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(54) **Title:** OXIDATIVE LEACHING OF CARBON-CONTAINING MIXED HYDROXIDE PRECIPITATES

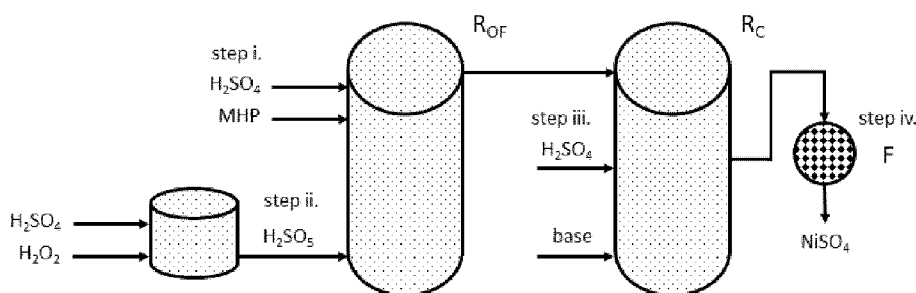


Figure 1

(57) **Abstract:** The present invention provides a process for selective leaching of nickel from a mixed hydroxide precipitate comprising nickel, cobalt, manganese and carbon, wherein carbon is comprised as organically bound carbon and/or graphite in an amount of 0.10 to 10.00 wt.% relative to the weight of said mixed hydroxide precipitate, said process comprising the steps of: i. providing a mixed hydroxide precipitate slurry, and at least partially leaching of nickel in said mixed hydroxide precipitate by adding sulphuric acid; ii. oxidizing the at least partially leached mixed hydroxide precipitate slurry from step i. with peroxymonosulphuric acid and/or a salt thereof in an acidic aqueous medium at a pH of at most 4; iii. acidifying the oxidized mixed hydroxide precipitate slurry obtained from step ii. by adding sulphuric acid to dissolve residual amounts of nickel in the solid phase, thereby obtaining a solid phase comprising cobalt and manganese and an aqueous phase comprising nickel sulphate; and iv. separating said solid phase and said aqueous phase.



## OXIDATIVE LEACHING OF CARBON-CONTAINING MIXED HYDROXIDE PRECIPITATES

### TECHNICAL FIELD

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The present invention relates to a process for manufacturing nickel sulphate suitable for the production of cathode materials for lithium-ion batteries.

### INTRODUCTION

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Secondary lithium-ion batteries (LIB) have found wide-spread application in portable devices and electric vehicles, as well as in specialized aerospace applications. Important characteristics of reusable batteries include charge/discharge efficiency, cycle durability, energy density and safety. Many developments have focused on improving the performance of the cathode of the LIB.

15

Next to lithium cobalt oxide, lithium manganese oxide and lithium iron phosphate, lithium nickel manganese cobalt oxide ("NMC",  $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ ) and lithium nickel cobalt aluminium oxide ("NCA",  $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ ) have received a lot of attention due to their superior performance. They can be easily obtained from mixing a suitable mixed metal precursor with a suitable lithium compound, and subsequent heat treatment of the mixture. Further processing steps are widely reported, e.g. for doping with further elements, providing a surface coating, improving crystallite size, etc.

20

The rising demand for electric vehicles (EV) has led to an increased demand for high purity nickel, especially for high purity nickel sulphate. Effectively, nickel refineries for preparing high purity nickel are considered of paramount importance for the supply of battery materials in the next decade. Such nickel refineries will need to allow for high capacities and high efficiency of the processes to yield the desired nickel sulphate in a desired quantity and high purity.

30

Known processes for refining of a raw nickel feed material such as mixed hydroxide precipitate comprise the steps of leaching in acid, optionally in presence of hydrogen

peroxide or sulphur dioxide; copper and iron removal in a hydrolysis step; and purification through one or more solvent extraction steps for obtaining a high purity nickel sulphate product. Typically, a specific solvent extraction step is foreseen for the purpose of removing cobalt. However, solvent extraction processes are cost intensive and do not allow for high variability of the feed solution.

CA 2 949 580 A1 describes a process for the selective leaching of nickel and cobalt from a mixed hydroxide intermediate that has been produced from the processing of a nickel ore or concentrate also containing manganese, the process including the steps of: a) providing a mixed hydroxide intermediate and forming a mixed hydroxide intermediate slurry; b) treating the mixed hydroxide intermediate slurry with an oxidizing agent to substantially oxidise the manganese present whilst minimising the oxidation of cobalt and nickel; and c) and either consecutively or simultaneously with the oxidation step, leaching the oxidised slurry in an acid sulphate medium, to produce a nickel and/or cobalt sulphate solution containing substantially all of the nickel and a major portion of the cobalt and a solid residue containing substantially all of the manganese in a resultant oxidised leach slurry. Yet, the aforementioned process does not allow for the obtained nickel sulphate solution to be processed as such for the production of cathode material precursors.

Novel processes are in demand to provide new processes which allow for ease of operation, high throughput, and optimized use of energy and reactants, and starting from raw feed materials. Furthermore, novel feed of mixed hydroxide precipitate may comprise higher amounts of carbon, which is not entirely eliminated through state-of-the-art processes. Such carbon forms a significant contamination which is to be considered in the downstream processing of the nickel sulphate solution and crystals. Problems which are to be overcome are contamination and degradation of solvents in solvent extraction units, inclusion of carbon during crystallization, foaming, etc. It is therefore an object of the present invention to reduce or even completely avoid the negative impact of carbon in the mixed hydroxide precipitate feed on the refining of nickel sulphate.

