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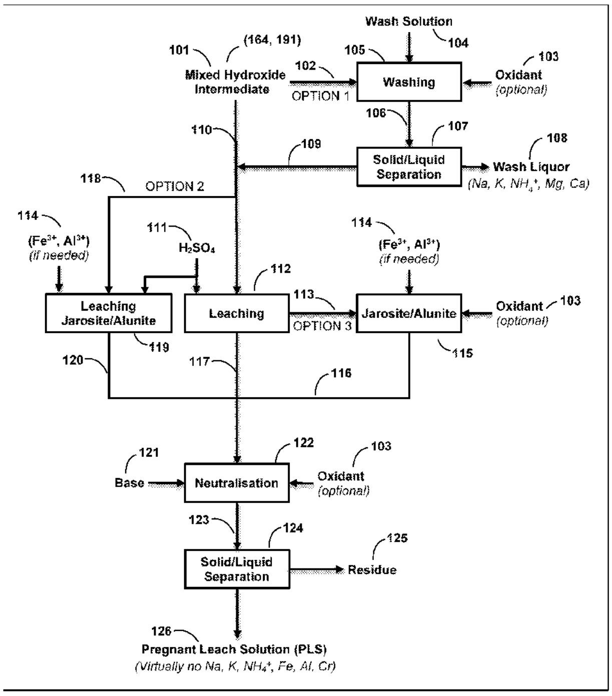

FIGURE 1

(57) Abstract: A process for separating nickel and/or cobalt salts from crude nickel and/or cobalt bearing materials is disclosed. The process comprises treating a crude nickel and/or cobalt bearing material with a salt of iron or aluminium under conditions to remove at least some of one or more alkali metal ion and/or monovalent cation species as a jarosite / alunite precipitate to provide a solution having a reduced content of one or more alkali metal ion and/or monovalent cation species; and subjecting the solution obtained to increasing pH in a stepwise manner under conditions to provide a feed solution for further purification to produce nickel and/or cobalt salts suitable for the production of battery grade nickel or cobalt salts. A process for obtaining purified nickel and cobalt from the feed solution is also disclosed.

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[Continued on next page]

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PRODUCTION OF HIGH PURITY NICKEL AND COBALT COMPOUNDS

PRIORITY DOCUMENT

[0001] The present application claims priority from Australian Provisional Patent Application No. 2021901424 titled "PRODUCTION OF HIGH PURITY NICKEL AND COBALT COMPOUNDS" and filed on 13 May 2021, the content of which is hereby incorporated by reference in its entirety.

TECHNICAL FIELD

[0002] The present disclosure relates to processes for obtaining high purity nickel and cobalt compounds from crude nickel and cobalt containing materials.

BACKGROUND

[0003] High purity nickel sulphate and cobalt sulphate are important precursors in the formation of lithium battery cathodes which are typically formed of nickel-cobalt-manganese (NCM) and nickel-cobalt-aluminium (NCA).

[0004] Currently there is no standard for high purity, battery grade nickel sulphate and cobalt sulphate. However, an example high purity or battery grade nickel sulphate hexahydrate ($NiSO_4.6H_2O$) having low levels of trace elements such as Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Na, Pb, Si, and Zn is shown in Table 1.

[0005] **Table 1** – Example specifications for high purity or battery grade nickel sulphate hexahydrate ($NiSO_4.6H_2O$).

Nickel, as Ni, %	>22
Cobalt, as Co, ppm	< 100
Manganese, as Mn, ppm	< 10
Iron, as Fe, ppm	< 10
Copper, as Cu, ppm	< 10
Sodium, as Na, ppm	< 30
Calcium, as Ca, ppm	< 20
Magnesium, as Mg, ppm	< 30
Zinc, as Zn, ppm	< 10
Lead, as Pb, ppm	< 10
Chromium, as Cr, ppm	< 10
Cadmium, as Cd, ppm	< 10
Aluminium, as Al, ppm	< 10
Silicon, as Si, ppm	< 10

[0006] A typical high purity or battery grade nickel sulphate hexahydrate ($NiSO_4.6H_2O$) having low levels of trace elements is shown in Table 2.

[0007] **Table 2** – Typical specifications for high purity or battery grade nickel sulphate hexahydrate ($NiSO_4.6H_2O$).

Nickel, as Ni, %	22-23
Cobalt, as Co, ppm	< 50
Manganese, as Mn, ppm	< 5
Iron, as Fe, ppm	< 5
Copper, as Cu, ppm	< 5
Sodium, as Na, ppm	< 20
Calcium, as Ca, ppm	< 10
Magnesium, as Mg, ppm	< 20
Zinc, as Zn, ppm	< 5
Lead, as Pb, ppm	< 5
Chromium, as Cr, ppm	< 5
Cadmium, as Cd, ppm	< 5
Aluminium, as Al, ppm	< 5
Silicon, as Si, ppm	< 10

[0008] Similarly, an example high purity or battery grade cobalt sulphate heptahydrate ($CoSO_4{\cdot}7H_2O$) having low levels of trace elements such as Al, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, Si, and Zn is shown in Table 3.

[0009] **Table 3** – Example specifications for high purity or battery grade cobalt sulphate heptahydrate ($CoSO_4{\cdot}7H_2O$).

Cobalt, as Co, %	> 20.5
Manganese, as Mn, ppm	< 10
Iron, as Fe, ppm	< 10
Nickel, as Ni, ppm	< 100
Copper, as Cu, ppm	< 10
Sodium, as Na, ppm	< 25
Calcium, as Ca, ppm	< 25
Magnesium, as Mg, ppm	< 20
Zinc, as Zn, ppm	< 10
Lead, as Pb, ppm	< 10
Chromium, as Cr, ppm	< 10
Cadmium, as Cd, ppm	< 10
Aluminium, as Al, ppm	< 10
Silicon, as Si, ppm	< 10

[0010] A typical high purity or battery grade cobalt sulphate heptahydrate ($CoSO_4.7H_2O$) having low levels of trace elements is shown in Table 4.

[0011] **Table 4** – Typical specifications for high purity or battery grade cobalt sulphate heptahydrate ($CoSO_4.7H_2O$).

Cobalt, as Co, %	20.5-22
Manganese, as Mn, ppm	< 5
Iron, as Fe, ppm	< 5
Nickel, as Ni, ppm	< 50
Copper, as Cu, ppm	< 5
Sodium, as Na, ppm	< 20
Calcium, as Ca, ppm	< 20
Magnesium, as Mg, ppm	< 10
Zinc, as Zn, ppm	< 5
Lead, as Pb, ppm	< 5
Chromium, as Cr, ppm	< 5
Cadmium, as Cd, ppm	< 5
Aluminium, as Al, ppm	< 5
Silicon, as Si, ppm	< 10

[0012] Traditionally, nickel sulphide has been an important starting material used in the production of battery grade nickel sulphate but as nickel sulphide deposits are being continually depleted, low grade nickel laterite deposits (accounting for 73% of world nickel resources) are becoming an increasingly important source of both nickel and cobalt for the battery industry. However, the profitable processing of these low-grade laterite ores to produce high purity, battery grade nickel sulphate and cobalt sulphate has been elusive. The existing refining processes for producing high purity, battery grade nickel sulphate and cobalt sulphate either require a costly step of physically extracting the major metal (i.e. nickel) by solvent extraction (SX) from relatively small amounts of relevant impurities (typically, at a mass ratio of impurities to nickel < 1/15), or can only produce nickel liquors suited for producing other forms of nickel products, typically nickel cathode by electrowinning or nickel powder by hydrogen reduction. These forms of nickel products in turn need further refining processes to produce high purity, battery grade nickel sulphate.

[0013] Nickel laterite ores are typically processed by direct acid leaching, followed by precipitation of major iron and aluminium impurities in the pregnant leach solution (PLS) by neutralisation or thermal hydrolysis. The nickel and cobalt are then usually recovered as intermediate products, either mixed sulphide precipitate (MSP), or mixed hydroxide precipitate (MHP) using a base chemical such as magnesia, lime, limestone or sodium hydroxide. In comparison with the MSP process which can exclude more of the common impurities, the MHP process is becoming increasingly popular because it eliminates the costly and undesirable H_2S precipitation step associated with the MSP process, and it yields a product that is readily soluble in ammonia or acid which assists in the purification and recovery processes. Since the specifications for battery grade nickel sulphate and cobalt sulphate require very low levels of impurities, the methods for separation and purification of these from the PLS formed via the dissolution of raw materials such as MHP are critical.

[0014] Although there are several existing commercial hydrometallurgical processes for processing nickel laterite ores and subsequently refining the intermediate products such as MSP and MHP, the products from these processes require further purification to meet the required specifications for battery grade nickel and cobalt products. Even nickel metal powder generated during hydrogen reduction, although being of LME grade, requires further purification to produce battery grade nickel sulphate.

[0015] Generally, known commercial nickel laterite processes can be separated into those that are acid-based and those that alkaline-based.

[0016] A typical alkaline leaching process is the modified Caron process that uses ammonia-ammonium carbonate lixiviant and was previously employed at the Queensland Nickel Industries (QNI), and nickel and cobalt refinery at Cawse Nickel Operations (Fittock, 1992; Fittock et al., 1994; Price and Reid, 1987). The refinery sections of these plants re-leached MHP with ammonia under mildly reducing conditions, followed by solvent extraction with LIX® 84 ketoxime to isolate nickel (Virnig et al., 1997). This was precipitated from solution as the carbonate and calcined to nickel oxide, which was further processed into a range of products, such as nickel metal produced by hydrogen reduction. Cobalt was recovered from the nickel-depleted raffinate by precipitation of cobalt sulphide using sodium hydrosulphide. The cobalt product could be further treated to produce high purity cobalt products.

[0017] A high pressure acid leaching (HPAL) process is employed at Murrin Murrin Operations of Minara Resources (Rodriguez, 2008; Rodriguez, 2009). MSP is produced to reject a large proportion of the impurities such as aluminium, magnesium and manganese found in the leach liquor. This is redissolved in the presence of oxygen, and the liquor purified by solvent extraction (SX) for zinc and then for cobalt removal using two Cyanex® 272 circuits to generate raffinate containing nickel that is recovered as metallic nickel by hydrogen reduction.

[0018] A problem with existing processes is that they are either unable to produce a qualified nickel liquor and/or cobalt liquor for direct crystallisation of high purity, battery grade nickel sulphate and/or cobalt sulphate, or the processes involve a costly step for extraction and separation of the major metal nickel from relatively small amounts of impurities in the PLS.

[0019] There are also challenges and limitations associated with the separation of some relevant impurities such as alkali metals (Na and K) which occur with nickel in the nickel ores and other nickel bearing materials and then enter the PLS after leaching and subsequent intermediate products such as MHP. More sodium ions, or monovalent species such as ammonium ions, may be introduced into an

MHP if sodium hydroxide or ammonium hydroxide is employed for neutralisation and precipitation of the MHP.

[0020] An MHP after precipitation may be washed to remove partially soluble species. In Canadian patent application number 2949580-A1 and Australian patent application number 2016256773-A1 (Clout and Perry), the washing of MHP is involved in the process as a step to remove or partially remove magnesium, calcium, sulphate, chloride, and sodium components from the MHP, but this is all for generally reduced level of soluble impurities in the leach liquor to meet the requirement for integration into the existing ammonia pressure leach processes to produce respective cobalt powder and nickel powder by pressure reduction with hydrogen.

[0021] Solvent extraction with an organophosphinic acid, e.g. Cyanex® 272 is typically required for separation of cobalt from nickel, wherein a base reagent, typically sodium hydroxide and ammonia / ammonium hydroxide, is required for neutralisation of the equivalent amount of acid produced or for pH control during the SX process. The alkali metal ions and ammonium ions end up with nickel in the raffinate, together with some alkaline earth meals such as calcium and magnesium, resulting in contamination through the formation of double sulphate salts involving these impurities if the raffinate is directly used for the crystallisation of nickel sulphate.

[0022] A problem in SX with a direct addition of ammonia to the concentrated nickel sulphate solution is the formation of nickel ammonium sulphate double salts. Attempts have been made in the prior art to deal with this problem by pre-neutralisation of the organophosphoric acid extractant and/or by preloading the organic phase with nickel.

[0023] Furthermore, most of the methods and schemes for pre-neutralisation and preloading were developed for preventing the formation of nickel double salts during the cobalt SX with a high concentration of nickel sulphate solution, and the raffinate nickel from the cobalt SX is recovered as nickel cathode by electrowinning or as metallic nickel by hydrogen reduction in the ammoniacal process. Although some prior art schemes have utilised pre-neutralisation and preloading methods for minimising the contamination of the cobalt and nickel main streams by the alkali metal and ammonium ions introduced from the neutralisation as base reagents, the cobalt and nickel liquors by these schemes are considerably contaminated with these impurities and not suitable for application to produce high purity, battery grade nickel sulphate.

[0024] It will be evident from the foregoing that the nickel produced in these processes tends to be considerably contaminated, and the processes do not provide complete enough separation of individual magnesium, cobalt and nickel streams to enable the production of high purity, battery grade nickel sulphate and cobalt sulphate.

[0025] Furthermore, the current practice for production of high purity, battery grade nickel sulphate involves the solvent extraction of nickel by an organocarboxylic acid, typically Versatic® 10, for the separation of nickel from the alkali metals, ammoniacal species, and alkaline earth metals (e.g. calcium and magnesium). The involvement of a major metal nickel SX step is very expensive, accounting for a major portion of the total operating and capital costs in the refining process.

[0026] There is a need for integrated processes to convert nickel / cobalt mixed hydroxide intermediates, e.g. MHP or other nickel bearing materials or solutions to high purity, battery grade nickel sulphate and cobalt sulphate without the costly separation step of major metal nickel. Alternatively, or in addition, there is a need for processes for producing high purity, battery grade nickel sulphate and cobalt sulphate that overcome one or more of the problems associated with prior art or known processes. Alternatively, or in addition, there is a need for useful alternatives to existing processes for producing high purity nickel sulphate and cobalt sulphate.

SUMMARY

[0027] The present disclosure arises from the inventors' research into processes for converting nickel / cobalt mixed hydroxide intermediates, such as MHP or other nickel bearing materials or solutions to high purity, battery grade nickel sulphate and cobalt sulphate. The processes described herein can generally be carried out in two phases.

[0028] In a first phase of the processes described herein, nickel laterite ores, other nickel bearing materials, intermediate products such as MHP or nickel bearing solutions, are converted to a feed solution which is substantially free of alkali metal and monovalent cation species and is suitable for further purification processes to produce high purity, battery grade nickel sulphate. This first phase may involve improving existing upstream processing of nickel laterite ores or other nickel containing materials for efficient production of feed solution or MHP suitable for subsequent refining processes. Optionally, a portion, or preferably a major portion, of manganese may be converted into stable Mn(III/IV) oxide in the MHP or in the leach slurry which is then separated to produce the feed solution with reduced manganese content for easy purification to produce high purity, battery grade nickel sulphate.

[0029] Thus, in a first aspect there is provided a process for separating nickel and/or cobalt salts from crude nickel and/or cobalt bearing materials, the process comprising:

a) treating a crude nickel and/or cobalt bearing material with a salt of iron or aluminium under conditions to remove at least some of one or more alkali metal ion and/or monovalent cation species as a jarosite/alunite precipitate to provide a solution having a reduced content of one or more alkali metal ion and/or monovalent cation species;

b) subjecting the solution from step a) to increasing pH in a stepwise manner under conditions to provide a feed solution for further purification to produce nickel and/or cobalt salts suitable for the production of battery grade nickel or cobalt salts;

wherein step b) removes at least some or any combination of any one or more of the following species:

i. iron,
ii. aluminium,
iii. chromium, and
iv. copper.

[0030] In certain embodiments of the first aspect, the process of the first aspect further comprises treating a crude nickel and/or cobalt bearing material prior to step a) with an aqueous solution comprising water and/or sulfuric acid under conditions to remove at least some of the one or more alkali metal ion and/or monovalent cation species. The step of treating the crude nickel and/or cobalt bearing material with an aqueous solution comprising water and/or sulfuric acid may be carried out at pH 7 or greater.

[0031] In certain embodiments of the first aspect, the feed solution is treated with an oxidant under conditions to oxidise any iron(II) to iron(III) and any manganese(II) to higher oxidation state manganese(III/IV) to provide a feed solution containing nickel and/or cobalt and having reduced concentrations of any one or more of alkali metal ions, monovalent cation species, iron, aluminium, chromium, copper and manganese relative to the crude nickel and/or cobalt bearing material.

