-enriched NaCl solution still contains divalent copper. The copper can be removed in a separate copper recovery step, which is advantageously cobalt solvent extraction 12, 23 or a minor metal removal 23 according to the present invention.

**Minor Metals Solvent Extraction (MM SX)**

Feed solution from solution purification stage is fed to the minor metals solvent extraction process 12,23 (MM SX). In the MM SX process minor
impurity metals like Co, Cu, Zn and Mn are extracted from the feed solution with a cationic extractant in a very high chloride environment. Multiple extraction stages are used.

Before the extraction stages a separate organic and/or crud removal circuit can be installed if needed. pH control can be done in the mixer-settlers or in the organic tank (pre-neutralization) or a combination of these neutralization systems can be used.

Loaded organic from the extraction stages can be scrubbed (chemical impurity removal) or washed (physical impurity removal) from the entrained nickel, chloride or some other impurity component. Need for the scrubbing and/or washing stages is determined by the feed quality to the MM SX process and the desired product quality from the MM SX process. One or more scrubbing/washing stages can be used.

Loaded organic from the extraction or scrubbing and/or washing stages is fed to the stripping stages, where metals from the organic phase are stripped with an acidic solution to the aqueous phase. Metals from the organic phase can be stripped in one or more solutions. Selective strip, where two or more stripping solutions are produced, are normally preferred solution, because selective strip increases the stripping liquid qualities. However, metals from a single strip solution can also be separated after the MM SX process for example with a selective precipitation process as carbonates, hydroxides or sulphides. One or more stripping stages can be used.

**Nickel Solvent Extraction**

Nickel solvent extraction (Ni SX) feed solution from the MM SX process, MM SX raffinate, is pumped to the nickel solvent extraction process 13, 24. Before solution from the MM SX is fed to the Ni SX extraction stages some organic entrainment removal processes and equipment must be installed
between MM SX and Ni SX. This equipment usually includes diluent wash, after settler, carbon filters and storage tanks. All or any combination of this equipment can be used.

After the organic removal Ni SX feed solution is fed to the nickel solvent extraction stages. In the nickel solvent extraction nickel is extracted selectively from the feed stream with a cationic extractant in a very high chloride environment. Multiple extraction stages are used. pH control can be done in the mixer-settlers or in the organic tank (pre-neutralization) or a combination of these neutralization systems can be used.

Loaded organic from the extraction stages can be scrubbed (chemical impurity removal) or washed (physical impurity removal) from the entrained impurities like chloride, magnesium and calcium. One or more scrubbing and/or washing stages are used.

Loaded organic from the scrubbing and/or washing stages is fed to the stripping stages, where nickel from the organic phase is stripped with an acidic solution to the aqueous phase. Produced stripping liquid, advance electrolyte, is used as a feed solution for a nickel electrowinning (Ni EW) process 13, 26. Used acid can be sulphuric or hydrochloride acid. Normally at this stage chloride based process is converted to a sulphate phase process and thus sulphuric acid is used for stripping.

Depending on the impurity levels in the advance electrolyte and Ni EW electrolyte quality requirements further purification of the advance electrolyte can be done for example with an ionic exchange process, where small amounts for example copper, cadmium, iron and zinc can be removed from the produced advance electrolyte.

**Magnesium removal**
Magnesium is a harmful substance in the nickel electrowinning 13, 26. Magnesium is removed from the nickel electrolyte in a magnesium removal stage 14, 25. Magnesium would be precipitated (process step 25 in Fig 2) by lye from the product solution, obtained from nickel solvent extraction, by raising the solution pH value to roughly 9, so that Mg was precipitated as magnesium hydroxide which also is a commercial product.

The quantity of magnesium is generally largest, and the dimensioning of the final solution purification such as ion exchange according to the Mg quantity becomes fairly expensive. One advantageous method according to the invention is to remove the magnesium from the solution in the Mg precipitation step 25 by using sodium hydroxide NaOH, formed in the chlorine-alkali electrolysis 14, 29, as the precipitation reagent. The solution pH is raised to within the range 9-10, in which case Mg is precipitated as magnesium hydroxide Mg(OH)_2. The hydroxide precipitate is subjected to thickening, and the underflow of the thickening is recycled to the precipitation step advantageously for improving the quality of the precipitate. When the hydrometallurgical treatment is completed with a separate magnesium recovery, it is possible thereby to treat concentrates where the magnesium quantity is hazardously high for treating the concentrate pyrometallurgically.