## SUMMARY

The current invention provides in a solution for at least one of the above mentioned problems by providing a process for selective leaching of nickel from a mixed hydroxide precipitate comprising nickel, cobalt, manganese and carbon, wherein carbon is comprised as organically bound carbon and/or graphite in an amount of 0.10 to 10.00 wt.% relative to the dry weight of said mixed hydroxide precipitate, said process comprising the steps of:

- i. providing a mixed hydroxide precipitate slurry, and at least partially leaching of nickel in said mixed hydroxide precipitate by adding sulphuric acid;
- ii. oxidizing the at least partially leached mixed hydroxide precipitate slurry from step i. with peroxymonosulphuric acid and/or a salt thereof in an acidic aqueous medium at a pH of at most 4;
- iii. consecutively or simultaneously to step ii., acidifying the oxidized mixed hydroxide precipitate slurry by adding sulphuric acid to a pH lower than 4, thereby obtaining a solid phase comprising cobalt and manganese and an aqueous phase comprising nickel sulphate; and
- iv. separating said solid phase and said aqueous phase.

The inventors have found that through proper steering of the process conditions as will be outlined below, specifically dosage of peroxymonosulphuric acid and/or a salt thereof and control of pH by addition of sulphuric acid and/or base in each process step allows to obtain a highly pure nickel sulphate solution which is free of cobalt and manganese. This reduces the intensity of solvent extractions or ion exchanges steps downstream of the process for obtaining a battery-grade nickel sulphate solution. The inventive process is schematically shown in Figure 1.

## DESCRIPTION OF THE FIGURES

By means of further guidance, figures are included to better appreciate the teaching of the present invention. Said figures are intended to assist the description of the invention and are nowhere intended as a limitation of the presently disclosed invention. The figures and symbols contained therein have the meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

Figure 1 shows schematically a process according to the invention.

Figure 2 shows schematically a process according to the invention, whereby step i.  
5 and step ii. are executed consecutively.

## **DETAILED DESCRIPTION OF THE INVENTION**

Unless otherwise defined, all terms used in disclosing the invention, including tech-  
10 nical and scientific terms, have the meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. By means of further guidance, term definitions are included to better appreciate the teaching of the present invention. As used herein, the following terms have the following meanings:

15 "A", "an", and "the" as used herein refers to both singular and plural referents unless the context clearly dictates otherwise. By way of example, "a compartment" refers to one or more than one compartment.

"About" as used herein referring to a measurable value such as a parameter, an  
20 amount, a temporal duration, and the like, is meant to encompass variations of +/- 20% or less, preferably +/-10% or less, more preferably +/-5% or less, even more preferably +/-1% or less, and still more preferably +/-0.1% or less of and from the specified value, in so far such variations are appropriate to perform in the disclosed invention. However, it is to be understood that the value to which the modifier  
25 "about" refers is itself also specifically disclosed. A steady influx is understood to be an influx at a rate which is substantially constant, or about constant, i.e., within a variability of +/-20% or less, preferably +/-10% or less, more preferably +/-5% or less, even more preferably +/-1% or less, and still more preferably +/-0.1% or less.

30 "Comprise," "comprising," and "comprises" and "comprised of" as used herein are synonymous with "include", "including", "includes" or "contain", "containing", "contains" and are inclusive or open-ended terms that specifies the presence of what follows e.g. component and do not exclude or preclude the presence of additional,

non-recited components, features, element, members, steps, known in the art or disclosed therein.

The recitation of numerical ranges by endpoints includes all numbers and fractions  
5 subsumed within that range, as well as the recited endpoints. All percentages are to be understood as percentage by weight, abbreviated as "wt.%" or as volume per cent, abbreviated as "vol.%", unless otherwise defined or unless a different meaning is obvious to the person skilled in the art from its use and in the context wherein it is used.

10  
In the context of the present invention, the term "MHP" is to be considered as an abbreviation of the term "mixed hydroxide precipitate." Mixed hydroxide precipitate (MHP) is an intermediate product of nickel metallurgy that is often derived from processing laterite ores which contains primarily nickel and a minor amount of cobalt. It  
15 can also be produced from other sources, for example as a by-product from Ni recovery out of side streams from various metallurgical or mining operations.

In a preferred embodiment, said mixed hydroxide precipitate comprises nickel in an amount of 25 to 60 wt.%, relative to the total dry weight of said mixed hydroxide  
20 precipitate, preferably in an amount of 33 to 53 wt.%. Preferably, said mixed hydroxide precipitate comprises cobalt in an amount of at least 0.1 wt.%, relative to the total dry weight of said mixed hydroxide precipitate, preferably in an amount of at least 0.2 wt.%, and more preferably in an amount of 0.9 to 3.7 wt.%. Preferably, said mixed hydroxide precipitate comprises manganese in an amount of at least  
25 0.001 wt.%, relative to the total dry weight of said mixed hydroxide precipitate, preferably in an amount of at least 0.01 wt.%, and more preferably in an amount of 0.1 to 7.0 wt.%. Preferably, said mixed hydroxide precipitate comprises carbon in an amount of 0.01 to 5.00 wt.%, relative to the total dry weight of said mixed hydroxide precipitate, more preferably in an amount of 0.01 to 3.00 wt.%, and more preferably  
30 in an amount of 0.01 to 1.00 wt.%. Preferably, said mixed hydroxide precipitate comprises zinc in an amount of 0.01 to 0.15 wt.%, relative to the total dry weight of said mixed hydroxide precipitate. Preferably, said mixed hydroxide precipitate comprises iron in an amount of 0.1 to 3.0 wt.%, relative to the total dry weight of said mixed hydroxide precipitate. Preferably, a wet mixed hydroxide precipitate comprises

water in an amount of 25 to 60 wt.%, relative to the total wet weight of said mixed hydroxide precipitate, preferably in an amount of 30 to 55 wt.%.

5 MHP is a solid product which is typically prepared by extracting nickel and cobalt from laterite ores. Alternatively or additionally, MHP may be obtained from nickel and/or cobalt containing hydroxide materials produced as production waste during preparation of cathode materials or obtained from battery recycling processes.