[0032] In certain embodiments of the first aspect, the salt of iron or aluminium in step a) is a sulphate, carbonate, oxide or a hydroxide of iron and/or aluminium.

[0033] In a second phase of the processes described herein, novel solvent extraction (SX) processes with minimum SX systems and circuits for separation of impurities from cobalt and nickel, and separation of cobalt from nickel to produce cobalt liquors suitable for crystallisation of high purity, battery grade cobalt sulphate, cobalt chloride, cobalt nitrate or other cobalt products, if desired, and a raffinate nickel suitable for direct crystallisation of high purity, battery grade nickel sulphate or other nickel products, if desired, without the separation step of major metal nickel are provided. Advantageously, the processes of the second phase avoid contamination from the neutralisation with a base reagent such as sodium hydroxide, sodium carbonate, ammonia or ammonium hydroxide in the SX processes. The processes of the second phase provide alternative processes to enable direct neutralisation during solvent extraction with ammonia / ammonium hydroxide and selective removal of the ammonium component from the final hydrated nickel sulphate as ammonia for recycling as a base reagent in the process.

[0034] Thus, in a second aspect there is provided a process for obtaining purified nickel and cobalt from the feed solution obtained according to the first aspect, the process comprising:

a) reducing the concentration of any zinc, calcium, manganese, copper, cadmium, lead or other metal impurities having higher affinity to an organic extractant than cobalt and nickel, in the feed solution by contacting it with an organophosphoric acid extractant in a hydrocarbon diluent, under solvent extraction conditions and separating the organic and aqueous phases to produce an aqueous raffinate comprising purified cobalt and nickel;
b) contacting the aqueous raffinate comprising purified cobalt and nickel with a cobalt selective extractant in a hydrocarbon diluent, under solvent extraction conditions and separating organic and aqueous phases to produce an organic phase comprising purified cobalt and an aqueous phase comprising purified nickel, followed by selective scrubbing and stripping of the organic phase to obtain an aqueous phase comprising purified cobalt;
c) purifying the aqueous phase comprising purified cobalt to produce a further aqueous phase comprising purified cobalt;
d) recovering cobalt from the further aqueous phase; and
e) recovering nickel from the aqueous phase comprising purified nickel.

[0035] It will be appreciated that the first and second phases described herein can be performed separately from one another, or they may be combined to provide an improved process for producing high purity, battery grade cobalt sulphate or other cobalt products and high purity, battery grade nickel sulphate from crude nickel and cobalt containing materials such as laterite ores.

[0036] In certain embodiments of the second aspect, step b) comprises:

a) (i) co-extracting both cobalt and magnesium in the aqueous raffinate from step a) into the organic phase; (ii) selectively scrubbing any co-extracted nickel from the organic phase with a scrub solution of sulphuric acid and/or cobalt sulphate at a relatively high equilibrium pH range to obtain the organic phase with nickel removed and a nickel rich scrub liquor (aqueous phase) which is recycled to step (i); (iii) further selectively scrubbing magnesium from the organic phase with a scrub solution of sulphuric acid and/or cobalt sulphate at a relatively low equilibrium pH range to obtain the organic phase with purified cobalt and a magnesium rich scrub liquor (aqueous phase); (iv) re-extracting any co-scrubbed cobalt in the magnesium rich scrub liquor (aqueous phase) with a minor portion of the organic phase to obtain a minor portion of cobalt loaded organic phase which is merged into the main portion of the organic phase in step (iii); and (v) stripping the organic phase from step (iii) to generate aqueous phase comprising purified cobalt ; or
b) (i) selectively extracting cobalt in the aqueous raffinate from step a) into the organic phase; (ii) scrubbing both co-extracted nickel and magnesium in the organic phase with a scrub solution of sulphuric acid and/or cobalt sulphate to obtain the organic phase with purified cobalt and a nickel and magnesium rich scrub liquor (aqueous phase) which is recycled to

step (i); (iii) stripping cobalt from the purified organic phase from step (ii) with an acid to obtain aqueous phase comprising purified cobalt (strip liquor); (iv) selectively extracting the magnesium from step (i) raffinate with a portion of the organic solution to obtain aqueous phase comprising purified nickel (the final raffinate) and magnesium rich organic phase; (v) scrubbing any co-extracted nickel in the organic phase with a scrub solution of sulphuric acid to obtain a nickel rich scrub liquor which is recycled to step (iv); and (vi) stripping the magnesium enriched organic to obtain aqueous phase comprising purified magnesium for recovery of magnesium by-product.

[0037] In certain embodiments of the second aspect the organophosphoric acid extractant has the formula $(RO)_2PO_2H$, wherein each R group, which may be the same or different, is an optionally substituted branched, straight chained or cyclic alkyl, alkenyl or alkynyl group.

[0038] In certain embodiments of the second aspect the organophosphoric acid extractant is di-2-ethylhexyl phosphoric acid (D2EHPA), or an organophosphoric acid having extraction characteristics similar to or the same as di-2-ethylhexyl phosphoric acid, such as mono-2-ethylhexyl phosphoric acid (M2EHPA) or di-p-octylphenyl phosphoric acid (OPPA).

[0039] In certain embodiments of the second aspect the cobalt selective extractant is an organophosphinic acid having the formula R_2PO_2H, in which the R groups, which may be the same or different, are selected from optionally substituted branched, straight chained or cyclic alkyl, alkenyl or alkynyl groups.

[0040] In certain embodiments of the second aspect the cobalt selective extractant is di-2,4,4-trimethylpentylphosphinic acid, or an organophosphinic acid having extraction characteristics similar to or the same as di-2,4,4-trimethylpentylphosphinic acid, such as di-2-ethylhexylphosphinic acid. By way of example only, di-2,4,4-trimethylpentylphosphinic acid is the functioning component in the commercial products Cyanex® 272 and Ionquest® 290.

[0041] In certain embodiments of the second aspect a phase modifier or modifiers may be present in the organic solutions. The modifier can be any suitable modifier that improves separation of the organic and aqueous phases, including, but not limited to, isodecanol, isotridecanol, 2-ethylhexanol and tri-n-butyl phosphate.

[0042] In certain embodiments of the second aspect the hydrocarbon diluent is an aliphatic or aromatic hydrocarbon solvent or a mixture thereof. In certain specific embodiments of the second aspect the hydrocarbon diluent is kerosene.

[0043] In certain embodiments of the second aspect the step c) purifying the aqueous phase comprising purified cobalt comprises:

contacting the aqueous phase comprising purified cobalt with an ion exchange (IX) resin under conditions to selectively bind impurities to the resin to form a loaded resin,

washing the loaded resin with an aqueous solution of water and/or an acid to recover co-loaded cobalt. In certain embodiments, the step c) further comprises eluting the loaded resin with an acid to remove the impurities and regenerate the resin.

[0044] In certain embodiments of the second aspect the step c) of purifying the aqueous phase comprising purified cobalt further comprises removing at least some of any copper from the aqueous phase comprising purified cobalt. The step of removing at least some of any copper from the aqueous phase comprising purified cobalt may comprise contacting the aqueous phase comprising purified cobalt with an iminodiacetic resin under conditions to bind copper and separating the copper loaded resin from the aqueous phase.

[0045] In certain embodiments of the second aspect the step c) of purifying the aqueous phase comprising purified cobalt further comprises removing at least some of any zinc from the aqueous phase comprising purified cobalt. The step of removing at least some of any zinc from the aqueous phase comprising purified cobalt may comprise contacting the aqueous phase comprising purified cobalt with a D2EHPA impregnated resin under conditions to bind zinc and separating the zinc loaded resin from the aqueous phase.

[0046] In certain embodiments of the second aspect the step c) of purifying the aqueous phase comprising purified cobalt optionally comprises simultaneously removing at least some of any zinc and at least some of any copper from the aqueous phase comprising purified cobalt. The step of simultaneously removing at least some of any zinc and at least some of any copper from the aqueous phase comprising purified cobalt may comprise contacting the aqueous phase comprising purified cobalt with an aminophosphonic acid resin under conditions to bind zinc and copper and separating the copper and zinc loaded resin from the aqueous phase.

[0047] In certain embodiments of the second aspect the step c) of purifying the aqueous phase comprising purified cobalt further comprises removing at least some of any manganese from the aqueous phase comprising purified cobalt. The step of removing at least some of any manganese from the aqueous phase comprising purified cobalt may comprise contacting the aqueous phase comprising purified cobalt with an oxidant under conditions to oxidise any manganese(II) to higher oxidation state manganese(III/IV) and separating the solid manganese(III/IV) oxide from the aqueous phase. The oxidant may be selected from the group consisting of ozone, a mixture of SO_2/O_2(air) at a ratio functioning as an oxidant, peroxymonosulfuric acid (Caro's acid) and peroxydisulfuric acid, if the aqueous phase comprising purified cobalt is sulphate, or selected from other groups of oxidants (e.g. chloride or nitrate) identical to the aqueous phase comprising purified cobalt.

[0048] In certain embodiments of the second aspect the step c) of purifying the aqueous phase comprising purified cobalt optionally comprises removing at least one of one or more of zinc, calcium, manganese, copper, cadmium, lead or other metal impurities in the aqueous phase comprising purified cobalt by contacting it with an organophosphoric acid extractant in a hydrocarbon diluent, optionally in the presence of a phase modifier, under solvent extraction conditions and separating the organic and aqueous phases to produce a further aqueous phase comprising purified cobalt.

[0049] In certain embodiments of the second aspect the step of recovering nickel from the aqueous phase comprising purified nickel comprises crystallising nickel sulphate from the aqueous phase comprising purified nickel.

[0050] In certain embodiments of the second aspect the process step a) further comprises scrubbing at least some of any co-extracted cobalt and nickel with a scrub solution containing water and/or sulphuric acid and/or metal sulphates from the organic phase to aqueous phase which is recycled to the extraction.

[0051] In certain embodiments of the second aspect the process further comprises stripping at least some of any one or more of zinc, calcium, manganese and copper, and other loaded impurities having higher affinity to the organic extractant than cobalt and nickel present in the organic phase obtained in step a) by either (a) treating the organic phase with sulfuric acid through control of the calcium concentration below its saturation to avoid gypsum formation, or (b) treating the organic phase with hydrochloric acid, if the calcium concentration in the system is relatively high with a risk of forming gypsum.

[0052] In certain embodiments of the second aspect the process further comprises periodically bleeding treatment of the organic phase in step a) by contacting the organic phase with a solution of hydrochloric acid (typically 6 molar HCl) to remove some of any one or more of iron, aluminium and other strongly binding metal ions from the organic phase.

[0053] In certain embodiments of the second aspect the step b), wherein selectively scrubbing the extracted nickel from the organic phase comprising purified cobalt is performed in a relatively high equilibrium pH range, preferably in equilibrium pH range of 4.5 – 6.5, and selectively scrubbing the extracted magnesium from the organic phase comprising purified cobalt in a relatively low equilibrium pH range, preferably in the equilibrium pH range of 3 – 5. The scrubbing of nickel and magnesium may be performed successively in a higher pH range for removal of nickel and then in a lower pH range for removal of magnesium to obtain two separate scrub liquors, or concurrently in a lower pH range for removal of both nickel and magnesium.

[0054] In certain embodiments of the second aspect, step b) further comprises co–extracting any magnesium present in the raffinate comprising purified cobalt and nickel into the organic phase. Magnesium may be separated from cobalt by further scrubbing the co-extracted magnesium with sulphuric acid at a preferable equilibrium pH range of 3 – 5, and selectively re-extracting the co-scrubbed cobalt from the magnesium rich scrub liquor into a portion of the organic phase which may be recycled and merged into the main portion of the organic phase at the point of scrubbing of the magnesium.

[0055] In certain embodiments of the second aspect the step b) purifying the organic phase comprising purified cobalt by scrubbing both co-extracted nickel and magnesium from the organic phase with a scrub solution of sulphuric acid and/or cobalt sulphate to obtain a nickel rich scrub liquor which may be recycled to the extraction step b) for recovering nickel.

[0056] In certain embodiments of the second aspect, step b) further comprises extracting any magnesium present in the raffinate comprising purified nickel with a portion of the organic, followed by scrubbing with sulphuric acid under conditions to remove the co-extracted nickel which is recycled to the extraction step b). The scrubbed organic is stripped with sulphuric acid to regenerate the organic and to produce the magnesium enriched aqueous phase for further recovery of magnesium by-products.

[0057] In certain embodiments of the second aspect, the process further comprises preloading one or more organic solution used in the process with sulphate, carbonate, oxide or hydroxide salts of nickel, cobalt and/or magnesium. The process may comprise preloading one or more organic solution used in the process with nickel sulphate. The process may further comprise treating with a base reagent such as nickel hydroxide, sodium hydroxide or carbonate, ammonia, ammonium hydroxide or carbonate and magnesium oxide / hydroxide or carbonate for neutralisation or pH control in the preloading. The process may further comprise pre-neutralising the organic solution with a base reagent to produce the pre-neutralised organic for preloading of nickel by exchange. The base reagent may be selected from the group consisting of sodium hydroxide, sodium carbonate, ammonia, ammonium hydroxide or ammonium carbonate. The process may further comprise washing the organic solutions preloaded with nickel sulphate with a scrub solution containing water and/or sulfuric acid and/or nickel sulphate to remove entrained and extracted sodium or ammonium ions.

[0058] In certain embodiments of the second aspect the process further comprises directly neutralising acid produced during the solvent extraction with ammonia, ammonium hydroxide or carbonate under conditions to avoid formation of nickel ammonium double salts, or ammonium sulphate salt and subsequently thermally decomposing the ammonium component in the hydrated nickel sulphate.

[0059] In certain embodiments of the second aspect the process comprises one or more stages of any extraction step, any scrubbing step and any stripping step in solvent extraction, and any loading step, any washing step and any elution step in ion exchange which may operate countercurrent mode or concurrent mode or the combination of the two modes.

[0060] In a third aspect, provided herein is a high purity nickel sulphate obtained by the process of the first aspect and/or the second aspect.

[0061] In a fourth aspect, provided herein is a high purity cobalt sulphate, and optionally cobalt chloride, cobalt nitrate, if desired, obtained by the process of the first aspect and/or the second aspect.

BRIEF DESCRIPTION OF THE FIGURES

[0062] Embodiments of the present disclosure will be discussed with reference to the accompanying figures wherein:

[0063] Figure 1 shows a schematic flowsheet of embodiments of the present disclosure with schemes and methods for treatment of MHP and or/PLS to produce final feed solution which is substantially free of alkali metal ion (Na^+ and K^+) and monovalent cation species (NH_4^+), iron, aluminium and cromium with an optional removal of a portion of manganese.

[0064] Figure 2 shows a schematic flowsheet of embodiments of the present disclosure with schemes and methods for processing of nickel laterite ores or nickel bearing materials and solutions for producion of an MHP with optimum ratios of iron and aluminium to the total amount of alkali metal ion (Na^+ and K^+) and monovalent cation species (NH_4^+) favorable for increased processing efficiency and subsequent refining processes shown in Figure 1, or alternatively for production of feed solution or MHP which is vritually free of alkali metal ion (Na^+ and K^+) and monovalent cation species (NH_4^+) and iron, aluminium and cromium with an optional removal of a portion of manganese.

[0065] Figure 3 shows a flowsheet of embodiments of the present disclosure with schemes and methods for purification of the feed solution produced from the processes shown in Figure 1 and Figure 2 by SX and IX, featuring (i) organic preloading; (ii) SX for removal of one or more impurities from the group of zinc, calcium, manganese, cadmium, copper, lead and any other impurities having higher affinity to the organic extractant than cobalt and nickel; (iii) one SX circuit for extraction of both cobalt and magnesium from nickel and then separation of magnesium from cobalt within the SX circuit; (iv) direct crystallisation of nickel sulphate from the final SX raffinate; (v) purification of the aqueous phase comprising purified cobalt from step (iii); and (vi) crystallisation of cobalt sulphate or other cobalt salts from the aqueous phase comprising purified cobalt from step (v).

[0066] Figure 4 shows a flowsheet of embodiments of the present disclosure for purification of the feed solution produced from the processes shown in Figure 1 and Figure 2 by SX and IX, featuring (i) direct neutralisation with ammonia/ammonium hydroxide in SX, (ii) SX for removal of one or more impurities from the group of zinc, calcium, manganese, copper, cadmium, lead and any other impurities having higher affinity to the organic extractant than cobalt and nickel, (iii) one SX circuit for extraction of both cobalt and magnesium from nickel and then separation of magnesium from cobalt within the SX circuit, (iv) direct crystallisation of nickel sulphate from the final SX raffinate, (v) thermal decomposition of ammonium sulphate component in the hydrated nickel sulphate to remove ammonium component as ammonia for recycling use as the base reagent, (vi) purification of the aqueous phase comprising purified cobalt from step (iii), and (vii) crystallisation of cobalt sulphate or orther cobalt salts from the aqueous phase comprising purified cobalt from step (vi).