When the quantity of other impurities, such as zinc and nickel left in the solution after magnesium removal 14, 25, is of the order milligrams per litre, the most advantageous method for removing them is ion exchange (brine purification 28 in Fig 2). Ion exchange is preferably carried out by means of a chelating ion exchange resin. Ion exchange functions according to known technique, so that the impurities bound in the resin are removed by means of hydrochloric acid, and the resin is regenerated with a NaOH solution. Consequently, the reagents needed in ion exchange are advantageously obtained from the chlorine-alkali electrolysis that forms part of the process.
The content of the NaCl solution, obtained from the brine treatment 14, 28, can be of the order 150-240 g/L NaCl, preferably 200 g/L. However, for the chlorine-alkali electrolysis it is necessary to raise the NaCl content in the solution up to the order of 160-300 g/L, preferably 280-300 g/L. The content increase is carried out in some suitable way, for example by means of a vacuum evaporator or immersion evaporator in the evaporation step. When necessary, the depleted NaCl solution created in the evaporation step can be conducted to the concentrate leaching process (not in the figure).

The purified and concentrated sodium chloride solution is conducted to chlorine-alkali electrolysis 14, 29 for producing the chlorine, hydrogen and sodium hydroxide needed in different steps of the nickel product process. The chlorine-alkali electrolysis functions in a known fashion. The NaCl saline solution is in the electrolysis conducted to the anode side, where the electric current disintegrates it, thus forming chlorine gas. Sodium ions proceed through a membrane placed in between the anode and cathode sides to the cathode side, where the electric current disintegrates water to hydrogen gas, thus forming sodium hydroxide. The NaCl solution conducted to electrolysis is depleted in the electrolysis in the proportion of the gases and lye produced there from. The NaCl content of the solution removed from electrolysis is of the order 150 - 240 g/L, preferably 200 g/L, and it is recycled back to the raw material leaching process.

As was maintained above, the sodium hydroxide formed in the chlorine-alkali electrolysis 14, 29 is used at least in the precipitation of magnesium hydroxide. Sodium hydroxide is also needed in the ion exchange regeneration, and when necessary, it can also be used in the removal of sulphates.

An advantageous method for leaching nickel bearing raw material is to feed oxygen to the final leaching step and to adjust the leach conditions by feeding hydrochloric acid therein according to reaction 3. The required
hydrochloric acid is advantageously made of the hydrogen and chlorine created in the electrolysis of the hydrochloric acid production process.

EXAMPLE 1

Nickel bearing feed material (e.g. nickel sulphide concentrate or ore or bulk concentrate containing mainly nickel and copper sulphides, scrap or matte) is leached in sodium chloride solution (50-200 g/l NaCl) containing divalent copper ions. Leaching is conducted in two or more counter-current leaching stages. The first leaching stage is operated in non-oxidative conditions and the subsequent stages in oxidative conditions.

In the first stage feed material is mixed with the process solution from the second leaching stage. Nickel sulphides are leached according to the reaction (1).

\[
2(Ni,Fe)_2S_8 + 18 CuCl_2 \rightarrow 9 NiCl_2 + 9 FeCl_2 + 9Cu_2S \downarrow + 7 S_6
\]  \hspace{1cm} (1)

Nickel and iron are transferred in solution while copper is precipitated in solid phase. Sulphide sulphur is converted mainly to elemental sulphur. Slurry from the first leaching stage is treated in a solid-liquid separation step. Solids are transferred to the subsequent oxidative leaching stage(s) and liquid is recovered as PLS, which is sent to solution purification stages. Temperature and pH in the first leaching stage is 80-110° and 0.5-3.0, respectively.