10 In the context of the present invention, the term "aqueous medium" is used for a water-based solution. The aqueous medium facilitates the handling of the contents of the reactor, such as mixing or pumping. The aqueous medium may already contain some of the other ingredients taking part in the reaction, or those can be added later. Said aqueous medium may in particular contain the mineral acid such as sulphuric acid.

15 In the context of the present invention, the term "slurry" is used for an aqueous mixture comprising a solid phase suspended in an aqueous phase. Slurries are typically treated in a reactor under vigorous stirring to avoid settling and to allow for contact of reagents in the aqueous phase and solids in the solid phase.

20 In the context of the present invention, the term "continuous process" is to be considered as a process in which the produced solution has a substantially constant composition. Specifically, a continuous process is a process in which the produced solution has a constant composition within the range of what are considered normal process variations. More specifically, the produced solution has a composition  
25 whereby the concentration of each ingredient is within the range of +/-20% or less, preferably +/-10% or less, more preferably +/-5% or less, even more preferably +/-3% or less of its average concentration. In a preferred embodiment, the present invention provides a continuous process which operates under steady-state conditions. Such a continuous process is typically by providing a steady influx of reagents  
30 and controlling the volumetric outflow of products in order to keep the process conditions and the volume occupied by the slurry in the reactor constant.

Alternatively, the influx of reagents is continuously adapted in order to stabilize process conditions and the volumetric flow and properties of the outgoing product.

Alternatively, the process is executed in cycles. In that case the inflow of products is controlled to maintain steady process conditions in the reactor during each cycle, yet the products are only periodically harvested at the end of every cycle. This means that there is no outflow during execution of the process itself, but the product accumulates in the reactor and the volume occupied by the slurry increases throughout a single cycle. Preferably, sulphuric acid and peroxymonosulphuric acid and/or a salt thereof are fed to the process according to the present invention at a substantially constant concentration and flow rate. Mixed hydroxide precipitate may be fed to the process intermittently or gradually. Preferably, the present invention provides a continuous process wherein the amount of mixed hydroxide precipitate is controlled in a reactor within the range of +/-20% or less, preferably +/-10% or less, more preferably +/-5% or less, even more preferably +/-3% or less of the average amount.

In a first aspect, the present invention provides a process for selective leaching of nickel from a mixed hydroxide precipitate comprising nickel, cobalt, manganese and carbon, wherein carbon is comprised as organically bound carbon and/or graphite in an amount of 0.10 to 10.00 wt.% relative to the dry weight of said mixed hydroxide precipitate, said process comprising the steps of:

- i. providing a mixed hydroxide precipitate slurry, and at least partially leaching of nickel in said mixed hydroxide precipitate by adding sulphuric acid;
- ii. oxidizing the at least partially leached mixed hydroxide precipitate slurry from step i. with peroxymonosulphuric acid and/or a salt thereof in an acidic aqueous medium at a pH of at most 4;
- iii. consecutively or simultaneously to step ii., acidifying the oxidized mixed hydroxide precipitate slurry by adding sulphuric acid to a pH lower than 4, thereby obtaining a solid phase comprising cobalt and manganese and an aqueous phase comprising nickel sulphate; and
- iv. separating said solid phase and said aqueous phase.



Preferably, nickel in said mixed hydroxide precipitate is leached in step i. by adding sulphuric acid and optionally one or more further acids, such as but not limited to hydrochloric acid, phosphoric acid, nitric acid, etc.

5 In a preferred embodiment, the oxidizing agent used in step ii. is peroxymonosulphuric acid. Using peroxymonosulphuric acid ensures the desired oxidation characteristics for the inventive process without introducing undesirable impurities into the process.

10 Preferably, said mixed hydroxide precipitate comprises nickel, cobalt, manganese and carbon, wherein carbon is comprised as organically bound carbon and/or graphite in an amount of 0.10 to 10.00 wt.% relative to the dry weight of said mixed hydroxide precipitate. The inventors found that the use of peroxymonosulphuric acid and/or a salt thereof allows for the oxidation of organically bound carbon and graphite present  
15 in the feed material. This is of specific interest for the processing of source materials that contain a carbon content resulting from battery recycling or for processing of ores that have a native organically bound carbon content. In a particular embodiment, said carbon is comprised as organically bound carbon and/or graphite in an amount of 0.15 to 10.00 wt.% relative to the dry weight of said mixed hydroxide precipitate,  
20 more particularly in an amount of 0.25 to 5.00 wt.%. Most notably, carbon is comprised as organically bound carbon and/or graphite in an amount of 0.40 to 2.50 wt.% relative to the dry weight of said mixed hydroxide precipitate, more particularly in an amount of 0.40 to 2.00 wt.%, such as 0.50 wt.%, 0.60 wt.%, 0.70 wt.%, 0.80 wt.%, 0.90 wt.%, 1.00 wt.%, 1.20 wt.%, 1.40 wt.%, 1.60 wt.%, 1.80 wt.%, or 2.00 wt.%,  
25 or any amount there in between.

In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, whereby said mixed hydroxide precipitate slurry from step i. is oxidized in step ii. with peroxymonosulphuric acid and/or a salt thereof,  
30 whereby peroxymonosulphuric acid and/or a salt thereof is administered in at least a stoichiometric amount relative to the total amount of Co, Mn and C comprised as organically bound carbon or graphite. By providing a sufficient amount of peroxymonosulphuric acid and/or a salt thereof as oxidizing agent, relative to the total amount of cobalt, manganese and organically bound carbon or graphite, it can be ascertained

that the carbon present is quantitatively oxidized to carbon dioxide, which is readily evacuated from the process via off-gasses. Preferably, said mixed hydroxide precipitate slurry from step i. is oxidized in step ii. with peroxymonosulphuric acid and/or a salt thereof, whereby peroxymonosulphuric acid and/or a salt thereof is administered in more than 95% of the stoichiometric amount relative to the total amount of Co, Mn and C comprised as organically bound carbon or graphite, preferably more than 100%, more than 110% or even more than 120%. Most preferably, peroxymonosulphuric acid and/or a salt thereof is administered in more than 130% and less than 250% of the stoichiometric amount relative to the total amount of Co, Mn and C comprised as organically bound carbon or graphite, specifically in an amount of 130%, 150%, 170%, or 190%, or any value there in between.