[0067] Figure 5 shows a flowsheet of embodiments of the present disclosure for the purification of the feed solution produced from the processes shown in Figure 1 and Figure 2 by SX and IX, featuring (i) organic preloading, (ii) SX for removal of one or more impurities from the group of zinc, calcium, manganese, copper, cadmium, lead and any other impurities having higher affinity to the organic extractant than cobalt and nickel, (iii) two separate SX circuits for separation of cobalt from magnesium and then magnesium from nickel, (iv) direct crystallisation of nickel sulphate from the final SX raffinate, (v) purification of the aqueous phase comprising purified cobalt from step (iii), and (vi) crystallisation of cobalt sulphate or other cobalt salts from the aqueous phase comprising purified cobalt from step (v).

[0068] Figure 6 shows a flowsheet of embodiments of the present disclosure for the purification of feed solution produced from the processes shown in Figure 1 and Figure 2 by SX and IX, featuring (i) direct neutralisation with ammonia/ammonium hydroxide in SX, (ii) SX for removal of one or more impurities from the group of zinc, calcium, manganese, copper, cadmium, lead and any other impurities having higher affinity to the organic extractant than cobalt and nickel, (iii) two separate SX circuits for the separation of cobalt from magnesium, and magnesium from nickel, (iv) direct crystallisation of nickel sulphate in the final SX raffinate, (v) thermal decomposition of ammonium sulphate component in the hydrated nickel sulphate to remove ammonium component as ammonia for recycling use as the base reagent, (vi) purification of the aqueous phase comprising purified cobalt from step (iii), and (vii) crystallisation of cobalt sulphate or other cobalt salts from the aqueous phase comprising purified cobalt from step (vi).

[0069] Figure 7 compares the conversion efficiency of Mn(II) to stable Mn(III/IV) oxide with air only and the mixture of SO_2/air.

[0070] Figure 8 shows the nickel preloading isotherms with 10% D2EHPA and 62 g/L nickel (sulphate) solution at pH ~5 and 50 °C.

[0071] Figure 9 shows the scrubbing isotherms of sodium from the preloaded 10% D2EHPA with 64.7 g/L nickel (sulphate) solution at pH 3.6 and 50 °C.

[0072] Figure 10 shows the extraction distribution isotherm with the Ni-preloaded 10% D2EHPA at pH 3.1 and 40 °C.

[0073] Figure 11 shows the McCabe-Thiele diagrams for extraction of Zn(II) and Cu(II) with the Ni-preloaded 10% D2EHPA at pH 3.1 and 40 °C.

[0074] Figure 12 shows the McCabe-Thiele diagrams for extraction of Mn(II) and Ca(II) with the Ni-preloaded 10% D2EHPA at pH 3.1 and 40 °C.

[0075] Figure 13 shows the nickel preloading isotherms with 25% Cyanex® 272 and 60 g/L nickel (sulphate) solution at 50 °C and pH 6.8 - 7.0.

[0076] Figure 14 shows the scrubbing isotherms of sodium from the preloaded 25% Cyanex® 272 at pH 5.5 and 50 °C.

[0077] Figure 15 shows the extraction distribution isotherms of Ni(II), Co(II) and Mg(II) with the Ni(II)-preloaded 25% Cyanex® 272 at 40 °C.

[0078] Figure 16 shows the McCabe-Thiele diagrams for extraction of Co(II) and Mg(II) with the Ni(II)-preloaded 25% Cyanex® 272 at 40 °C.

[0079] Figure 17 shows McCabe-Thiele diagrams for nickel scrubbing from the loaded 25% Cyanex® 272 at pH ~4.2 and pH ~5 and 40 °C.

[0080] Figure 18 shows McCabe-Thiele diagrams for magnesium scrubbing from the loaded 25% Cyanex® 272 at pH ~3.5 and pH ~4.2 and 40 °C.

DESCRIPTION OF EMBODIMENTS

[0081] Details of terms and processes are given below to provide greater clarity concerning compositions, processes and the use(s) thereof for the purpose of guiding those of ordinary skill in the art in the practice of the present disclosure. The terminology in this disclosure is understood to be useful for the purpose of providing a better description of particular embodiments and should not be considered limiting.

[0082] In the context of the present disclosure, the term “about” when referring to a measurable value such as an amount, a temporal duration, and the like, is intended to encompass variations of ±20%, ±10%, ±5%, ±1%, or ±0.1% from the specified value, as such variations are appropriate to perform the disclosed processes.

[0083] In the context of the present disclosure, the terms “purified”, “purity” and related terms are intended to mean a composition, compound or material that has had some of the impurities or substances that adulterate or contaminate a substance removed. The term purified is a relative term and does not require absolute purity. Thus, for example, a purified compound is one in which the compound is more enriched than the compound is in its natural environment or preceding any purifying treatment.

[0084] In the context of the present disclosure, the terms “high purity” and “battery grade” when used in reference to nickel salts or cobalt salts means that the material has a minimum level of nickel or cobalt and/or low levels of trace elements such as Al, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Na, Pb, Si, and Zn that make them suitable for battery applications. For example, a “high purity” and/or “battery grade” nickel salt may have a nickel content of at least 21 wt%, such as from about 22 wt% to about 23 wt%. For example, a nickel salt (such as nickel sulphate hexahydrate: $NiSO_4{\cdot}6H_2O$) having a nickel content of 22.0 wt%, 22.1 wt%, 22.2 wt%, 22.3 wt%, 22.4 wt%, 22.5 wt%, 22.6 wt%, 22.7 wt%, 22.8 wt%, 22.9 wt% or 23.0 wt% is considered high purity or battery grade. Similarly, a “high purity” and/or “battery grade” cobalt salt may have a cobalt content of at least 20 wt%, such as at least 21 wt% or such as from about 20 wt% to about 22 wt%. For example, a cobalt salt (such as cobalt sulphate heptahydrate: $CoSO_4{\cdot}7H_2O$) having a cobalt content of 20.0 wt%, 20.1 wt%, 20.2 wt%, 20.3 wt%, 20.4 wt%, 20.5 wt%, 20.6 wt%, 20.7 wt%, 20.8 wt%, 20.9 wt%, 21.0 wt%, 21.1 wt%, 21.2 wt%, 21.3 wt%, 21.4 wt%, 21.5 wt%, 21.6 wt%, 21.7 wt%, 21.8 wt%, 21.9 wt% or 22.0 wt% is considered high purity or battery grade.

[0085] In the context of the present disclosure, the term “soluble” is intended to mean capable of becoming molecularly or ionically dispersed in a solvent to form a homogeneous solution. Solubility can be determined by visual inspection, by turbidity measurements or by dynamic light scattering.

[0086] A person of ordinary skill in the art would recognise that the definitions provided above are not intended to include impermissible combinations. Unless otherwise explained, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. The singular terms “a,” “an,” and “the” include plural referents unless context clearly indicates otherwise. The term “comprises” means “includes.” Therefore, comprising “A” or “B” refers to including A, including B, or including both A and B. Although processes and materials similar or equivalent to those described herein can be used in the practice or testing of the present disclosure, suitable processes and materials are described herein. In case of conflict, the present specification, including explanations of terms, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

[0087] Generally described herein are processes whereby high purity cobalt sulphate and high purity (battery grade) nickel sulphate can be produced from nickel and cobalt containing crude feedstocks, such as mixed hydroxide precipitate (MHP), without requiring the costly nickel extraction step via SX, resulting in an economic advantage. The processes described herein comprise one or more of the following steps:

a) Washing a nickel / cobalt MHP or other nickel containing material to remove most or substantially all of the alkali metal ion (e.g. Na^+ and K^+) and monovalent cation species (e.g. NH_4^+), and simultaneously to partially remove other soluble impurities such as magnesium and calcium, and optional conversion of divalent manganese ions to stable Mn(IV) oxides with an oxidant, whilst retaining the nickel and cobalt as solid hydroxides;

b) Redissolution of nickel and cobalt, optionally followed by jarosite / alunite precipitation for removal of residual alkali metals and monovalent cation species, if needed. This removal step can be performed either concurrently or successively;

c) Neutralisation of the leach solution to precipitate the remaining iron and aluminium as goethite, alumina or hydroxides, together with chromium hydroxide and partial copper hydroxides, and optional oxidative precipitation of Mn(IV) oxides with an oxidant to provide a feed solution;

d) Solid / liquid separation to obtain nickel and cobalt pregnant leach solution (PLS) containing nickel, cobalt, zinc, calcium, manganese (minor), copper, magnesium, and being substantially free of alkali metals and monovalent cation species, and iron, aluminium and chromium;

e) SX-based extraction and thus separation of zinc, manganese, copper and calcium and other impurities (e.g. cadmium, lead) having higher affinities to the organic extractant than cobalt and nickel from the PLS using an organophosphoric acid extractant (e.g. D2EHPA), leaving a PLS containing cobalt, nickel and magnesium in the raffinate;

f) SX-based extraction of both cobalt and magnesium, either successively or concurrently, from the PLS using an organophosphinic acid extractant (e.g. Cyanex® 272), leaving a nickel-rich PLS solution substantially free of impurities;

g) Separation of the loaded magnesium from cobalt arising from concurrent separation in step f) using a novel scrubbing scheme within the SX circuit;

h) Stripping of cobalt from the purified cobalt loaded organic with an acid to produce the strip liquor comprising purified cobalt and regenerate the organic;

i) Purification of the strip liquor comprising purified cobalt by ion exchange (IX) to remove minor impurities such as copper and zinc, and by oxidative precipitation to remove minor manganese, if needed, or by SX similar to step e) to remove various minor impurities such as zinc, manganese, copper and calcium, cadmium and lead;

j) Crystallisation of high purity, battery grade cobalt sulphate or other cobalt salts from the above purified cobalt loaded strip liquor (step i); and

k) Direct crystallisation of high purity, battery grade nickel sulphate from the above final SX raffinate (step f) - the purified nickel liquor.

[0088] The processes described herein provide novel refining approaches and schemes to enable an important economic value chain for unlocking crude nickel and/or cobalt bearing materials, such as nickel laterite ore deposits, for production of high purity, battery grade nickel sulphate and cobalt sulphate products as lithium battery cathode precursor materials for lithium battery industries.

[0089] Advantageously, the processes described herein can be retrofitted to conventional and existing commercial processes for production of improved intermediate products or solutions suitable for subsequent refining processes as described herein. Furthermore, the processes described herein provide a great potential to expand existing operations or justify investment in green field operations and revitalise nickel laterite industries.

[0090] In a first aspect of the present disclosure, disclosed herein is a process for separating nickel and/or cobalt salts from crude nickel and/or cobalt bearing materials, the process comprising:

a) treating a crude nickel and/or cobalt bearing material with a salt of iron or aluminium under conditions to remove at least some of one or more alkali metal ion and/or monovalent cation species as a jarosite /alunite precipitate to provide a solution having a reduced content of one or more alkali metal ion and/or monovalent cation species;
b) subjecting the solution from step a) to increasing pH in a stepwise manner under conditions to provide a feed solution for further purification to produce nickel and/or cobalt salts suitable for the production of battery grade nickel or cobalt salts;

wherein step b) removes at least some or any combination of any one or more of the following species:

i. iron,
ii. aluminium,
iii. chromium, and
iv. copper.

[0091] Thus, the processes of this first aspect include jarosite / alunite precipitation to remove alkali metal ions and monovalent cation species (Figure 1 and Figure 2).

[0092] Jarosite / alunite precipitation is used for a deep removal of the alkali metal ion (Na^+, K^+) and monovalent cation (NH_4^+) species, which can be used alone or in successive steps after the washings. The schemes of the treatment processes described herein include only washing, only jarosite / alunite treatment and an optimum combination of washing with jarosite / alunite, depending on specific conditions associated with cost effective factors such as the contents of the alkali metal ions and monovalent cation species, water balance from washings, available solid / liquid separation facilities of high efficiency, contents of iron and aluminium in the MHP and/or available iron and aluminium forms / sources suitable for jarosite / alunite precipitation.

[0093] The jarosite / alunite precipitation can be performed in leaching concurrently or successively after the leaching. If needed, various iron and aluminium forms, preferably their sulphates or carbonate and oxides or hydroxides, can be added to obtain an optimum ratio to the alkali metal ion and monovalent cation species for efficient jarosite / alunite precipitation. An oxidant may be present to oxidise iron(II) to iron (III), which may also oxidise manganese(II) to stable manganese(IV) oxides.

[0094] A typical nickel laterite ore contains rich iron and aluminium, which partially enters the PLS and are removed as hydroxides by neutralisation prior to the precipitation of the MHP. A portion of the iron and aluminium hydroxides could be utilised as a source of iron for the jarosite process, if desired.

[0095] A known issue of the iron and aluminium hydroxide precipitation in a conventional process is the co-precipitation of nickel and cobalt which becomes significant at a higher pH for more complete removal of iron and aluminium to meet the standard specification of the MHP. To minimise the loss of nickel and cobalt in the iron and aluminium hydroxides, staged precipitations of the iron and aluminium and recycling the last stage precipitate to leaching is conventionally employed, but heavy recycling loads would significantly decrease the process efficiency and increase the operating costs.

[0096] The presently disclosed processes not only provide schemes for treating an intermediate product, e.g. MHP, but they are also useful and beneficial for improving the overall nickel laterite ore process. With the present processes, it is not necessary to deep remove iron and aluminium, as the presence of stoichiometric amounts of iron and aluminium species relative to the alkali metal ions (Na^+,

K^+) and monovalent cation (NH_4^+) species is required for the jarosite / alunite precipitation to remove these critical impurities. Therefore, an MHP can contain a desirable ratio of the iron / aluminium to the total of alkali metal and monovalent cation components for subsequent the jarosite / alunite precipitation.

[0097] Alternatively, the jarosite / alunite process is applicable for removal of alkali metal ion (Na^+, K^+) and monovalent cation (NH_4^+) species in leaching nickel laterite ores or after the leaching prior to the MHP precipitation. It is known that the co-precipitation of nickel and cobalt in the jarosite precipitate is very low.

[0098] In either primary leaching process or the MHP refining process, a stoichiometric portion of the MHP with respect to that of total alkali metal ion (Na^+, K^+) and monovalent cation (NH_4^+) species can be utilised for neutralisation of the acid produced during the jarosite / alunite precipitation, or in other words, the acid produced is simultaneously utilised for dissolving equivalent amount of the MHP without need for addition of other base reagents to avoid introduction of impurities. In application, a portion of the jarosite can be recycled to seed the solution at a proper dose to improve the kinetics of jarosite precipitation.

[0099] Once the jarosite precipitation is completed, the slurry pH is raised, preferably in stages from lower to higher pH to precipitate a major portion of the remaining iron(III) as well crystalline forms such as goethite so as to minimise the loss of nickel and cobalt, and similarly the remaining aluminium as alunite / alumina versus iron and aluminium hydroxides. A base reagent, preferably nickel hydroxide, magnesium oxide / hydroxide, limestone / lime, can be added for the neutralisation process. The neutralisation process would also remove chromium and a portion of copper as hydroxides.

[0100] Optionally, the processes of this first aspect can also comprise a washing step to remove alkali metal ions and monovalent cation species (Figure 1 and Figure 2). Thus, the process may further comprise treating the crude nickel and/or cobalt bearing material prior to step a) with an aqueous solution comprising water or dilute sulfuric acid under conditions to remove at least some of one or more alkali metal ion and monovalent cation species.

[0101] Although washing of an MHP may be involved in the conventional and existing refining processes, it is not specially designed for the removal of a substantial portion, or preferably substantially all the alkali metal ion (Na^+, K^+) and monovalent cation (NH_4^+) species.

[0102] Washing is the first step of the present process for the treatment of an MHP, wherein the MHP is repulped with a wash solution containing water and/or sulphuric acid to remove a substantial portion or preferably substantially all the alkali metal ions (Na^+, K^+), monovalent cation species (NH_4^+) with minimum dissolution of nickel and cobalt. The washing step may be carried out at a pH of 7 or greater.

Multiple washings may be performed to achieve a desirable degree of washing efficiency. The washings would simultaneously remove significant portions of other soluble species such as calcium and magnesium as an additional benefit favourable for subsequent purification by SX. It is optional to simultaneously convert a portion, or preferably a major portion of Mn(II) into stable solid Mn(IV) oxide with an oxidant.