Solids from the first leaching stage are mixed with depleted brine from the chlor-alkali electrolysis and further leached in oxidative leaching stages. Leach is oxidised with hydrochloric acid and oxidising gas such as oxygen, air, oxygen enriched air or chlorine. As a result copper sulphide precipitated in the first leaching stage is leached. Copper is released in solution as divalent copper ions, which in turn are consumed in nickel and iron sulphide leaching according to reaction (2).
2(Ni,Fe)_3S_8 + 36 CuCl_2 → 9 NiCl_2 + 9 FeCl_2 + 36 CuCl + 16 S^0 \quad (2)

Again sulphur in metal sulphides in converted mainly into elemental sulphur.

Copper(I) chloride produced in the reaction (2) is re-oxidised according to reaction (3) back to copper(II) chloride.

4 CuCl + O_2 + 4 HCl → 4 CuCl_2 + 2 H_2O \quad (3)

Hydrochloric acid used in leaching is produced in chlor-alkali electrolysis.

In the second leaching stage leached iron is oxidised and precipitated as iron oxides or hydroxides. In reactions (4) and (5) iron oxidation and precipitation as goethite is shown as an example.

FeCl_2 + 2 CuCl_2 → FeCl_3 + CuCl \quad (4)

FeCl_3 + 2 H_2O → FeOOH↓ + 3 HCl \quad (5)

After the oxidative leaching stages solid-liquid mixture is subjected to solid-liquid separation step where iron and sulphur residue is separated from nickel containing solution. Residue is sent to tailings facility. Additional residue stabilisation step may be applied. Liquid from the solid-liquid separation step is transferred to the preceding leaching stage.

If gold is present in the feed material, it is leached in the oxidative leaching stages and recovered.

During the leaching process iron and sulphur (as sulphate) are also leached. Iron and sulphates are removed in solution purification. Oxidising gas (O_2, air, oxygen enriched air, chlorine) is injected in PLS in order to oxidise iron and the pH of the solution is adjusted with sodium hydroxide and/or calcium carbonate/hydroxide to precipitate iron as iron hydro-oxides and sulphur as gypsum. Resulting solids are separated from PLS and recycled to oxidative leaching stages. Treated PLS is transferred to cobalt solvent extraction.
EXAMPLE 2

Sulphidic nickel concentrate was leached according to the method of the invention. The major part of the nickel contained in the concentrate was bound in pentlandite. Other main minerals were antigorite, millerite and pyrrhotite. The chemical analysis of the concentrate was:

<table>
<thead>
<tr>
<th>Ni</th>
<th>Fe</th>
<th>S</th>
<th>Co</th>
<th>Cu</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>3.78</td>
<td>29.3</td>
<td>16.3</td>
<td>0.23</td>
<td>0.2</td>
<td>19.23</td>
</tr>
</tbody>
</table>

Leaching step 1

Nickel concentrate (690g) was leached in a solution (2500 ml), the initial content of which was:

<table>
<thead>
<tr>
<th>Ni</th>
<th>Fe</th>
<th>S</th>
<th>Co</th>
<th>Cu</th>
<th>Mg</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>g/l</td>
<td>mg/l</td>
<td>g/l</td>
</tr>
<tr>
<td>7.62</td>
<td>1.2</td>
<td>1680</td>
<td>670</td>
<td>6.8</td>
<td>1680</td>
<td>30.5</td>
</tr>
</tbody>
</table>

Oxidant was not used in the leaching, and the pH value of the solution was 2-3 during the leaching process. Copper was precipitated from the solution as chalcochite \( \text{Cu}_2\text{S} \), and at the same time iron was dissolved. After leaching three hours at the temperature of 95\(^\circ\)C, there was obtained a solution (leach product solution, PLS), the composition of which was:

<table>
<thead>
<tr>
<th>Ni</th>
<th>Fe</th>
<th>S</th>
<th>Ca</th>
<th>Co</th>
<th>Cu</th>
<th>Mg</th>
<th>Na</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>g/l</td>
<td>g/l</td>
<td>mg/l</td>
</tr>
<tr>
<td>10.3</td>
<td>2760</td>
<td>2470</td>
<td>614</td>
<td>670</td>
<td>&lt; 5</td>
<td>11200</td>
<td>41.2</td>
<td>37.3</td>
</tr>
</tbody>
</table>