In a particular embodiment, said mixed hydroxide precipitate slurry from step i. is oxidized in step ii. with peroxymonosulphuric acid and/or a salt thereof, whereby peroxymonosulphuric acid and/or a salt thereof is administered in at least a stoichiometric amount relative to the total amount of Co, Mn and C comprised as organically bound carbon and graphite. The inventors found that the administration of at least a stoichiometric amounts of peroxymonosulphuric acid and/or a salt thereof allowed for the full conversion of cobalt to  $\text{Co}^{3+}$ , manganese to  $\text{Mn}^{4+}$  and carbon to carbon dioxide. Accordingly, carbon is easily removed from the feed via off-gasses.

In one embodiment, step i. and ii. may be performed simultaneously. In another embodiment, steps ii. and iii. may be performed simultaneously. Preferably, steps i., ii. and iii. are not performed simultaneously; yet, either steps i. and ii. are performed simultaneously and step iii. is performed subsequently, or steps ii. and iii. are performed simultaneously and step i. is performed prior to steps ii. and iii. Most preferably, steps i. and ii. are performed simultaneously and step iii. is performed subsequently. Step iv. is always performed subsequent to step iii. In another embodiment, steps i., ii., iii. and iv. are performed sequentially. In one embodiment, steps i., ii. and/or iii. are performed sequentially in one reactor. In another embodiment, steps i., ii. and/or iii. are performed in two or more reactors placed in a serial sequence.

The present invention has the advantage that Co and Mn can at least partly, and preferably predominantly, be separated from the Ni-rich feed material via a solid-

liquid separation, such as filtration. Methods according to the prior art, in contrast, rely largely on the removal of Co and/or Mn via one or more dedicated solvent extractions. Such processes are energy intensive and require specific equipment. Moreover, such processes are generally not flexible in terms of the feed which can be processed, and have a rigid process window. Also, such processes generate a large amount of waste salts. Therefore, upfront separation of Co and Mn in a process according to the present invention is preferred. Complete or partial removal of Co and Mn, and optionally further impurities, through the process according to the invention limits the need for further impurity removal through solvent extractions or ion exchange.

Preferably, sulphuric acid is added in step i. at a pH above 4, more preferably at a pH between 4 and 6. Preferably, peroxymonosulphuric acid and/or a salt thereof is added in step ii. together with sulphuric acid. The pH in step ii. is preferably maintained to a value below 4, preferably between 3 and 4. The inventors have found that the specific pH control in step i. and ii. as herein described results in an optimal yield and purity of nickel sulphate obtained after step ii. This allows for a reduced need for further purification, i.e., by solvent extraction units, to further reduce the amount of cobalt and manganese present in the obtained nickel sulphate solution. In addition, improved filtration characteristics were observed.

In step i., water is added to a mixed hydroxide precipitate to form a slurry. A slurry is more easily handled than the wet mixed hydroxide precipitate. Generally, the mixed hydroxide precipitate has a composition as in Table 1.

Table 1. Composition of a typical mixed hydroxide precipitate.

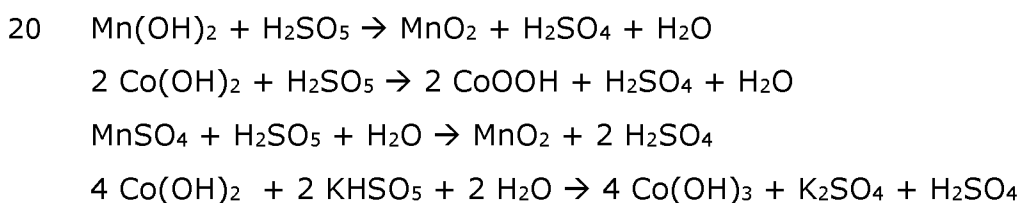
Element	wt.% <sup>a</sup>
Ni	33 - 53
Co	0.95 - 3.7
Mn	0.13 - 6.4
Mg	0.66 - 3.1
Ca	0.04 - 0.29
Cr	traces
Fe	0.12 - 2.20

Si	0.02 - 0.37
Zn	0.01 - 0.46
U	traces
B	traces
C	0.01 - 0.92
S	2.9 - 7.5
Cl	traces
N	traces

<sup>a</sup> on a dry basis, to be complemented with oxygen and hydrogen to 100% dry mass and to be complemented by water to obtain the corresponding mass of a moist MHP product.

- 5 The mixed hydroxide precipitate slurry is partially leached in step i. by addition of sulphuric acid. Generally, 0.01 to 0.80 parts of the mixed hydroxide precipitate slurry are leached with sulphuric acid in step i. Ni(II), Co(II) and Mn(II) compounds present in the mixed hydroxide precipitate slurry are converted to the respective sulphate compounds. Upon addition of the acid the pH will decrease from an initial pH > 6,  
 10 typically to a range between 4 and 6 while the hydroxide compounds in the MHP neutralize the sulphuric acid as the leaching reaction proceeds.

In step ii., the slurry comprising Ni(II), Co(II) and Mn(II) compounds is subjected to oxidation to oxidize Co(II) and Mn(II) to water-insoluble Co(III) and Mn(IV) compounds, which precipitate and report to the solid phase in the slurry. Preferably, a  
 15 pH of at most 4 is maintained by addition of sulphuric acid and/or by the release of free sulphuric acid during oxidation of Co and Mn, for example according to the reactions below.