[0103] Optionally, the processes of this first aspect can also comprise oxidative conversion of divalent Mn(II) to stable Mn(III/IV) forms. Thus, the process may comprise treating the first nickel and/or cobalt bearing material extract, the second nickel and/or cobalt bearing material extract and/or the third nickel and/or cobalt bearing material extract with an oxidant under conditions to oxidise any iron(II) to iron (III) and any manganese(II) to manganese(III/IV) to provide a pregnant liquor solution containing nickel and/or cobalt and having reduced concentrations of any one or more of alkali metal ions, monovalent cation species, iron, aluminium, chromium, copper and manganese relative to the crude nickel and/or cobalt bearing material, wherein the pregnant liquor solution is suitable for further purification to produce high purity, battery grade nickel and/or cobalt salts.

[0104] A proper oxidant may be optionally added in the above neutralisation process under controlled conditions, termed as oxidative neutralisation, to convert any iron(II) to iron(III) and Mn(II) into stable Mn(III/IV) oxide, if desired. An early rejection of a major portion of manganese is preferred to make the subsequent purification by solvent extraction easier.

[0105] It is known that the loss of nickel and cobalt in the solid forms such as jarosite / alunite, goethite and Mn(IV) oxides is minimal, compared to the amorphous iron and aluminium hydroxides. In addition, these forms of the solid phase make easier the liquid and solid separation by filtration or other separation means.

[0106] After the above treatments, the feed solution produced is substantially free of alkali metal ion (Na^+, K^+) and monovalent cation (NH_4^+) species, iron, aluminium and chromium, with partially removed copper and manganese, which contains major metal – nickel, cobalt, zinc, remaining copper and manganese, calcium and magnesium in the feed solution for further purification.

[0107] In the second aspect of the present disclosure, disclosed herein is a process for obtaining purified nickel and cobalt from a feed solution produced according to the first aspect. The process comprises:

a) reducing the concentration of any zinc, calcium, manganese, copper, cadmium, lead or other metal impurities having higher affinity to an organic extractant than cobalt and nickel, in the feed solution by contacting it with an organophosphoric acid extractant in a hydrocarbon diluent, under solvent extraction conditions and separating organic and aqueous phases to produce an aqueous raffinate comprising purified cobalt and nickel;

b) contacting the aqueous raffinate with a cobalt selective extractant in a hydrocarbon diluent, under solvent extraction conditions and separating organic and aqueous phases to produce an organic phase comprising purified cobalt and an aqueous phase comprising purified nickel;
c) selectively scrubbing and stripping the organic phase to obtain an aqueous phase comprising purified cobalt ;
d) purifying the aqueous phase comprising purified cobalt to produce a further aqueous phase comprising purified cobalt;
e) recovering cobalt from the further aqueous phase; and
f) recovering nickel from the aqueous phase comprising purified nickel.

[0108] In certain embodiments, the feed solution produced in the process of the first aspect is further purified by SX and IX to separate impurities from cobalt, and cobalt from nickel, wherein cobalt rich liquor is further purified by ion exchange (IX) or SX to remove various minor impurities such as zinc and copper to generate purified cobalt liquor for crystallisation of cobalt sulphate, while the major metal nickel in the final SX raffinate is directly fed to the crystallisation to produce high purity nickel sulphate. The purification process comprises the following schemes.

[0109] **Impurity SX** (Figure 3, Figure 4, Figure 5, Figure 6)

[0110] The impurities of zinc, calcium, manganese and copper, cadmium, lead and other impurities having higher affinity to the organic extractant than cobalt and nickel in the feed solution are extracted and separated from cobalt and nickel with an organophosphoric acid (D2EHPA) extractant in a hydrocarbon diluent such as Exxsol D80 and Escaid 110 and optionally in the presence of a phase modifier, leaving cobalt and nickel together with partial magnesium in the raffinate. There are options for stripping the impurities loaded organic: (a) with sulfuric acid through control of the calcium concentration below its saturation to avoid gypsum formation, if the calcium concentration in the system is low; and (b) with hydrochloric acid, if the calcium concentration in the system is relatively high with a risk of forming gypsum.

[0111] **Separation of cobalt and magnesium** (Figure 3, Figure 4, Figure 5, Figure 6)

[0112] An organophosphinic acid (e.g. Cyanex® 272 or Ionquest® 290) in a hydrocarbon diluent such as Exxsol D80 and Escaid 110 and optionally in the presence of a phase modifier can be employed to separate cobalt, magnesium and nickel into respective liquors. Two SX schemes may be used.

[0113] *Co and Mg SX Scheme Option 1* (Figure 3, Figure 4): In certain embodiments, the cobalt and magnesium are co-extracted and separated from nickel, and the loaded magnesium is separated from cobalt by an internal scrubbing scheme within the SX circuit, wherein the coextracted nickel is first scrubbed from the loaded organic to obtain a nickel rich scrub liquor which is recycled to the extraction and then the extracted magnesium is scrubbed from the loaded organic to produce a magnesium rich liquor containing some co-scrubbed cobalt which is then extracted by a minor stream of the organic solution and recycled to the main scrubbing section. This scheme can separate respective magnesium and cobalt streams from nickel in just one SX circuit.

[0114] *Co and Mg SX Scheme Option 2* (Figure 5, Figure 6): In certain other embodiments, the cobalt is selectively extracted and the co-extracted nickel and magnesium are scrubbed and recycled to the extraction, and thus the cobalt is separated from magnesium and nickel. The magnesium in the raffinate is then extracted and separated from nickel using a portion of the same organic solution in a separate solvent extraction circuit.

[0115] **Cobalt liquor purification and crystallisation** (Figure 3, Figure 4, Figure 5, Figure 6)

[0116] The cobalt loaded strip liquor is purified by ion exchange (IX) to remove minor impurities such as copper with an iminodiacetic type resin and zinc with D2EHPA impregnant resin, or alternatively, simultaneous removal of both copper and zinc with an aminophosphonic acid resin. Minor manganese can be selectively removed by oxidative precipitation with a suitable oxidant, such as ozone, the mixture of SO_2/O_2(air) at a ratio for functioning as an oxidant, or peroxymonosulfuric acid (Caro's acid) and peroxydisulfuric acid. Optionally, various minor impurities including zinc, copper, manganese, calcium, cadmium, and lead can be removed from the cobalt loaded strip liquor by SX with an organophosphoric acid (D2EHPA) extractant as described above, if desired. The purified cobalt liquor is fed to crystallisation to produce high purity cobalt sulphate or other cobalt salts.

[0117] **Direct crystallisation of nickel sulphate** (Figure 3, Figure 4, Figure 5, Figure 6)

[0118] The final raffinate - purified nickel liquor is directly fed to the crystallisation to produce high purity nickel sulphate without involving an expensive step of nickel separation by SX.

[0119] **SX Neutralisation**

[0120] The stoichiometric amount of acid equivalent to the divalent metals extracted would be produced during the SX processes with an acidic extractant such as an organophosphoric acid (e.g. D2EHPA) and an organophosphinic acid (e.g. Cyanex® 272). Therefore, it is critical for the SX schemes to be able to produce the final high purity nickel sulphate product without contamination. Two approaches and schemes may be used.

[0121] *Scheme 1 - Organic preloading* (Figure 3 and Figure 5)

[0122] Certain embodiments utilise a direct preloading of organic solutions with nickel sulphate available within the process. Although other metal sulphates, or carbonate, or oxide / hydroxide may be employed for the preloading such as cobalt sulphate and magnesium sulphate, or their oxide / hydroxide, the nickel sulphate or carbonate, or oxide / hydroxide is preferred because any nickel introduced into the feed solution does not need further separation, compared to the cobalt or magnesium salts which need to be again separated in the subsequent SX schemes. A proper base reagent such as nickel hydroxide, sodium hydroxide or carbonate, ammonia / ammonium hydroxide or carbonate and magnesium oxide / hydroxide or carbonate can be used for neutralisation or pH control in the preloading.

[0123] Alternatively, the stripped organic can be pre-neutralised with a base reagent such as sodium hydroxide or carbonate, or ammonia / ammonium hydroxide or carbonate to produce the pre-neutralised organic for preloading of nickel by exchange.

[0124] The nickel preloaded organic solutions are then washed with a scrub solution containing water and/or sulfuric acid and/or nickel sulphate to remove the entrained and extracted sodium or ammonium ions to avoid contamination of the system. The scrubbed organic solutions are then fed to respective main SX circuits to extract the metal ions through exchange of the preloaded nickel with minimum or no pH control.

[0125] *Scheme 2 - Direct neutralisation and thermal treatment* (Figure 4 and Figure 6)

[0126] An alternative approach employs direct neutralisation of the acid produced during the SX with ammonia / ammonium hydroxide under controlled conditions to avoid formation of nickel ammonium double salt or ammonium sulphate salt, and subsequent selective thermal decomposition of the ammonium component in the hydrated nickel sulphate, preferably as ammonia which can be recycled in the process as the base reagent.

[0127] The present disclosure also provides schemes for improving overall upstream processing of nickel laterite ores or other nickel containing materials or solutions, including the following schemes.

[0128] *Upstream Scheme 1:* Controlled neutralisation of iron and aluminium precipitation to produce MHP containing a desirable ratio of iron and aluminium to alkali metal ions (Na^+ and K^+) and monovalent cation (NH_4^+) species for subsequent jarosite / alunite precipitation in the refining processes described herein.

[0129] *Upstream Scheme 2:* leaching and jarosite precipitation concurrently or successively followed by neutralisation and solid / liquid separation to produce a feed solution which is substantially free of alkali metal ions (Na^+ and K^+) and monovalent cation (NH_4^+) species. This feed solution can be directly fed to the subsequent purification schemes by SX and IX described herein, or to the production of MHP which is substantially free of alkali metal ions (Na^+ and K^+) and monovalent cation (NH_4^+) species for subsequent leaching option as illustrated in Figure 1.

[0130] Further details of embodiments of processes disclosed herein will now be described with reference to the accompanying figures.

[0131] **Schemes for Treatment of MHP** (Figure 1)

[0132] The methods and schemes described herein for the treatment of various MHP to produce feed solution (126) suitable for subsequent purification processes to produce respective high purity, battery grade cobalt sulphate and nickel sulphate without costly separation step of major metal – nickel are illustrated in Figure 1.

[0133] The methods for removing alkali metal ions (Na^+, K^+) and monovalent cation (NH_4^+) species include washing (105) and/or concurrent leaching – jarosite / alunite (119) or successive leaching (112) and jarosite / alunite (115). Washing (105) or jarosite / alunite (119, 112 and 115) can be used alone or in combination.

[0134] The steps of the treatment schemes shown in (Figure 1) are described below.

[0135] **Washing (105).** A typical MHP from the conventional and existing nickel laterite processes (101) or the MHP (164, 191) produced from the upstream nickel laterite process described herein (Figure 2), is washed with a wash solution (104) of water or deionised water, or dilute sulphuric acid at an appropriate liquid to solid ratio to remove a portion of, preferably a major portion of, and desirably the complete portion of alkali metal ion (Na^+, K^+) and monovalent cation (NH_4^+) species (108). Other soluble components such as alkaline earth metals, Ca(II) and Mg(II), and nitrate and chloride ions can be partially removed as well. The washings can be performed in various ways, including single or multiple re-pulping, rinsing the filter cakes, and a combination of these means, or continuous counter-current decantation in multiple stages.

[0136] In washing, an oxidant (103) may be added to convert a portion, preferably a major portion of Mn(II) ions into stable solid Mn(IV) oxides. The oxidant may be selected from, but not limited, air, oxygen, ozone, oxides, persulphuric acid, peroxides, peroxymonosulphuric acid (Caro's Acid), the oxidising mixtures of sulphur dioxide (SO_2) with air or oxygen at a right ratio. The addition of an oxidant is controlled through monitoring the slurry potential and pH to minimise the oxidation of Co(II) and Ni(II) into Co(III) and Ni(III) oxides. An oxidant of week to medium oxidising power such as air, oxygen and their mixture with sulphur dioxide at a right ratio, and Caro's Acid are preferred for continuous addition and easy control to minimise the oxidation of Co(II) and Ni(II). The oxidation process is preferably performed under the condition that a substantial portion (> 95%) of the MHP is undissolved in the solid state to minimise the oxidation of Co(II) and Ni(II) into solid forms of Co(III) and Ni(III) oxides.

[0137] The liquid and solid in the washings are separated (107) to produce the washed MHP (109) with desirable washing efficiency of alkali metal ion and monovalent cation species and reduced contents of other soluble species such as Ca(II), Mg(II), Mn(II), nitrate and chloride ions.

[0138] **Leaching (112) and Jarosite / Alunite (115 & 119).** In leaching, a quantitative amount of sulfuric acid at a net stoichiometric ratio to the amount of MHP is added either in doses or continuously to dissolve the MHP. Depending on the contents of alkali metal ions (Na^+, K^+) and monovalent cation (NH_4^+) species, jarosite / alunite precipitation (119) may be operated either simultaneously with leaching (119) or successively after leaching (115). The jarosite / alunite proceeds according to the reaction:

$$A^+ + 3M^{3+} + 2SO_4^{2-} + 6H_2O \rightarrow AM_3(OH)_6(SO_4)_2 + 6H^+ \qquad (1)$$

where A^+ = monovalent cations: Na^+, K^+, NH_4^+ and $M^{3+} = Fe^{3+}, Al^{3+}$

[0139] In either simultaneous or successive leaching and jarosite / alunite treatment, an equivalent portion of the MHP is added to neutralise the acid produced during the jarosite / alunite precipitation (119) according to reaction (1) to control a pH range desirable for the jarosite / alunite precipitation (119) without need for use of other base reagents which may introduce more impurities. In this way, the acid produced is simultaneously utilised for dissolution of an equivalent portion of the MHP.

[0140] If the contents of Fe(III) and Al(III) are insufficient with respect to the formation of jarosite / alunite to completely remove the monovalent cation species (Na^+, K^+ and NH_4^+) according to reaction (1), various iron and aluminium forms, preferably Fe(III) and Al(III) hydroxides, oxides and sulphates can be added at equal or above 3:1 stoichiometric ratios of Fe(III)/Al(III) to $Na^+/K^+/NH_4^+$, preferably in the range of 4:1 – 5:1 ratios.

[0141] The iron and aluminium hydroxides from the conventional upstream precipitate process are a potential iron and hydroxide source. An improved upstream processing of nickel laterite ores for controlled Fe/Al precipitation to allow the presence of desirable ratios of (Fe + Al) to (Na^+ + K^+ + NH_4^+) in the feed solution and in the MHP is as shown in Figure 2, which will be described later.

[0142] The jarosite precipitation can be operated in the range of 60 – 100 °C and pH 1.6 – 2.0, preferably at 85 – 95 °C and pH 1.8 – 2.0, and redox potential (Eh) at the stability region of jarosite formation. Recycle of a portion of jarosite as seed is preferred to promote the kinetics of jarosite / alunite precipitation. If needed, an oxidant may be added to oxidise any lower oxidation valance of iron species, e.g. Fe(II) to Fe(III).

[0143] After the completion of the jarosite precipitation, the alunite precipitation may be performed successively under the conditions of preferably 85 – 95 °C and pH 3.5 – 5.0 ranges, wherein the slurry pH is raised by neutralisation (122), preferable in stages, e.g. pH 2.5, pH 3.5 and pH 4 - 4.5 to precipitate the remaining iron(III) to goethite, oxide / hydroxide, and aluminium as alunite and alumina / hydroxide, while chromium and a portion of copper would be simultaneously precipitated as hydroxides. There are several candidates of the base reagents (121) for the neutralisation (122), including nickel oxide / hydroxide, magnesium oxide / hydroxide, limestone / lime, and sufficiently washed MHP which is substantially free of alkali metal ions and monovalent cation species depending on the specific requirement. An oxidant (103) can be optionally present, termed as "oxidative neutralisation" (122), to oxidise Fe(II) to Fe(III) and/or a major portion of Mn(II) to solid Mn(III/IV) oxides.

[0144] The slurry (123) from the neutralisation (122) is then transferred to the liquid and solid separation (124), to dispose the residue (125) containing jarosite, alunite, goethite, hydroxides of Fe(III), Al(III), Cr(III) and Cu(II), and optional manganese(III/IV) oxides, while the feed solution (126) obtained is substantially free of alkali metal ion (Na^+, K^+) and monovalent cation (NH_4^+) species as well as iron, aluminium, chromium, containing nickel (major), cobalt, zinc, calcium, manganese (minor) and partially reduced copper, and magnesium, which is suitable for subsequent purification processes described herein as shown in Figure 3, Figure 4, Figure 5 and Figure 6.