After three hours, the composition of solids was:

<table>
<thead>
<tr>
<th>Ni</th>
<th>Fe</th>
<th>S</th>
<th>Co</th>
<th>Cu</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>3.7</td>
<td>29.4</td>
<td>17</td>
<td>0.24</td>
<td>2.3</td>
<td>11.1</td>
</tr>
</tbody>
</table>

Leaching step 2
Solids, i.e. the leach residue from the first leaching step were leached oxidatively in a solution containing 130 g/l NaCl and 12 g/l Cu\textsuperscript{2+}. Oxygen and hydrochloric acid were fed in the leaching process for oxidizing the sulphides. The pH value was maintained within the range 2.0 – 2.5. The duration of the leaching process was 8 hours, where after the compositions of the solution and the solids were:

**Solution**

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Fe</th>
<th>S</th>
<th>Ca</th>
<th>Co</th>
<th>Cu</th>
<th>Mg</th>
<th>Na</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/l</td>
<td>10.2</td>
<td>11.5</td>
<td>1180</td>
<td>372</td>
<td>678</td>
<td>10.7</td>
<td>671</td>
<td>49</td>
<td>27.9</td>
</tr>
</tbody>
</table>

**Solids**

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Fe</th>
<th>S</th>
<th>Co</th>
<th>Cu</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>0.09</td>
<td>28.5</td>
<td>14.0</td>
<td>0.01</td>
<td>0.38</td>
<td>9.5</td>
</tr>
</tbody>
</table>

The total yields to the solution, calculated from the iron balance, were (leaching step 1 + leaching step 2):

Nickel 98.2 %

Cobalt 97.2 %
CLAIMS:

1. A hydrometallurgical method of producing metallic nickel from nickel bearing raw material, the method comprising the steps of:
   a) providing a nickel sulphide containing material;
   b) leaching the nickel sulphide containing material with a chloride leach solution at atmospheric pressure in a leaching stage to form a pregnant leach solution containing dissolved nickel and a concentration of chloride;
   c) extracting the dissolved nickel from the leach solution with solvent extraction to produce a nickel sulphate containing electrolyte;
   d) recovering nickel from the electrolyte at a nickel electrowinning stage;
   e) regenerating depleted chloride containing process solutions from process steps c) to d) in a chlorine-alkali electrolysis stage to recover chlorine, hydrogen and sodium hydroxide back to the process.

2. The method according to claim 1, wherein the nickel bearing raw material is selected from the group consisting of: nickel sulphide concentrate; ore; and scrap.

3. The method according to claim 1, wherein the leach solution from the leaching step b) contains dissolved chloride more than 100 g/l.

4. The method according to any one of claims 1 to 3, wherein the nickel bearing raw material is leached in an aqueous solution containing sodium chloride and copper (II) chloride in atmospheric conditions so as to form a nickel enriched nickel chloride pregnant leach solution (PLS) and a leach residue.
5. The method according to claim 1, wherein the leach the pregnant leach solution from step b) is subjected to a precipitation of dissolved iron and sulphates.

6. The method according to claim 1, wherein the liquid from step b) is fed to a solvent extraction process where in very high chloride concentration using a cationic organic reagent minor metal are removed from the solution and conducted thereafter to the process step of c).

7. The method according to claim 6, wherein the minor metal is selected from the group consisting of: cobalt; copper; zinc; and manganese.

8. The method according to claim 1, wherein in the nickel solvent extraction step c) nickel is extracted from the solution with a cationic extractant and stripped to a sulphate solution.

9. The method according to claim 1, wherein the feed to the chlorine-alkali electrolysis stage of step e) is purified from magnesium.

10. The method according to claim 1, wherein other divalent dissolved impurity residues are removed from the chlorine-alkali electrolysis stage feed by means of ion exchange.

11. The method according to claim 1, wherein in a first leaching step, raw material is leached in non-oxidative conditions in a non-oxidative leaching step by means of copper (II) chloride, so that part of the sulphides of the raw material is dissolved, and copper is precipitated as copper sulphide.
12. A method according to claim 11, wherein the pH value of the non-oxidative leaching step is within the range 0.5 - 3.0.
Fig. 1