- 25 In step iii., the leaching of Ni is maximized by further addition of sulphuric acid. This ensures a high recovery rate for Ni, however at the expense of higher amounts of Co

which may dissolve in the aqueous phase. As further elaborated below, the inventors have contemplated that neutralizing the slurry after the final leaching step allows to reduce the amount of Co in the aqueous phase, thereby increasing the selectivity.

5 In step iv., the leached and oxidised slurry undergoes a solid-liquid separation step to produce a nickel sulphate solution and a solid residue comprising cobalt and manganese. Minor amounts of nickel may be entrained with the solid residue. The nickel sulphate solution may be further treated with a base to increase the pH and induce the precipitation of iron and/or aluminium. The nickel sulphate solution may be further  
10 subjected to a solvent extraction process or to an ion exchange process to eliminate impurities such as calcium and zinc.

In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, wherein said aqueous phase obtained in step iii. is  
15 neutralized to a pH of at least 4 prior to step iv. Neutralization through adding an alkaline solid or solution allows to precipitate part of the dissolved cobalt, hence reducing the amount of cobalt in the aqueous phase and increasing the selectivity of recovering Ni from the MHP product. Preferably, said aqueous phase is neutralized to a pH between 4 and 7, more preferably between 4 and 6, and even more preferably  
20 between 4 and 5. Also, preferably, said aqueous phase is neutralized until at least 50% of the dissolved cobalt precipitates, more preferably at least 70%, and even more preferably at least 90%. Most preferably, said aqueous phase is neutralized until at least 95%, at least 98% or even at least 99% of the dissolved cobalt precipitates.

25 In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, wherein said aqueous phase in the neutralization step after step iii. is neutralized by addition of a calcium base, a magnesium base and/or a nickel base. Preferably, said calcium, magnesium and nickel base are selected from the group consisting of nickel hydroxide, nickel carbonate, calcium hydroxide, calcium carbonate, magnesium oxide, magnesium hydroxide, magnesium carbonate, or a combination of two or more of the aforementioned. Most preferably,  
30 calcium hydroxide and/or calcium carbonate are used as a neutralizing agent. The

aforementioned bases are of interest as, for the case of Ni base, it does not contaminate the nickel sulphate solution, and for the case of Ca and Mg base, the cations can easily be sequestered from the nickel sulphate solution post neutralization.

5 In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, whereby step i. and step ii. are performed sequentially. Preferably, step i. and step ii. are performed in a separate reactor with agitator. Alternatively, both step i. and step ii. are performed in a series of two or more separate reactors with agitators that operate in a cascade configuration. The agitator or  
10 mixing device ensures intense mixing of the reaction medium. This is especially relevant during step ii. while adding peroxymonosulphuric acid and/or a salt thereof. It was observed that intense mixing improves the efficiency of the leaching operation and the selectivity of the nickel recovery. In addition, intense mixing counteracts accumulation of foam on the bath surface in the reactor. This foam can be formed  
15 during the oxidation reaction.

In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, whereby step iii. is performed in a collector reactor. The collector reactor receives the oxidized slurry from the reactor in which step ii. is  
20 performed and is further acidified by addition of sulphuric acid to complete the nickel leaching reaction, and thereby maximizing the efficiency of nickel recovery. As a side reaction, the amount of cobalt in the aqueous solutions increases during this operation. Therefore, the aqueous solutions is subsequently neutralized through addition of a base to precipitate cobalt in the aqueous solution.

25 In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, whereby a fraction of the slurry in said collector reactor is recirculated to a reactor in which step ii. is performed. Recirculation of a fraction of the slurry in the collector reactor allows to further process slurries which  
30 are not sufficiently oxidized.

In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, whereby the molar ratio of sulphuric acid to the Ni contained in the mixed hydroxide precipitate in step i. is at least 0.01, preferably

between 0.05 and 0.8, and more preferably between 0.1 and 0.6, and most preferably between 0.15 and 0.5. This allows to leach the predominant amount of nickel from said MHP and to ensure that the targeted cobalt and manganese are sufficiently available to be oxidized in the subsequent oxidations step.

5 In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, whereby the pH of said acidic aqueous medium in step ii. is controlled by addition of sulphuric acid.

10 In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, whereby the temperature in step ii. is maintained at a temperature higher than 30°C and lower than 80°C, preferably higher than 35°C and lower than 70°C, and more preferably at a temperature higher than 40°C and lower than 60°C. Most preferably, said temperature is between 50°C and 60°C.

15 In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, whereby the excess of peroxymonosulphuric acid and any salts thereof relative to the total amount of cobalt and manganese in said mixed hydroxide precipitate is between 0.4 and 3.5, preferably between 0.5 to 3.0.

20 In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, whereby the total amount of peroxymonosulphuric acid and any salts thereof is equal to at least the sum of an amount projected for oxidation of Co present in the mixed hydroxide precipitate, an amount projected for  
25 oxidation of Mn present in the mixed hydroxide precipitate, and an amount projected for oxidation of C bound as organically bound carbon and graphite present in the mixed hydroxide precipitate. The amount projected for Co oxidation is calculated as a molar ratio of peroxymonosulphuric acid and any salts thereof relative to the total amount of Co between 0.25 and 2.25, preferably between 0.75 and 2. The amount  
30 projected for Mn oxidation is calculated as a molar ratio of peroxymonosulphuric acid and any salts thereof relative to the total amount of Mn between 0.5 and 4.5, preferably between 1 and 4. Use of an excess of oxidizing agent ensures that oxidation of impurities present in the starting product does not result in an inadequate amount of oxidizing agent for oxidizing cobalt, manganese and carbon.