[0145] **Schemes for Overall Processing** (Figure 2)

[0146] The present disclosure not only provides the schemes as shown in Figure 1 for refining a MHP intermediate product from a conventional or existing nickel laterite process, but also provides schemes as shown in Figure 2 for upstream processing of nickel laterite ores or other nickel bearing materials and solutions to directly produce qualified feed solution suitable for subsequent purification processes (Figure 3, Figure 4, Figure 5 and Figure 6), or alternatively to produce a MHP (Figure 2) desirable for the refining using the schemes described herein as shown in Figure 1. The scheme options for overall processing of nickel laterite ores or nickel bearing materials and solutions are described as follows:

[0147] *Scheme Options 1 - Modified conventional process to produce feed solution / MHP free of alkali metals*

[0148] Jarosite / alunite precipitation was employed in prior arts for removal or control of iron and aluminium concentrations and/or for generation of acid, wherein alkali metal salts (Na_2CO_3 or Na_2SO_4) or ammonium salt such as $(NH_4)_2SO_4$ are added. The present processes aim to utilise the jarosite / alunite precipitation for removal of alkali metal ions (Na^+, K^+) or monovalent cation (NH_4^+) species wherein preferably above the stoichiometric amounts of Fe^{3+} and Al^{3+} according to reaction (1) are required.

[0149] It is advantageous to utilise the rich iron and aluminium components in the feed material such as nickel laterite ores in leaching for early removal of these monovalent components by the jarosite / alunite precipitation. The forms of jarosite and alunite are easy to be separated by filtration or other liquid and solid separation technologies. The loss of nickel and cobalt by precipitation in jarosite and alunite is known to be very small. Scheme Options 1 comprises the following steps:

[0150] Leaching with conventional leaching methods such as high-pressure acid leaching (HPAL) and atmospheric leaching (AL) can be simultaneously performed with the jarosite / alunite precipitation in one step (156) or performed in successive steps of leaching (152) and jarosite / alunite (154) under the conditions as described above for step (115) (Figure 1).

[0151] The slurry (155 or 157) is neutralised (158) with a base reagent (121) to remove remaining iron as goethite / hydroxide and aluminium as alumina / hydroxides, together with other metal hydroxides such as chromium and copper hydroxides. An oxidant (103) can be optionally added to oxidise any Fe(II) to Fe(III) and Mn(II) to stable solid Mn(IV) oxides under the conditions as described above for the neutralisation step (122) (Figure 1).

[0152] The slurry (159) from the neutralisation (158) goes through the solid / liquid separation (160) to obtain the feed solution (162) which is substantially free of monovalent cations (Na^+, K^+, NH_4^+), iron, aluminium and chromium and to dispose the residue (161) containing jarosite / alunite, goethite, alumina and hydroxides of iron, aluminium, chromium and copper, and Mn(III/IV) oxides.

[0153] The feed solution (162) can be, if desired, fed to the subsequent purification schemes as shown in Figure 3, Figure 4, Figure 5 and Figure 6. Depending on the concentration of nickel and/or cobalt, the feed solution (162) may be concentrated by means of water separation, e.g. by membrane distillation, before being fed to the subsequent purification schemes as shown in Figure 3, Figure 4, Figure 5 and Figure 6.

[0154] Alternatively, the feed solution (162) goes through the mixed hydroxide precipitation (163) to produce MHP (164) which is then leached in step (112) (Figure 1) to produce the feed solution (126) for further purification using the schemes shown in Figure 3, Figure 4, Figure 5 and Figure 6 to produce high purity, battery grade nickel sulphate and cobalt sulphate.

[0155] *Scheme Options 2 - Modified conventional process to produce MHP with a desirable Fe/Al to Na/K ratio*

[0156] In conventional nickel laterite process, a challenging issue is the loss of nickel and cobalt by adsorption / precipitation with the iron and aluminium hydroxide precipitate. To minimise the loss, the iron and aluminium precipitation is typically operated in multiple stages with recycling the last stage of the iron and aluminium hydroxide precipitate to leaching, which significantly decreased the process efficiency and increased process costs.

[0157] As described above, the MHP feeding the flowsheet shown in Figure 1 allows the presence of iron and aluminium at a desirable ratio relatively to the alkali metal ions and monovalent cation species required for subsequent jarosite / alunite precipitation. Therefore, a deep removal of the iron and aluminium by primary neutralisation is not necessary, and the recycling of the last stage iron and aluminium hydroxide precipitate as practiced in the conventional process can be reduced or eliminated. The major steps of Scheme Options 2 and principles for control of iron and aluminium contents in the MHP are described below.

[0158] After leaching (152) and the solid / liquid separation (181), the PLS (183) is neutralised with a base reagent such as limestone or lime (185) to precipitate iron and aluminium (184) under controlled conditions to leave partial Fe(III) and Al(III) relative to monovalent cations ($Na^+ + K^+ + NH_4^+$) in the PLS which is measured based on their ratios in the MHP (191), preferably in the range of (3 – 6):1, and more preferably at (4 - 5):1.

[0159] After the liquid and solid separation (187) of the slurry (186), the residue (188) is disposed, and the PLS (189) is fed to the mixed hydroxide precipitation (190) by addition of a base reagent such as magnesium oxide / hydroxide (14) to produce the MHP (191) with a desirable ratio of [Fe(III) + Al(III)] to ($Na^+ + K^+ + NH_4^+$) for jarosite / alunite precipitation (115 or 119) to remove the monovalent cations ($Na^+ + K^+ + NH_4^+$) in subsequent refining processes.

[0160] **Impurities (typically Zn(II), Mn(II), Cu(II) and Ca(II)) Solvent Extraction** (Figure 3, Figure 4, Figure 5 and Figure 6)

[0161] The impurities of Zn(II), Mn(II), Cu(II) and Ca(II), Cd(II), Pb(II) and other impurities having higher affinities to the organic extractant than cobalt and nickel in the feed solution (126, 162) are extracted with an organophosphoric acid, e.g di(2-ethylhexyl)phosphoric acid (D2EHPA). This SX scheme comprises the following steps:

[0162] The stripped organic (211) is preloaded (212) with nickel sulphate (126 or 162, or 221 or 331) shown in Figure 3 and (419 or 503) shown in Figure 5 with a base reagent (213) such as sodium hydroxide or carbonate or ammonia / ammonium hydroxide to produce the nickel preloaded organic (216) and sodium sulphate or ammonium sulphate by-products (215). Alternatively, the stripped organic can be pre-neutralised (222) with a base reagent (213) such as sodium hydroxide or carbonate or ammonia / ammonium hydroxide to produce the pre-neutralised organic (223) for preloading (212) of nickel by exchange.

[0163] The preloaded organic (216) is scrubbed (217) with a scrub solution (218) containing water and/or dilute sulphuric acid and/or nickel sulphate to remove the extracted and entrained sodium or ammonium ions to scrub liquor (219) which is recycled to the preloading (212).

[0164] The scrubbed / preloaded organic (220) is fed to Impurity Extraction (201), wherein the impurities of Zn(II), Mn(II), Cu(II) and Ca(II), Cd(II), Pb(II) and other impurities having higher affinities to the organic extractant than cobalt and nickel in the feed solution (126 or 162) are extracted into the organic phase by exchange of the preloaded nickel into the aqueous phase. Minimum pH control with sulphuric acid for maintaining a desirable pH profile for the multiple stages of extraction may be optionally employed, if desired.

[0165] The loaded organic (202) is scrubbed (203) with a scrub solution (205) of water and/or sulphuric acid and/or metal sulphates to remove the extracted nickel and cobalt to the scrub liquor (204) which is recycled to the extraction (201).

[0166] The scrubbed organic (206) is stripped (207) with a strip solution (208) of sulphuric acid or hydrochloric acid (HCl) to regenerate the organic (211) for feeding the preloading (212) or optionally feeding the pre-neutralisation (222).

[0167] The selection of an acid, H_2SO_4 or HCl (208), for the stripping (207) depends on the concentration of calcium. If the calcium concentration is significantly below its saturation to form gypsum, sulphuric acid for stripping under controlled conditions to avoid formation of gypsum is preferred due to the identical sulphate matrix. If the concentration of calcium is high, hydrochloric acid can be employed to avoid the formation of gypsum. If hydrochloric acid is used, washing stage(s) may be required to remove the entrained chloride ions in the organic phase before transferring the stripped organic (211) for preloading (212) or pre-neutralisation (222).

[0168] The strip liquor (210) containing the impurities (typically Zn(II), Mn(II), Cu(II) and Ca(II)) can be further treated to separate and recover specific metals of interest. For example, the zinc can be separated from other impurities through selective stripping to produce a separate by-product, if desired.

[0169] It is aware that trace amounts of iron and aluminium and other high valence ions would be strongly extracted by D2EHPA, and a periodic bleed treatment of the organic with 6 M HCl may be needed, depending on the loading and capacity requirement.

[0170] **Extraction of Cobalt and Magnesium in One SX Circuit with Preloaded Organic** (Figure 3)

[0171] The present disclosure provides the SX scheme using an organophosphinic acid, e.g. bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex$^{®}$ 272 or Ionquest$^{®}$ 290) in a hydrocarbon diluent and optionally in the presence of an organic phase modifier to extract both cobalt and magnesium (301) from the raffinate (221) and separation of the magnesium from cobalt within the circuit. This scheme comprises of the following steps:

[0172] The stripped organic (324) is preloaded (325) with nickel sulphate (221 or 331) available within the process with a base reagent (213) such as ammonium hydroxide or carbonate, or sodium hydroxide for neutralisation to produce the nickel preloaded organic (326) and ammonium sulphate or sodium sulphate by-products (215). Alternatively, the stripped organic (324) can be pre-neutralised (332) with a base reagent (213) such as sodium hydroxide or carbonate, or ammonium hydroxide to produce the pre-neutralised organic (333) for preloading (325) of nickel by exchange.

[0173] The preloaded organic (326) is scrubbed (327) with a scrub solution (328) of water and/or sulphuric acid and/or nickel sulphate to remove the extracted and entrained sodium and ammonium ions from the organic phase into the scrub liquor (329) which is recycled to the preloading (325).

[0174] Both cobalt and magnesium in the raffinate (221) are extracted (301) with the scrubbed / preloaded organic (330) and separated from nickel which remains in the raffinate (331).

[0175] The loaded organic (302) is firstly scrubbed (303) with a scrub solution (304) of water and/or sulphuric acid and/or cobalt sulphate to selectively remove the extracted nickel from the organic phase to the scrub liquor (305) which is recycled to the Co/Mg extraction (301).

[0176] The nickel scrubbed organic (306) is further scrubbed (307) with a scrub solution (308) of water and/or sulphuric acid and/or cobalt sulphate solution to remove the extracted magnesium from the organic phase to obtain the magnesium rich scrub liquor (309) with some co-scrubbed cobalt.

[0177] The co-scrubbed cobalt in the magnesium rich scrub liquor (309) is then extracted (310) with a minor portion of the stripped organic (321), wherein a base reagent (311) such as ammonia / ammonium hydroxide or sodium hydroxide or carbonate can be directly used for the neutralisation, if desired. Alternatively, the stripped organic (321) can be preloaded (334) with a solution of magnesium sulphate ($MgSO_4$) (312) and a base reagent (311) for pH adjustment, preferably magnesium oxide / hydroxide and/or ammonia / ammonium hydroxide, or sodium hydroxide or carbonate, and then fed for the extraction of cobalt (310) through the exchange of the preloaded base metal.

[0178] The entrained or extracted ammonium or sodium in the organic phase in the above steps (334 and 310) can be removed from the organic phase by a scrubbing step (314) to the scrub liquor (316) which is recycled to the extraction (310).

[0179] The magnesium rich raffinate (312) can be further processed to produce magnesium sulphate, or magnesium oxide or hydroxide for recycling as a base (311) for preloading and neutralisation in the process.

[0180] The minor stream of cobalt loaded organic (317) is merged with the main stream of nickel scrubbed organic (306) as the feed (318) for scrubbing of magnesium (307).

[0181] The magnesium scrubbed organic (319) is stripped (320) with a strip solution (323) of sulfuric acid to obtain cobalt loaded strip liquor (322) and to regenerate the organic (321 and 324) which is recycled to the preloading (325 or 334). If desired, the cobalt can be stripped by other acids such as hydrochloride acid and nitric acid, respectively, for production of other salt products, wherein washing steps before and after the stripping may be needed to avoid cross contaminations by organic phase carrying-over.

[0182] The cobalt loaded strip liquor (322) containing minor zinc and copper can be purified by IX (601) using a type of iminodiacetic acid resin such as Lewatit® TP 207 for removal of copper, followed by zinc IX with a D2EHPA impregnated resin such as Lewatit® VP OC 1026. Alternatively, aminophosphonic acid chelating resin such as Purolite® S950 can be potentially employed for removal of both copper and zinc.

[0183] If needed, it is known that nickel can be separated from cobalt by bis-picolylamine chelating resin such as Dowex® M4195.

[0184] Minor manganese may also be present in the cobalt loaded strip liquor (322), which can be selectively precipitated as Mn(III/IV) oxide with an oxidant such as ozone, a mixture of SO_2/O_2(air) at a ratio functioning as an oxidant, peroxymonosulfuric acid (Caro's acid) and peroxydisulfuric acid.

[0185] The purified cobalt liquor (603) is fed to cobalt crystallisation (604) to produce high purity, battery grade hydrated cobalt sulphate (605).

[0186] The raffinate (331) from the Co/Mg SX (301) is directly fed to crystallisation (701) to produce high purity, battery grade hydrated nickel sulphate (702).

[0187] Optionally, the cobalt loaded strip liquor (322) can be purified to remove various minor impurities such as zinc, copper, calcium, manganese, cadmium, lead and other impurities by SX with an orgnophosphoric acid (D2EHPA) extractant as described above, if desired.

[0188] **Extraction of Cobalt and Magnesium in One SX Circuit with Direct Neutralisation** (Figure 4)

[0189] An alternative SX scheme (Figure 4) to use direct neutralisation of the acid produced during the SX processes (201) and (301) with ammonia / ammonium hydroxide (222), instead of the preloading as shown in Figure 3.

[0190] The major SX schemes with D2EHPA (201) for separation of the impurities (typically Zn(II), Mn(II), Cu(II) and Ca(II)) and then the extraction of cobalt and magnesium (301) are the same as those shown in Figure 3. The ratios of the aqueous to the organic (A/O) is chosen and controlled to avoid the formation of ammonium nickel sulphate double salt during the SX process.

[0191] The ammonium sulphate produced in the neutralisations (201 and 301) will end up with nickel in the SX raffinate (331). Partial ammonium sulphate would be crystallised with the hydrated nickel sulphate (703) as ammonium nickel sulphate double salt.

[0192] A thermal decomposition step (704 or 706) is designed to convert the double sulphate salt to nickel sulphate (708), wherein the ammonium sulphate can be decomposed into ammonia, sulphur trioxide and nitrogenous gases (705) at temperature above 280 °C. It is preferable to selectively decompose only the ammonium component to ammonia (222) for recycling as the base regent, for which an oxide / hydroxide such as nickel oxide /hydroxide (707) may be added to form nickel sulphate (708). Nitrate, nitrite, nitrous components, if exists, would be at least partially removed in this step.

[0193] **Extraction of Cobalt and Magnesium by Separate SX Circuits with Preloaded Organic** (Figure 5)

[0194] The present disclosure provides alternative SX schemes to firstly extract cobalt from magnesium and nickel, and then to extract magnesium from nickel with the same Cyanex® 272 as shown in Figure 5. The SX scheme for removal of the impurities (typically Zn(II), Mn(II), Cu(II) and Ca(II)) with D2EHPA are the same as that described above and shown in Figure 3.

[0195] The alternative SX schemes for extraction and separation of cobalt and magnesium by separate SX circuits include the following steps:

[0196] The stripped Cyanex® 272 (410 and 511) is preloaded (411) with nickel sulphate (419 or 503) available within the process, which produces nickel loaded organic (413) and ammonium sulphate or sodium sulphate by-products (215) with a base reagent (213) such as sodium hydroxide or carbonate, or ammonia / ammonium hydroxide. Alternatively, the stripped organic (410 and 511) can be pre-neutralised (420) with a base reagent (213) to produce the pre-neutralised organic (421) for preloading (411) of nickel by exchange.

[0197] The preloaded organic (413) is scrubbed (414) with a scrub solution (415) of water and/or sulphuric acid, and/or nickel sulphate to remove the extracted and entrained sodium or ammonium ions from the organic phase into the scrub liquor (416) which is recycled to the preloading (411).

[0198] The cobalt in the raffinate (221) from the impurity SX (201) is extracted (401) with a portion of the scrubbed / preloaded organic (418) by exchange and separated from magnesium and nickel in the raffinate (419).

[0199] The cobalt loaded organic (402) is scrubbed (403) with a scrub solution (404) comprising water, and/or sulphuric acid, and/or cobalt sulphate to remove the extracted nickel and magnesium into the scrub liquor (405) which is recycled to the cobalt extraction (401).

[0200] The nickel and magnesium scrubbed organic (406) is stripped (407) with a strip solution (408) of sulfuric acid to regenerate the organic (410) which is recycled to the preloading (411).

[0201] The cobalt loaded strip liquor (409) containing minor zinc and copper is purified by IX (601) as described above. If needed, minor nickel can be removed by IX (601) using bis-picolylamine chelating resin and minor manganese can be removed by oxidation with an oxidant such as Caro's acid.

[0202] Optionally, the cobalt loaded strip liquor (409) can be purified (601) to remove various minor impurities such as zinc, copper, calcium, manganese, cadmium, lead and other impurities by SX with an orgnophosphoric acid (D2EHPA) extractant as described above, if desired.

[0203] The purified cobalt liquor (603) is fed to cobalt crystallisation (604) to produce high purity, battery grade hydrated cobalt sulphate (605).

[0204] The magnesium in the cobalt extraction raffinate (419) is extracted (501) with a portion of the preloaded organic (502).

[0205] The magnesium loaded organic (504) is scrubbed (505) with a scrub solution (506) comprising water, and/or sulphuric acid to remove the extracted nickel into the scrub liquor (507) which is recycled to the magnesium extraction (501).

[0206] The scrubbed organic (508) is stripped (509) with a strip solution (510) of sulfuric acid to obtain magnesium loaded strip liquor (512) and to regenerate the organic (511) which is recycled to the preloading (411).

[0207] The magnesium loaded strip liquor (512) contain magnesium sulphate (513) can be crystallised to produce magnesium sulphate by-product or can be further processed to produce MgO / $Mg(OH)_2$ by-products which can be used in the process as a base reagent.

[0208] The raffinate (503) from the magnesium solvent extraction (501) containing nickel is directly fed to nickel crystallisation (701) to produce high purity, battery grade hydrated nickel sulphate (702).

[0209] **Extraction of Cobalt and Magnesium by Separate SX Circuits with Direct Neutralisation** (Figure 6)

[0210] The present disclosure provides an alternative approach and scheme (Figure 6) using direct neutralisation of the acid produced during the SX processes (201), (401) and (501) with ammonia / ammonium hydroxide (222), instead of the preloading approach and scheme as shown in (Figure 5). The ratios of the aqueous to the organic (A/O) is chosen and controlled to avoid the formation of ammonium nickel sulphate double salt during the SX process.

[0211] The major SX scheme with D2EHPA (201) for separation of the impurities (Zn(II), Mn(II), Cu(II) and Ca(II)), and separation of cobalt (401) and magnesium (501) using two separate SX circuits are the same as those shown in Figure 5.

[0212] The ammonium sulphate produced from the neutralisation of the acid in the SX processes (201, 401 and 501) end up with nickel in the final SX raffinate (503). Partial ammonium sulphate would be crystallised with nickel sulphate (703) as ammonium nickel sulphate double salt.

[0213] A thermal decomposition step (704 or 706) is designed to convert the double sulphate salt to nickel sulphate (708), wherein the ammonium sulphate can be decomposed into ammonia, sulphur trioxide and nitrogenous gases (705) at a temperature above 280 °C. It is preferable to selectively decompose only the ammonium component to ammonia (222) for recycling as the base regent, for which an oxide / hydroxide such as nickel oxide /hydroxide (707) may be added to form nickel sulphate (708). Nitrate, nitrite, nitrous components, if existing, would be at least partially removed in this step.

EXAMPLES

[0214] **Example 1** - *Washing MHP*

[0215] Wet MHP (4.2 kg, 48.9% moisture) was repulped with deionised water at 40 °C with constant agitation for 30 minutes followed by filtration through a pressure filter. This repulping / filtration procedure was repeated for multiple washings. The conditions and results are given in Table 5.

[0216] The sodium and potassium contents in the feed MHP decreased with washings, corresponding to increases in the Ni/Na and Ni/K ratios.

[0217] After three washings, the ratios of Ni/Na and Ni/K increased from 142 to 3929 and from 378 to 3522, respectively, corresponding to 25 ppm Na and less than 28 ppm K in the feed solution normalised to 100 g/L Ni, if the washed MHP is fully dissolved.

[0218] After six washings, the ratios of Ni/Na and Ni/K increased from 142 to 26281 and 378 to 12533, respectively, corresponding to less than 10 ppm Na and less than 20 ppm K in the final nickel sulphate product containing 22.3% Ni, assuming that all the Na and K enter the nickel sulphate product.

[0219] Therefore, in principle, the contents of sodium and potassium in the MHP could be removed by washings and efficient filtration such as pressure filtration to very low levels to meet the requirements and specifications of a final nickel sulphate product. However, this does not limit the cost-effective combinations of the washings with the jarosite / alunite precipitation method described in the examples below.

[0220] The contents of magnesium and calcium in the MHP were also significantly reduced through the washings, which would be beneficial for the subsequent purification processes.

[0221] **Table 5** - Washing of MHP

Wash	Solid assays (%)											Ratio	
	Ni	Co	Cu	Zn	Fe	Mn	Al	Mg	Ca	Na	K	Ni/Na	Ni/K
Feed	13.73	1.23	1.18	1.71	0.02	0.88	0.23	9.51	0.54	0.097	0.036	142	378
1	25.38	2.31	2.25	3.22	0.04	1.26	0.42	4.32	0.21	0.021	0.014	1191	1826
3	33.40	4.35	1.79	2.65	0.04	1.81	0.18	3.21	0.16	0.009	0.009	3929	3522
4	34.45	4.56	1.86	2.84	0.03	1.85	0.51	6.52	0.19	0.006	0.004	6061	9025
5	36.46	4.77	1.99	2.99	0.04	2.01	0.19	2.12	0.05	0.003	0.004	14586	8942
6	37.66	4.97	1.98	3.09	0.04	2.00	0.19	1.82	0.03	0.001	0.003	26281	12533

[0222] **Example 2** - *Jarosite precipitation and neutralisation*

[0223] This example presents the jarosite precipitation using a feed with the compositions shown in Table 6. The feed was heated to 95 °C with agitation and aeration, while 20 grams of jarosite seed produced from a previous jarosite precipitation was added. The slurry pH was adjusted and maintained in the pH range of 1.8 – 2.0 by addition of washed MHP obtained as described in Example 1. At 7.3 hours, the slurry was filtered by vacuum using Macherey-Nagel MN615 filter paper. The compositions of the final solution and the washed solid are given in Table 6.

[0224] The sodium in the solution decreased from the feed 118 mg/L to 3.1 mg/L, corresponding to 99.8% Na precipitation efficiency and an increase of the Ni/Na ratio from 770 to 31119. The nickel and cobalt in the jarosite precipitate were measured at 0.03% and 0.07%, respectively.

[0225] This example demonstrates that the sodium ions can be deeply removed by the jarosite precipitation to a very low level which meets the requirement and specifications of the feed solution suitable for subsequent purification by SX and IX to produce high purity, battery grade nickel sulphate.

[0226] **Table 6** - *Jarosite precipitation*

Time (h)	pH	Liquor Analysis (mg/L)						Solid Analysis (%)					
		Ni	Co	Fe	Al	Na	K	Ni	Co	Fe	Al	Na	K
Feed	1.6	91079	7858	3200	7.7	118	<0.2	-	-	-	-	-	-
7.3	1.8	96821	8434	1180	9.5	3.1	<0.2	0.055	0.010	28.82	0.009	2.764	0.005

[0227] After the above jarosite precipitation, lime was added in doses to increase the slurry pH in stages: pH 2.1 (95 °C), pH 2.4 (62 °C), pH 3.6 (62 °C) and pH 4.4 (62 °C), while the slurry temperature was allowed to decrease from 95 °C to 62 °C after 80 minutes. The test conditions and results are given in Table 7.

[0228] The remaining iron and aluminium in the solution decreased to below 1 mg/L at pH 4.4 (62 °C), while the total nickel and cobalt co-precipitated in the final washed solid in the jarosite and neutralisation were ~0.04% and ~0.08%, respectively.

[0229] **Table 7** - *Neutralisation*

Time (min)	T (°C)	pH	Liquor Analysis (mg/L)						Solid Analysis (%)					
			Ni	Co	Fe	Al	Na	K	Ni	Co	Fe	Al	Na	K
0	95	2.1	88158	7581	1298	13.96	15.6	<0.2						
80	95	2.1	86975	7506	1131	13.07	5.15	<0.2	0.059	0.011	31.14	0.006	2.957	0.011
200	62	2.4	78050	6794	290	11.89	1.81	<0.2	0.055	0.010	27.47	0.008	2.614	0.007
320	62	3.6	74643	6502	7.20	2.27	2.62	<0.2	0.061	0.010	25.56	0.007	2.400	0.011
420	62	4.4	75994	6563	0.42	0.20	3.33	<0.2	0.055	0.010	25.94	0.007	2.413	0.011

[0230] **Example 3** - *Oxidative conversion of Mn(II) to Mn(IV) oxides*

[0231] This example shows the conversion of the soluble Mn(II) to stable solid Mn(IV) oxides in a MHP (44.46% Ni, 4.6% Co, 0.88% Mn) with air and SO_2/air mixture. The MHP was repulped in deionised water at 29% (dry solid) pulp density and 60 °C. The slurry was constantly agitated with a continuous sparging of air or the mixture of sulphuric dioxide (SO_2) and air at 0.5 – 1% (v/v) SO_2.

[0232] The slurry samples were periodically taken and filtered by vacuum through Macherey-Nagel MN615 filter paper. The solid cakes from the filtration were leached with 1M sulfuric acid solution and then the insoluble leach residue samples were fully dissolved in 6M HCl solution. The leach liquor samples were assayed by ICP-AES/MS for the concentrations of nickel, cobalt and manganese, based on which, the conversion efficiencies of the manganese and precipitated nickel and cobalt were calculated. The results for the conversion with sparging of air only, and sparging of the mixture of SO_2/air are compared in Figure 7.

[0233] With air alone, the conversion rate was initially fast, but decreased with time at about 60% conversion at 60 minutes. With alterative air and the SO_2/air mixture, the conversion increased almost linearly with > 97% conversion efficiency at 170 minutes, corresponding to < 0.1 g/L Mn relative to 100 g/L Ni in the leach solution, if the MHP is dissolved.

[0234] Further analysis of the data indicated that the kinetic behaviour of the conversion with air alone could be approximated by a second order rate reaction with respect to the content of soluble Mn(II), while that with the SO_2/air mixture featured zero order rate kinetics, i.e. independent of the Mn(II) content. In application, the conversion can be run with initial sparging of air alone to obtain a rapid conversion of a major portion of Mn(II), followed by sparging of the SO_2/air gas mixture for more complete conversion.

[0235] In principle, a complete conversion of Mn(II) can be achieved, if desired. In this process, the complete conversion of Mn(II) is optional, as the remaining Mn(II) at a lower level can be removed by subsequent SX scheme with D2EHPA.

[0236] The precipitated cobalt and nickel in the final solid residue were 0.88% and 0.08%, respectively, with air only for 90 minutes and 3.37% and 0.09%, respectively, with alternatively SO_2/air mixture and air for 300 minutes. Therefore, the parameters for the conversion such as pH, flowrate, SO_2/air(O_2) ratio, and residence time can be optimised for desirable conversion efficiency of Mn(II) with minimum conversion of nickel and cobalt.

[0237] **Example 4** - *Nickel preloading of D2EHPA*

[0238] The preloading distribution isotherms shown in this example were established with 10% D2EHPA in Exxsol D80 and a feed solution of 62.6 g/L Ni (sulphate) at 50 °C and about pH 5 with sodium hydroxide for neutralisation and pH control. The results are shown in Figure 8. McCabe-Thiele diagram suggests two to three theoretical stages for extraction of nickel at an operating A/O ratio of 1:10 (Figure 8).

[0239] **Example 5** - *Scrubbing the preloaded D2EHPA*

[0240] This example shows that the entrained and loaded sodium from sodium hydroxide as the base reagent for neutralisation in the preloading could be scrubbed from the loaded organic.

[0241] The scrubbing distribution isotherms shown in this example were performed at 50 °C and about pH 3.6 using 10% D2EHPA in Exxsol D80 preloaded with nickel and a scrub solution of 64.8 g/L Ni (sulphate). The scrubbing results are shown in Figure 9.

[0242] The McCabe-Thiele diagram constructed based on the data suggests two to three theoretical stages for scrubbing the loaded sodium at an operating A/O ratio of about 1:10. The scrubbing of the nickel was reasonably in the range of 10 – 15%, which is recycled to the preloading section in a continuous operation. The scrubbing conditions with respect to the composition of the scrub solution, scrubbing pH, A/O ratios and stages can be further optimised. In a continuous SX process with multiple stages, an optimum pH profile can be applied.

[0243] **Example 6** - *Extraction of impurities with the preloaded D2EHPA*

[0244] This example presents the extraction distribution isotherms for extraction of the impurities (Zn(II), Cu(II), Mn(II) and Ca(II)) with the nickel (6.3 g/L) preloaded 10% (v/v) D2EHPA in Exxsol

D80. Portions of the nickel preloaded organic were separately contacted with respective portions of a synthetic PLS (g/L: 93.1 Ni, 9.23 Co, 2.80 Mg, 3.2 Zn, 0.08 Mn, 0.034 Ca and 0.087 Cu) at various A/O ratios, pH ~3.1 and 40 °C for 10 minutes with a constant mechanical stirring.

[0245] The metal distribution isotherms are shown in Figure 10. The negative extraction efficiency of nickel indicated that the metal impurities were extracted through the replacement of the preloaded nickel. The McCabe-Thiele diagrams shown in Figure 11 and Figure 12 suggest three theoretical extraction stages for extraction and separation of the impurities (Zn(II), Mn(II), Cu(II) and Ca(II)) from nickel and cobalt with 10% D2EHPA at an operating A/O ratio of 1.5.

[0246] **Example 7** - *Nickel preloading of Cyanex® 272*

[0247] This example presents the preloading of 25% Cyanex® 272 in Exxsol D80 with 56 g/L Ni (sulphate) at 50 °C and pH 6.8 – 7.0 with sodium hydroxide for neutralisation and pH control. The distribution isotherms and McCabe-Thiele diagram for nickel preloading are shown in Figure 13, predicting two to three theoretical stages for extraction of nickel at an operating A/O ratio of 1:4.

[0248] **Example 8** - *Scrubbing sodium from the preloaded Cyanex® 272*

[0249] This example demonstrates the scrubbing distribution isotherms for removal of the entrained and extracted sodium from the preloaded 25% Cyanex® 272 in Exxsol D80 at pH 5.5 using a scrub solution of 65 g/L Ni (sulphate). The metal distribution isotherms and McCabe-Thiele diagram constructed based on the data are shown in Figure 14, suggesting two to three theoretical stages for scrubbing of the sodium at an operation A/O ratio of 1:15 with reasonable scrubbing of nickel which can be further minimised in multiple stage operation with an optimum pH profile. The scrub liquor can be recycled to the preloading section for recovery of nickel in a continuous operation.

[0250] **Example 9** - *Extraction of cobalt and magnesium with Cyanex® 272*

[0251] As shown in Figure 3, the present disclosure provides an SX scheme for extraction of both cobalt and magnesium and then separate the loaded magnesium from cobalt through a scrubbing scheme within the SX circuit. This example presents the metal distribution isotherms for the extraction of cobalt and magnesium and separation from nickel using the nickel preloaded (14.44 g/L Ni) organic solution of 25% (v/v) Cyanex® 272 in Exxsol D80 and a synthetic solution containing (g/L) 103 Ni, 11.4 Co and 3.2 Mg.

[0252] The test results are shown in Figure 15. The negative extraction efficiency of nickel indicates that the preloaded nickel was exchanged by the extraction of cobalt and magnesium. McCabe-Thiele diagrams predicts that both cobalt and magnesium can be extracted with two to three (theoretical) extraction stages with 25% Cyanex® 272 at an operating A/O of 0.6:1 (Figure 16).