In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, whereby peroxymonosulphuric acid and/or a salt thereof are provided in a stoichiometric excess, relative to the total amount of cobalt, manganese and organically bound carbon and graphite in said mixed hydroxide precipitate. Using a stoichiometric excess of oxidizing agent thus ensures a high selectivity for nickel and the partial or even full removal of carbon early in the process scheme, thereby avoiding tedious carbon removal steps later in the process.

10 In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, whereby said mixed hydroxide precipitate slurry is treated in step ii. with peroxymonosulphuric acid and/or a salt thereof in an acidic aqueous medium at a pH between 2 and 5, preferably at a pH between 3 and 4.

15 In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, whereby said mixed hydroxide precipitate slurry is treated in step ii. with peroxymonosulphuric acid. Preferably, said peroxymonosulphuric acid is prepared by mixing sulphuric acid and hydrogen peroxide prior to feeding the generated peroxymonosulphuric acid to the leached MHP slurry obtained in step i.

20

In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, wherein one or more additional oxidising agents are used in step ii., said oxidising agent selected from the group consisting of persulphates, peroxide, sulphur dioxide – oxygen mixtures, permanganates, perchlorates, ozone, oxides, oxygen and chlorine.

25

In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, wherein said mixed hydroxide precipitate further comprises one or more impurities selected from the group comprising magnesium, calcium, iron, silicon, zinc, uranium, chloride, carbon, sulphur and/or nitrogen compounds, whereby said impurities are comprised in a total amount of 2 to 20 wt.%, relative to the weight of said mixed hydroxide precipitate. The inventive process as described above allows to process mixed hydroxide precipitate comprising impurities.

30



Hence, no additional pre-treatments for reducing the amount of impurities in the feed MHP materials is required.

In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, wherein said solid phase obtained in step iv. comprises Co(III) and Mn(IV) compounds, together with a minimal amount of Ni and impurities in solid form, such as silicon compounds, iron compounds, etc. Said solid residue may be leached in an acidic liquid medium under reducing conditions, in presence of one or more further solid feeds comprising Co and/or Mn. Said reducing conditions may be achieved by introducing a reducing agent to the reaction. Suitable reducing agents are, but not limited to, SO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, or a combination thereof. Alternatively, solid metallic reagents can be used as a reducing agent, such as for example Co metal powder, Fe metal powder or Mn flakes. In this context, suitable solid feeds comprising Co and/or Mn are cobalt hydroxide precipitate, cobalt hydroxide intermediate precipitate, mixed metal oxides comprising nickel, cobalt and manganese from lithium-ion battery production or recycling, or a blend thereof.

In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, wherein said mixed hydroxide precipitate comprises carbon in an amount of 0.01 to 10.00 wt.%, relative to the weight of said mixed hydroxide precipitate. In this context, carbon comprised in said mixed hydroxide precipitate is comprised as organically bound carbon or graphite. The inventors have found that under the reaction conditions of the inventive process, organically bound carbon and graphite are efficiently removed from the solution into the atmosphere by oxidation to gaseous compounds and therefore eliminating any impact of the presence of organically bound carbon in downstream processes or products.

In a preferred embodiment, the present invention provides a process according to the first aspect of the invention, whereby said aqueous phase obtained in step iv. is subjected to a purification step to reduce the concentration of one or more impurities in said aqueous phase, whereby said impurities comprise one or more selected from the list comprising Cu, Zn, Co, Mn, Fe, Al, F, Cl, C, Ca, Si, U, P, As, Cd, Sb and Mg. In a preferred embodiment, a base is added to said aqueous phase obtained in step iv. to react with the residual amount of sulphuric acid present in said concentrated

nickel sulphate solution, prior to subjecting said aqueous phase to a further purification step, whereby said base is selected from the group consisting of potassium hydroxide, potassium carbonate, nickel hydroxide, nickel carbonate, calcium hydroxide, calcium carbonate, sodium hydroxide, sodium carbonate, lithium hydroxide, lithium carbonate, magnesium oxide, magnesium hydroxide, magnesium carbonate, or a combination of two or more of the aforementioned. Preferably, said base is added until the pH of the aqueous phase comprising nickel sulphate is between 3 and 5, preferably between 4 and 5.

10 In a preferred embodiment, the present invention provides a process according to the first aspect, whereby said aqueous phase comprising nickel sulphate as obtained in step iv. has a nickel content of between 70 and 170 g Ni/L, preferably between 80 and 150 g Ni/L and more preferably between 90 and 145 g Ni/L. Preferably, said aqueous phase comprising nickel sulphate has a nickel content of between 110 and 15 140 g/L, more preferably between 120 and 130 g/L.

### EXAMPLE

The following example is intended to further clarify the present invention, and is nowhere intended to limit the scope of the present invention.

Figure 2 shows schematically a process according to the present invention. An MHP material with a composition according to Table 1 is subjected to the inventive process, whereby carbon is comprised in said MHP material as organically bound carbon or graphite in an amount of 0.5 to 0.6 wt.%, relative to the dry weight of said MHP material. In a first step, the MHP material is suspended in water to obtain a suspension with a dry weight content of about 30 wt.%, relative to the total weight of the suspension. The MHP suspension is fed to an overflow reactor  $R_{OF}$  and is agitated intensively with a mechanical stirrer. A sulphuric acid solution with a concentration of about 1300 g/L sulphuric acid is added to obtain a suspension with a pH of about 3.

Subsequently, peroxymonosulphuric acid prepared from sulphuric acid and hydrogen peroxide in a 3:1 ratio, is added to the overflow reactor  $R_{OF}$  to oxidize all cobalt and

manganese present in the slurry. At the end of the oxidation reaction, sulphuric acid is added to reduce the pH of the slurry to a value below 4. The slurry from the overflow reactor is then brought to the collector reactor RC and sulphuric acid is added to complete the leaching process. A pH of about 3 is achieved at the end of the leaching  
5 reaction. Then, calcium hydroxide is added until the pH is above 4. Thereby, cobalt which may have dissolved during the leaching reaction precipitates.