[0253] **Example 10** - *Scrubbing nickel and magnesium from the loaded organic*

[0254] These examples show the scrubbing distribution isotherms of the loaded nickel at a higher pH range and then scrubbing the loaded magnesium at a lower pH range from the 25% (v/v) Cyanex® 272 in Exxsol D80 preloaded at 6.477 g/l Co, 1.632 g/L Ni and 1.722 g/L Mg. The scrubbing distribution isotherms at pH 5, pH 4.2 and pH 3.5 are shown in Figure 17 and Figure 18, respectively.

[0255] The distribution isotherms and the McCabe-Thiele diagrams suggest one to two theoretical extraction stages with 25% Cyanex® 272 at an operating A/O of 1:7 for scrubbing of the loaded nickel in the pH range of 4.2 – 5 (Figure 17). The nickel rich scrub liquor is recycled to the extraction sections in a continuous operation.

[0256] The distribution isotherms and the McCabe-Thiele diagrams suggest three to four scrubbing stages for scrubbing the loaded magnesium in the pH range of 3.5 – 4.2 and an operating A/O ratio in the range of 1:4 – 1:9 (Figure 18), which can be further optimised in a continuous operation for the scrubbing efficiency of magnesium and selectivity over cobalt in multiple stage operation with an optimum pH profile.

[0257] Some significant features and advantages of the processes described herein are summarised as follows:

1) For production of high purity, battery grade nickel sulphate and cobalt sulphate, the conventional and existing refining processes require costly SX-based extraction and subsequent stripping of the major metal, nickel, using an organocarboxylic acid such as Versatic 10, away from the relatively small amount of impurities present (normally at the ratio of impurities / nickel < 1/15 in the original MHP). In addition, two additional SX stages are required. This disclosure avoids the most costly nickel SX step, resulting in just two SX steps being required, resulting in reduced capital and operating costs.
2) This disclosure provides a process to enable simple separation of alkali metals and monovalent cation species.
3) This disclosure provides novel SX schemes for extraction and separation of respective cobalt and magnesium from nickel in one SX circuit, or in two separate SX circuits. Both schemes for separation of magnesium from nickel are novel and the former in one SX circuit offers minimum SX requirement and thus minimum capital and operating costs.
4) This disclosure provides two approaches and schemes for neutralisation of the acid produced in the SX processes: (a) preloading the organic with nickel sulphate available

within the process to avoid contamination of the system from the base reagents, or (b) direct neutralisation with ammonia / ammonium hydroxide which is then removed from the final hydrated nickel sulphate by thermal decomposition preferably to ammonia for recycling as the base reagent in the process.

5) This disclosure provides oxidative precipitation methods for conversion of the soluble divalent manganese ions, Mn(II), into stable solid Mn(III/IV) oxides with minimum loss of nickel and cobalt in washing stage, and/or in subsequent oxidative neutralisation step for early rejection of manganese favourable for easy separation in subsequent purification by SX.
6) The rich iron and aluminium contents in nickel laterite ores are conventionally leached and removed as hydroxides by neutralisation with heavy recycling the last stage precipitate to minimise the loss of nickel and cobalt, which significantly decreases the process efficiency and increases the processing costs.
7) This disclosure offers approaches and schemes for improvement of overall process efficiency of nickel laterite processing, including:
   (a) A controlled neutralisation for iron and aluminium hydroxide precipitation to allow desirable ratios of iron and aluminium to the alkali metal ion (Na^+ and K^+) and monovalent cation (e.g. NH_4^+) species in the MHP for subsequent refining processes described herein to remove these monovalent cations and species as jarosite / alunite so that a deep removal of iron and aluminium and heavy recycling in the conventional upstream process for product MHP is not necessary; and
   (b) Jarosite / alunite precipitation for removal of alkali metal ions (Na^+ and K^+) and monovalent cation (e.g. NH_4^+) species which can be operated concurrently with leaching or successively after leaching to produce feed solution or MHP which is substantially free of these monovalent cations and species and can be fed to the subsequent simplified refining and purification processes described herein.

[0258] This disclosure relates to refining processes for production of high purity, battery grade nickel sulphate and cobalt sulphate products from a wide range of feed materials, including, but not limited to:

- Nickel and cobalt containing intermediate products such as MHP;
- Nickel laterite ores or other nickel and cobalt containing materials;
- Nickel and cobalt containing solutions;
- Spent battery materials;
- Manganese ocean nodules; and
- Waste materials and tails containing nickel and cobalt.

[0259] It will be understood that the terms “comprise” and “include” and any of their derivatives (e.g. comprises, comprising, includes, including) as used in this specification, and the claims that follow, is to be taken to be inclusive of features to which the term refers, and is not meant to exclude the presence of any additional features unless otherwise stated or implied

[0260] The reference to any prior art in this specification is not, and should not be taken as, an acknowledgement of any form of suggestion that such prior art forms part of the common general knowledge.

[0261] In some cases, a single embodiment may, for succinctness and/or to assist in understanding the scope of the disclosure, combine multiple features. It is to be understood that in such a case, these multiple features may be provided separately (in separate embodiments), or in any other suitable combination. Alternatively, where separate features are described in separate embodiments, these separate features may be combined into a single embodiment unless otherwise stated or implied. This also applies to the claims which can be recombined in any combination. That is a claim may be amended to include a feature defined in any other claim. Further a phrase referring to “at least one of” a list of items refers to any combination of those items, including single members. As an example, “at least one of: a, b, or c” is intended to cover: a, b, c, a-b, a-c, b-c, and a-b-c.

[0262] It will be appreciated by those skilled in the art that the disclosure is not restricted in its use to the particular application or applications described. Neither is the present disclosure restricted in its preferred embodiment with regard to the particular elements and/or features described or depicted herein. It will be appreciated that the disclosure is not limited to the embodiment or embodiments disclosed, but is capable of numerous rearrangements, modifications and substitutions without departing from the scope as set forth and defined by the following claims.

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[0267] Rodriguez, M., 2008. Hydrometallurgical leaching for nickel comprises combining nickel sulfide ore with nickel laterite and milling to form slurry, leaching combined slurry in pressure acid leach circuit, and providing oxidant to pressure acid leach circuit. Patent No. AU2008100563-A4; AU2008100563-B4.

[0268] Rodriguez, M., 2009. Hydrometallurgical method for leaching nickel from nickel ore composition, involves adding sulfide ore to autoclave of high-pressure acid leach circuit including nickel laterite feed material, and adding oxidant to autoclave. Patent No. AU2008101213-A4; AU2008101213-B4; AU2008101213-A8; AU2008101213-B8.

[0269] Virnig, M.J., Mackenzie, J. and Mackenzie, J.M., 1997. Nickel recovery from laterite ore using oxime extractant - by acid leaching, precipitating nickel hydroxide, re-leaching with aqueous ammonia, extracting with water-insoluble oxime in water-immiscible hydrocarbon, acid stripping and electrowinning. Patent No. WO9743023-A1; AU9730543-A; EP915727-A1; US5976218-A; AU727561-B; CA2252592-C.

CLAIMS

1. A process for separating nickel and/or cobalt salts from crude nickel and/or cobalt bearing materials, the process comprising:

   a) treating a crude nickel and/or cobalt bearing material with a salt of iron or aluminium under conditions to remove at least some of one or more alkali metal ion and/or monovalent cation species as a jarosite /alunite precipitate to provide a solution having a reduced content of one or more alkali metal ion and/or monovalent cation species;

   b) subjecting the solution from step a) to increasing pH in a stepwise manner under conditions to provide a feed solution for further purification to produce nickel and/or cobalt salts suitable for the production of battery grade nickel or cobalt salts;

wherein step b) removes at least some or any combination of any one or more of the following species:

   i. iron,
   ii. aluminium,
   iii. chromium, and
   iv. copper.

2. The process of claim 1, further comprising treating a crude nickel and/or cobalt bearing material prior to step a) with an aqueous solution comprising water and/or sulfuric acid under conditions to remove at least some of the one or more alkali metal ion and/or monovalent cation species.

3. The process of either claim 1 or claim 2, further comprising treating the feed solution obtained from step b) with an oxidant under conditions to oxidise any iron(II) to iron(III) and any manganese(II) to higher oxidation state manganese(III/IV).

4. The process of any one of claims 1 to 3, wherein the iron or aluminium salt in step a) is selected from the group consisting of sulphate, carbonate, oxide, and hydroxide salts.

5. A process for obtaining purified nickel and cobalt from the feed solution obtained according to any one of claims 1 to 4, the process comprising

   a) reducing the concentration of any zinc, calcium, manganese, copper, cadmium, lead or other metal impurities having higher affinity to an organic extractant than cobalt and nickel, in the feed solution by contacting it with an organophosphoric acid extractant in a hydrocarbon diluent, under solvent extraction conditions and separating organic and aqueous phases to produce an aqueous raffinate comprising purified cobalt and nickel;

b) contacting the aqueous raffinate with a cobalt selective extractant in a hydrocarbon diluent, under solvent extraction conditions and separating organic and aqueous phases to produce an organic phase comprising purified cobalt and an aqueous phase comprising purified nickel;

c) selectively scrubbing and stripping the organic phase to obtain an aqueous phase comprising purified cobalt ;

d) purifying the aqueous phase comprising purified cobalt to produce a further aqueous phase comprising purified cobalt;

e) recovering cobalt from the further aqueous phase; and

f) recovering nickel from the aqueous phase comprising purified nickel.

6. The process of claim 5, wherein step b) comprises:

a) (i) co-extracting both cobalt and magnesium in the aqueous raffinate from step a) into the organic phase; (ii) selectively scrubbing any co-extracted nickel from the organic phase with a scrub solution of sulphuric acid and/or cobalt sulphate at a relatively high equilibrium pH range to obtain the organic phase with nickel removed and a nickel rich scrub liquor (aqueous phase) which is recycled to step (i); (iii) further selectively scrubbing magnesium from the organic phase with a scrub solution of sulphuric acid and/or cobalt sulphate at a relatively low equilibrium pH range to obtain the organic phase with purified cobalt and a magnesium rich scrub liquor (aqueous phase); (iv) re-extracting any co-scrubbed cobalt in the magnesium rich scrub liquor (aqueous phase) with a minor portion of the organic phase to obtain a minor portion of cobalt loaded organic phase which is merged into the main portion of the organic phase in step (iii); and (v) stripping the organic phase from step (iii) to generate aqueous phase comprising purified cobalt ; or

b) (i) selectively extracting cobalt in the aqueous raffinate from step a) into the organic phase; (ii) scrubbing both co-extracted nickel and magnesium in the organic phase with a scrub solution of sulphuric acid and/or cobalt sulphate to obtain the organic phase with purified cobalt and a nickel and magnesium rich scrub liquor (aqueous phase) which is recycled to step (i); (iii) stripping cobalt from the purified organic phase from step (ii) with an acid to obtain aqueous phase comprising purified cobalt (strip liquor); (iv) selectively extracting the magnesium from step (i) raffinate with a portion of the organic solution to obtain aqueous phase comprising purified nickel (the final raffinate) and magnesium rich organic phase; (v) scrubbing any co-extracted nickel in the organic phase with a scrub solution of sulphuric acid to obtain a scrub liquor comprising purified nickel (aqueous phase) which is recycled to step (iv); and (vi) stripping the magnesium enriched organic to obtain aqueous phase comprising purified magnesium for recovery of magnesium by-product.

7. The process of any one of claims 5 or 6, wherein the organophosphoric acid extractant has the formula $(RO)_2PO_2H$, wherein each R group, which may be the same or different, is selected from optionally substituted branched, straight chained or cyclic alkyl, alkenyl or alkynyl groups.

8. The process of claim 7, wherein the organophosphoric acid is di-2-ethylhexyl phosphoric acid, or an organophosphoric acid having extraction characteristics similar to or the same as di-2-ethylhexyl phosphoric acid.

9. The process of any one of claims 5 to 8, wherein the cobalt selective extractant is an organophosphinic acid having the formula R_2PO_2H, wherein each R group, which may be the same or different, is selected from optionally substituted branched, straight chained or cyclic alkyl, alkenyl or alkynyl groups.

10. The process of claim 9, wherein the organophosphinic acid is di-2,4,4-trimethylpentyl phosphinic acid (bis(2,4,4-trimethylpentyl) phosphinic acid), or an organophosphinic acid having extraction characteristics similar to or the same as di-2,4,4-trimethylpentyl phosphinic acid.

11. The process of any one of claims 5 to 10, wherein the hydrocarbon diluent is an aliphatic or aromatic hydrocarbon solvent, or a mixture thereof.

12. The process of claim 11, wherein the hydrocarbon diluent is kerosene.

13. The process of any one of claims 6 to 12, wherein step a. and/or step b. is carried out in the presence of a phase modifier or a combination of phase modifiers present in any of the hydrocarbon diluents.

14. The process of claim 13, wherein the phase modifier is selected from one or more of the group consisting of isodecanol, isotridecanol, 2-ethylhexanol and tri-n-butyl phosphate.

15. The process of any one of claims 5 to 14, wherein step c) of purifying the aqueous phase comprising purified cobalt comprises removing at least some of any copper from the aqueous phase comprising purified cobalt.

16. The process of claim 15, wherein the step of removing at least some of any copper from the aqueous phase comprising purified cobalt comprises contacting the aqueous phase comprising purified cobalt with an iminodiacetic resin under conditions to bind copper and separating the copper loaded resin from the aqueous phase.

17. The process of any one of claims 5 to 16, wherein the step c) of purifying the aqueous phase comprising purified cobalt comprises removing at least some of any zinc from the aqueous phase comprising purified cobalt.

18. The process of claim 17, wherein the step of removing at least some of any zinc from the aqueous phase comprising purified cobalt comprises contacting the organic phase comprising purified cobalt with a D2EHPA impregnated resin under conditions to bind zinc and separating the zinc loaded resin from the aqueous phase.

19. The process of any one of claims 5 to 18, wherein the step c) of purifying the aqueous phase comprising purified cobalt comprises removing at least some of any manganese from the aqueous phase comprising purified cobalt.

20. The process of claim 19, wherein the step of removing at least some of any manganese from the aqueous phase comprising purified cobalt comprises contacting the aqueous phase comprising purified cobalt with an oxidant under conditions to oxidise any manganese(II) to higher oxidation state manganese(III/IV) and separating the manganese(III/IV) from the aqueous phase.

21. The process of claim 20, wherein the oxidant is selected from the group consisting of oxygen (air), ozone, a mixture of SO_2/O_2(air) at a ratio functioning as an oxidant, peroxymonosulfuric acid (Caro's acid), and peroxydisulfuric acid.

22. The process of any one of claims 5 to 21, wherein the step c) of purifying the aqueous phase comprising purified cobalt comprises removing one of one or more of zinc, calcium, manganese, copper, cadmium, lead or other metal impurities in the aqueous phase comprising purified cobalt by contacting it with an organophosphoric acid extractant in a hydrocarbon diluent under solvent extraction conditions and separating the organic and aqueous phases to produce a further aqueous phase comprising purified cobalt.

23. The process of claim 22, wherein the organophosphoric acid extractant has the formula $(RO)_2PO_2H$, wherein each R group, which may be the same or different, is selected from optionally substituted branched, straight chained or cyclic alkyl, alkenyl or alkynyl groups.

24. The process of claim 23, wherein the organophosphoric acid is di-2-ethylhexyl phosphoric acid, or an organophosphoric acid having extraction characteristics similar to or the same as di-2-ethylhexyl phosphoric acid.

25. The process of any one of claims 5 to 24, wherein the step of recovering cobalt from the aqueous phase comprising purified cobalt comprises crystallising cobalt sulphate from the aqueous phase comprising purified cobalt.

26. The process of any one of claims 5 to 25, wherein the step of recovering nickel from the aqueous phase comprising purified nickel comprises crystallising nickel sulphate from the aqueous phase comprising purified nickel.

27. The process of any one of claims 5 to 26, further comprising stripping at least some of any one or more of zinc, calcium, manganese and copper present in the organic phase obtained in step a) by either (a) treating the organic phase with sulfuric acid through control of the calcium concentration below its saturation to avoid gypsum formation; or (b) treating the organic phase with hydrochloric acid, if the calcium concentration in the system is relatively high with a risk of forming gypsum.

28. The process of claim 27, further comprising periodically bleeding treatment of the organic phase in step a) by contacting the organic phase with a solution of hydrochloric acid to remove some of any one or more of iron, aluminium and other strongly binding metal ions from the organic phase.

29. The process of any one of claims 5 to 28, further comprising preloading one or more organic solution used in the process with sulphate, carbonate, oxide or hydroxide salts of nickel, cobalt and/or magnesium.