Finally, the slurry is filtered to obtain a solid residue on a filter F and an aqueous nickel sulphate solution. The yield of Ni recovery is typically higher than 95%, and  
10 yields higher than 98% can easily be achieved. The obtained aqueous nickel sulphate solution comprises typically about 120 g Ni/L. The amount of cobalt and manganese in the aqueous nickel sulphate solution is less than 20 mg/L Co and less than 5 mg/L Mn, indicating a high selectivity for Ni. Carbon present in the MHP feed was effectively  
15 reduced. The filtrate further comprises about 4 g/L Mg, 1 g/L Zn, 0.1 g/L Ca, 0.4 g/L Si, and minor amounts of Cu, Fe and Cl. These impurities are subsequently removed from the filtrate by solvent extraction to obtain a high-purity battery-grade nickel sulphate solution.

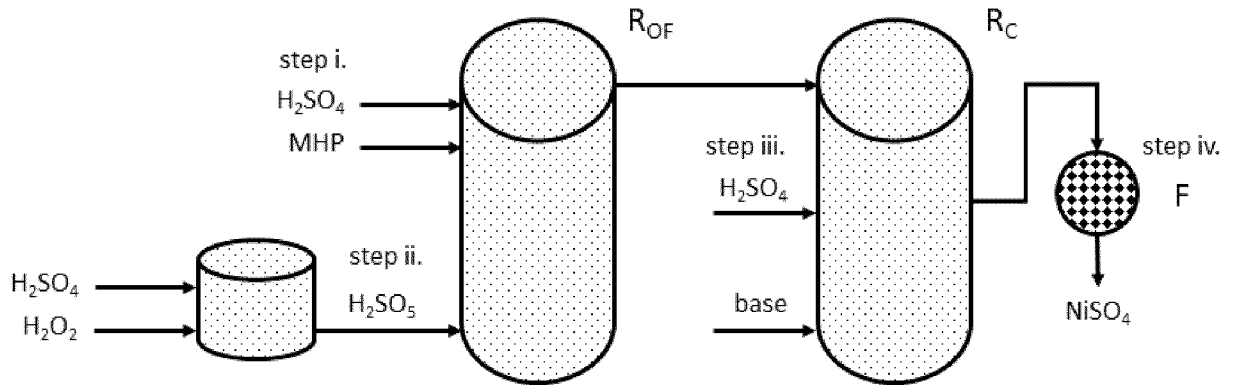
**CLAIMS**

1. A process for selective leaching of nickel from a mixed hydroxide precipitate comprising nickel, cobalt, manganese and carbon, wherein carbon is comprised  
5 as organically bound carbon and/or graphite in an amount of 0.10 to 10.00 wt.% relative to the weight of said mixed hydroxide precipitate, said process comprising the steps of:
  - i. providing a mixed hydroxide precipitate slurry, and leaching of nickel in  
said mixed hydroxide precipitate by adding sulphuric acid;
  - 10 ii. oxidizing the leached mixed hydroxide precipitate slurry from step i. with peroxymonosulphuric acid and/or a salt thereof in an acidic aqueous medium at a pH of at most 4;
  - iii. consecutively or simultaneously to step ii., acidifying the oxidized mixed  
hydroxide precipitate slurry obtained from step ii. by adding sulphuric  
15 acid to dissolve residual amounts of nickel in the solid phase, thereby obtaining a solid phase comprising cobalt and manganese and an aqueous phase comprising nickel sulphate; and
  - iv. separating said solid phase and said aqueous phase.
- 20 2. Process according to claim 1, wherein carbon is comprised as organically bound carbon and/or graphite in an amount of 0.15 to 10.00 wt.% relative to the weight of said mixed hydroxide precipitate, preferably in an amount of 0.25 to 5.00 wt.%.
- 25 3. Process according to claim 1 or 2, wherein said mixed hydroxide precipitate slurry from step i. is oxidized in step ii. with peroxymonosulphuric acid and/or a salt thereof, whereby peroxymonosulphuric acid and/or a salt thereof is administered in at least a stoichiometric amount relative to the total amount of Co, Mn and C comprised as organically bound carbon or graphite present in  
30 said mixed hydroxide precipitate slurry.
4. Process according to any of claims 1 to 3, wherein sulphuric acid is added in step i. to obtain a pH between 4 and 6, and wherein the pH in step ii. is maintained at a value between 3 and 4.

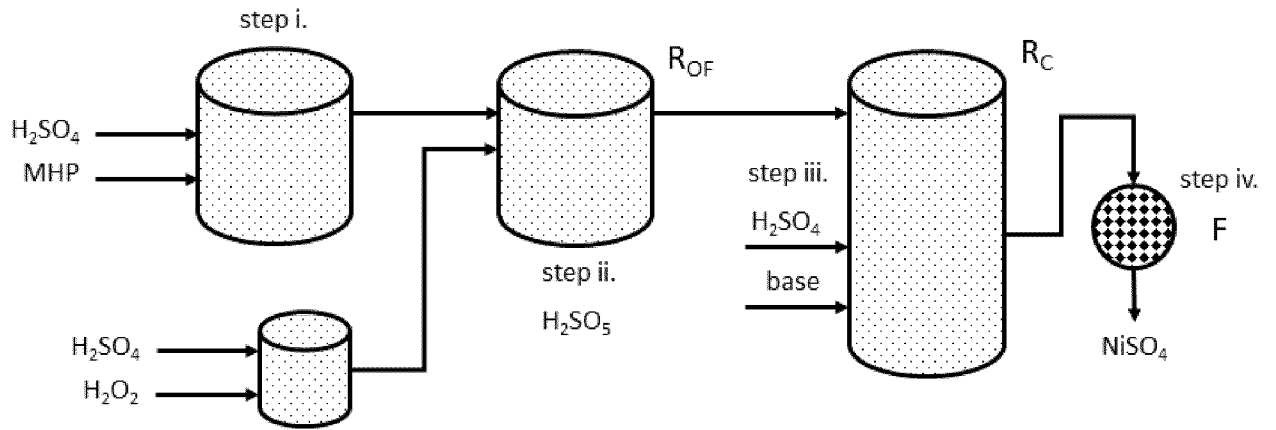
5. Process according to any of claims 1 to 4, wherein said aqueous phase obtained in step iii. is neutralized to a pH of at least 4 prior to step iv.
- 5 6. Process according to any of claims 1 to 5, whereby step i. and step ii. are performed in separate reactors with agitator.
7. Process according to claims 5 and 6, whereby a fraction of the slurry in said collector reactor is recirculated to step ii.
- 10 8. Process according to any of claims 1 to 7, whereby the molar ratio of sulphuric acid to the Ni contained in the mixed hydroxide precipitate in step i. is between 0.01 and 0.80.
- 15 9. Process according to any of claims 1 to 8, whereby the pH of said acidic aqueous medium in step ii. is controlled by addition of sulphuric acid.
10. Process according to any of claims 1 to 9, whereby the temperature in step ii. is maintained at a temperature higher than 40°C and lower than 60°C.
- 20 11. Process according to any of claims 1 to 10, whereby the stoichiometric ratio of peroxymonosulphuric acid and any salts thereof relative to the total amount of cobalt and manganese in said mixed hydroxide precipitate is between 0.5 and 4.5.
- 25 12. Process according to any of claims 1 to 11, whereby said mixed hydroxide precipitate slurry is treated in step ii. with peroxymonosulphuric acid and/or a salt thereof in an acidic aqueous medium at a pH between 2 and 5.
- 30 13. Process according to any of claims 1 to 12, whereby said solid phase obtained in step iv. is leached in an acidic liquid medium under reducing conditions.

14. Process according to any of claims 1 to 13, wherein said mixed hydroxide precipitate further comprises one or more impurities selected from the group comprising magnesium, calcium, iron, silicon, zinc, uranium, chloride, carbon, sulphur and/or nitrogen compounds, whereby said impurities are comprised in a total amount of 2 to 20 wt.%, relative to the weight of said mixed hydroxide precipitate.
- 5
15. Process according to any of claims 1 to 14, wherein said mixed hydroxide precipitate comprises carbon in an amount of 0.01 to 2.00 wt.%, relative to the weight of said mixed hydroxide precipitate.
- 10
16. Process according to any of claims 1 to 15, whereby said aqueous phase obtained in step iv. is subjected to a purification step to reduce the concentration of one or more impurities in said aqueous phase, whereby said impurities comprise one or more selected from the list comprising Cu, Zn, Fe, Al, F, Cl, C, Ca, Si, P, As, Cd, U, Sb and Mg.
- 15

**FIGURES**



**Figure 1**



**Figure 2**

**INTERNATIONAL SEARCH REPORT**

International application No  
**PCT/EP2023/078919**

**A. CLASSIFICATION OF SUBJECT MATTER**  
**INV. C22B3/00 C01G53/10**  
**ADD.**

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)  
**C22B C01G**

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)

**EPO-Internal**

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
<b>X</b>	<b>CA 2 949 580 A1 (BHP BILLITON NICKEL WEST</b>	<b>1-12,</b>
<b>Y</b>	<b>PTY LTD [AU]) 9 June 2017 (2017-06-09)</b>	<b>14-16</b>
	<b>page 2 - page 7</b>	<b>1-16</b>
	<b>First Embodiment;</b>	
	<b>page 7 - page 8</b>	
	<b>page 11; example 1; table 1</b>	
	<b>figures 1-2</b>	
	<b>claims 1-29</b>	
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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	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search	Date of mailing of the international search report
<b>13 January 2024</b>	<b>25/01/2024</b>

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  <b>Neibecker, Pascal</b>
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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2023/078919

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DELINA RUTH ESTHER ET AL: "Chromium occurrence in a nickel laterite profile and its implications to surrounding surface waters", CHEMICAL GEOLOGY, ELSEVIER SCIENCE PUBLISHER B.V., AMSTERDAM, NL, vol. 558, 12 September 2020 (2020-09-12), XP086386897, ISSN: 0009-2541, DOI: 10.1016/J.CHEMGEO.2020.119863 [retrieved on 2020-09-12] Section 2.3</p> <p style="text-align: center;">-----</p>	1-16
A	<p>DELINA RUTH ESTHER ET AL: "Supporting Information: Chromium occurrence in a nickel laterite profile and its implications to surrounding surface waters", CHEMICAL GEOLOGY., vol. 558, 1 December 2020 (2020-12-01), page 119863, XP093119142, NL ISSN: 0009-2541, DOI: 10.1016/j.chemgeo.2020.119863 examples RL, YL; table S1</p> <p style="text-align: center;">-----</p>	1-16
Y	<p>CA 1 180 903 A (INTEROX CHEMICALS LTD) 15 January 1985 (1985-01-15) claims 1-19</p> <p style="text-align: center;">-----</p>	1-16
Y	<p>CA 2 396 972 A1 (IP CANADA CO [CA]) 10 February 2003 (2003-02-10) page 7, line 20 - line 23 figures 1-2 claims 1-23</p> <p style="text-align: center;">-----</p>	13

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

**PCT/EP2023/078919**

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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			<b>CA 1180903 A</b>
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<b>CA 2396972</b>	<b>A1</b>	<b>10-02-2003</b>	<b>NONE</b>
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