30. The process of claim 29, comprising preloading one or more organic solution used in the process with nickel sulphate.

31. The process of any one of claims 29 to 30, further comprising treating with a base reagent selected from the group consisting of nickel hydroxide, sodium hydroxide or carbonate, ammonia, ammonium hydroxide or carbonate, and magnesium oxide / hydroxide or carbonate for neutralisation or pH control in the preloading.

32. The process of any one of claims 29 to 30, comprising pre-neutralising the organic solution with a base reagent to produce the pre-neutralised organic for preloading of nickel by exchange.

33. The process of claim 32, wherein the base reagent is selected from the group consisting of sodium hydroxide or carbonate, ammonia, and ammonium hydroxide or carbonate.

34. The process of any one of claims 30 to 33, further comprising washing the organic solutions preloaded with nickel sulphate with a scrub solution containing water and/or sulfuric acid and/or nickel sulphate to remove entrained and extracted sodium or ammonium ions.

35. The process of any one of claims 5 to 34, further comprising directly neutralising acid produced during the solvent exchange with ammonia, ammonium hydroxide or carbonate under conditions to avoid formation of nickel ammonium double salts and subsequently thermally decomposing the ammonium sulphate component in the hydrated nickel sulphate to remove the ammonium component.

36. The process of any one of claims 5 to 35, wherein any extraction step, any scrubbing step and any stripping step in solvent extraction, and any loading step, any washing step and any elution step in ion exchange, comprise one or more stages operating in counter-current mode or concurrent mode or the combination of the two modes.

37. High purity nickel sulphate obtained using the process of any one of claims 5 to 36.

38. High purity cobalt sulphate obtained using the process of any one of claims 5 to 36.

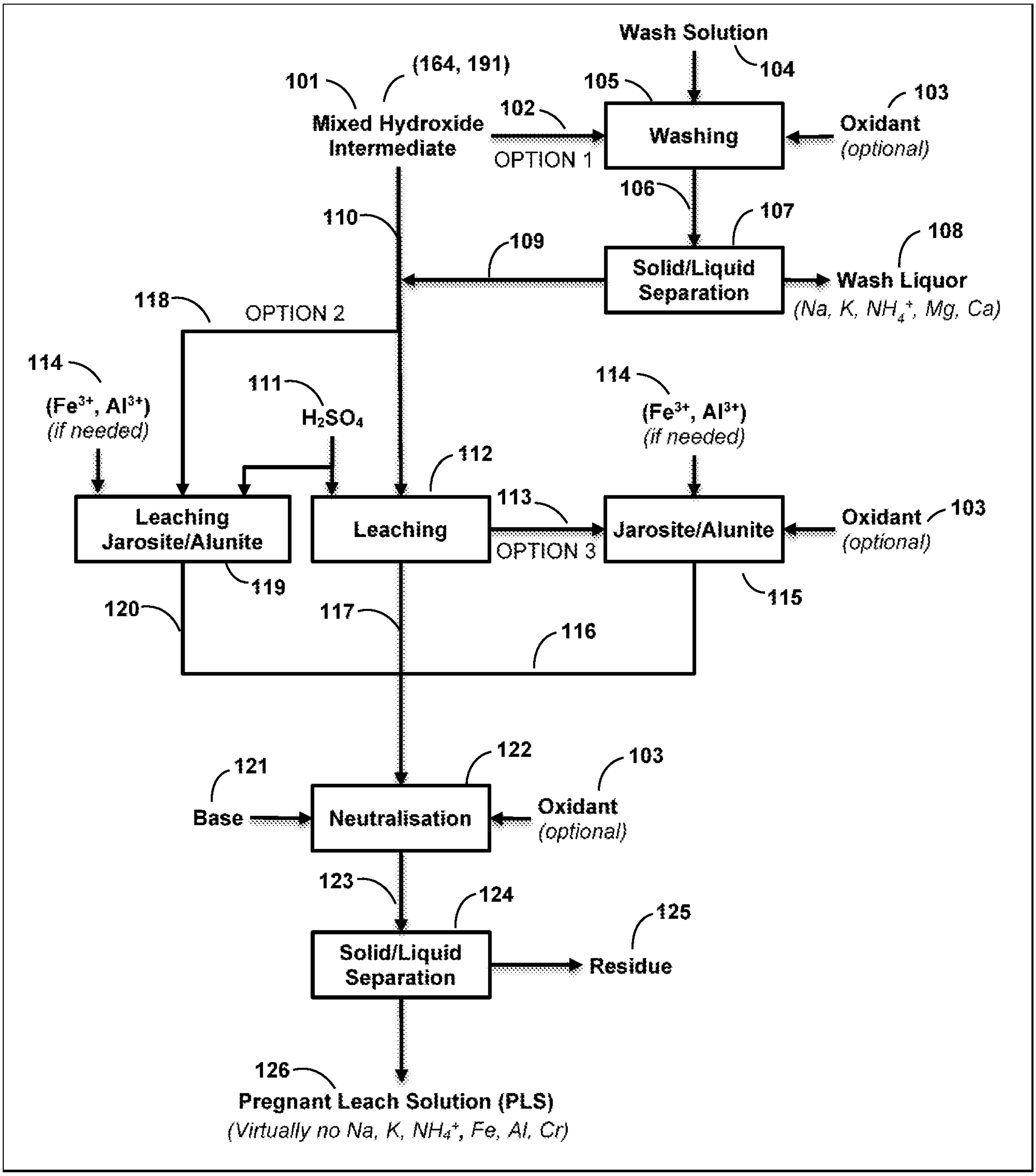

Wash Solution
104
101
(164, 191)
105
103
Mixed Hydroxide Intermediate
102
Washing
Oxidant
(optional)
OPTION 1
106
110
107
108
109
Solid/Liquid Separation
Wash Liquor
(Na, K, NH4+, Mg, Ca)
118
OPTION 2
114
111
114
(Fe3+, Al3+)
(if needed)
H2SO4
(Fe3+, Al3+)
(if needed)
112
113
103
Leaching Jarosite/Alunite
Leaching
Jarosite/Alunite
Oxidant
(optional)
OPTION 3
119
115
120
117
116
122
103
121
Base
Neutralisation
Oxidant
(optional)
123
124
125
Solid/Liquid Separation
Residue
126
Pregnant Leach Solution (PLS)
(Virtually no Na, K, NH4+, Fe, Al, Cr)

FIGURE 1

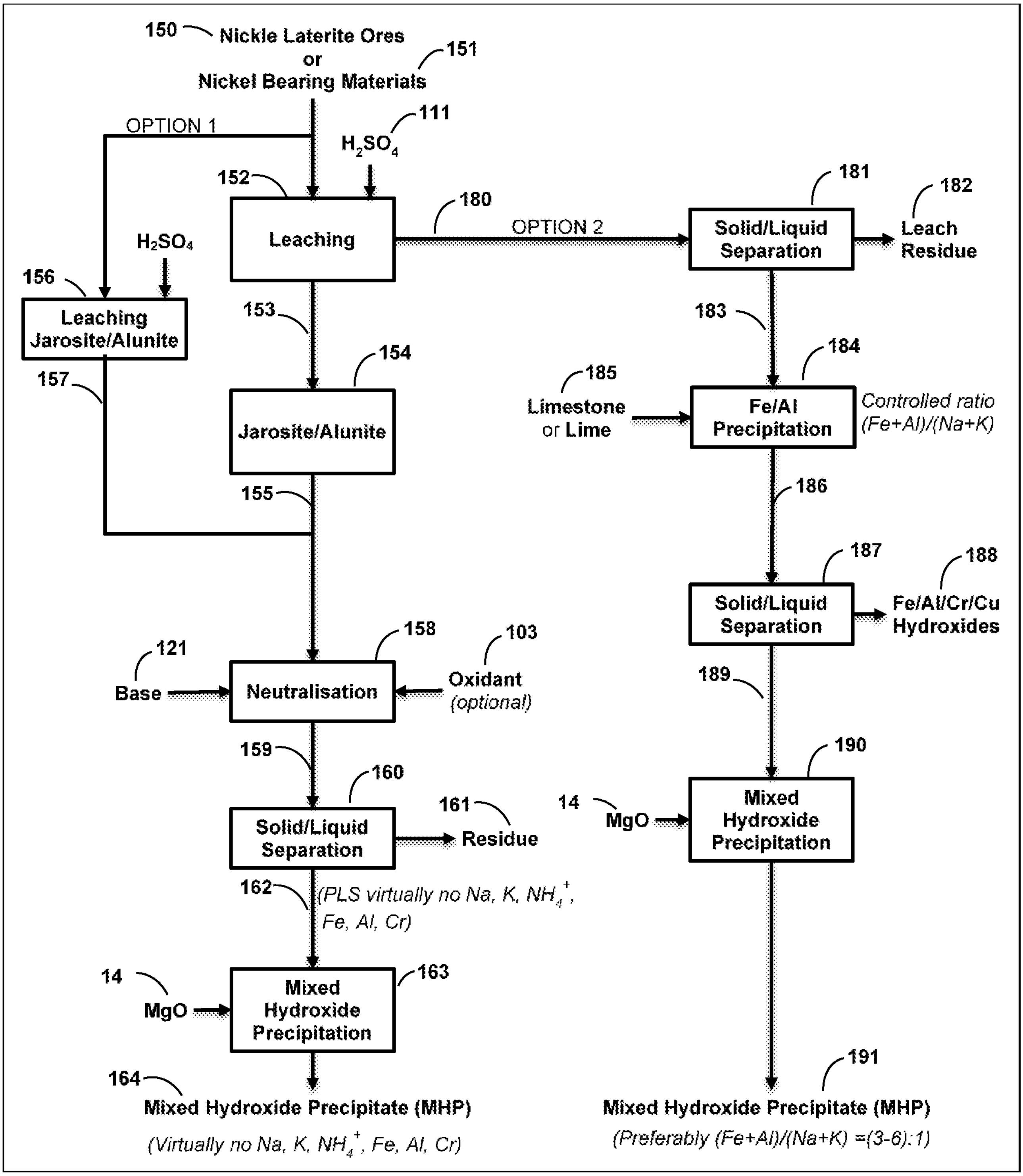

150
Nickle Laterite Ores
or
Nickel Bearing Materials
151
OPTION 1
111
H_2SO_4
152
Leaching
180
OPTION 2
181
Solid/Liquid Separation
182
Leach Residue
H_2SO_4
156
Leaching Jarosite/Alunite
153
154
Jarosite/Alunite
157
183
184
185
Limestone or Lime
Fe/Al Precipitation
Controlled ratio (Fe+Al)/(Na+K)
155
186
187
188
Solid/Liquid Separation
Fe/Al/Cr/Cu Hydroxides
158
103
121
Base
Neutralisation
Oxidant (optional)
189
190
159
160
161
Solid/Liquid Separation
Residue
14
MgO
Mixed Hydroxide Precipitation
162
(PLS virtually no Na, K, NH_4^+, Fe, Al, Cr)
14
MgO
Mixed Hydroxide Precipitation
163
164
Mixed Hydroxide Precipitate (MHP)
(Virtually no Na, K, NH_4^+, Fe, Al, Cr)
191
Mixed Hydroxide Precipitate (MHP)
(Preferably (Fe+Al)/(Na+K) =(3-6):1)

FIGURE 2

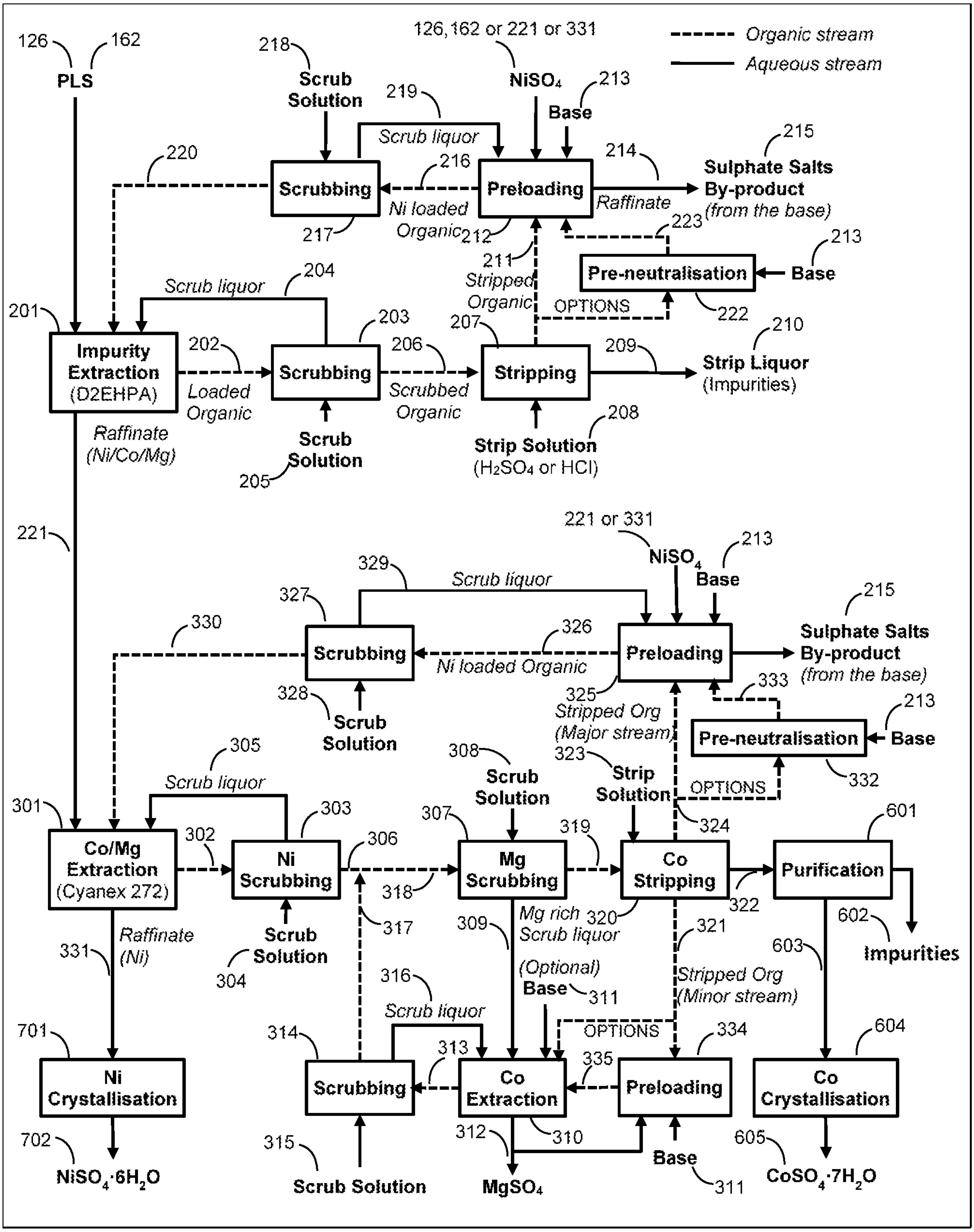

126
162
PLS
218
Scrub Solution
219
Scrub liquor
126,162 or 221 or 331
NiSO4
213
Base
Organic stream
Aqueous stream
220
216
Scrubbing
Preloading
214
215
Sulphate Salts By-product (from the base)
Raffinate
Ni loaded Organic
217
212
223
213
Base
211
Stripped Organic
Pre-neutralisation
222
OPTIONS
Scrub liquor
204
201
203
207
209
210
Impurity Extraction (D2EHPA)
202
Scrubbing
206
Stripping
Strip Liquor (Impurities)
Loaded Organic
Scrubbed Organic
208
Raffinate (Ni/Co/Mg)
Scrub Solution
Strip Solution (H2SO4 or HCl)
205
221
221 or 331
NiSO4
213
Base
329
Scrub liquor
327
330
326
Scrubbing
Preloading
215
Sulphate Salts By-product (from the base)
Ni loaded Organic
328
325
333
Scrub Solution
Stripped Org (Major stream)
213
Pre-neutralisation
Base
305
308
Scrub Solution
323
Strip Solution
332
Scrub liquor
OPTIONS
301
303
324
601
307
319
302
306
Co/Mg Extraction (Cyanex 272)
Ni Scrubbing
Mg Scrubbing
Co Stripping
Purification
318
322
317
309
Mg rich Scrub liquor
320
602
Raffinate (Ni)
321
603
331
Scrub Solution
Impurities
304
Stripped Org (Minor stream)
316
(Optional) Base
311
701
Scrub liquor
OPTIONS
334
604
314
313
335
Ni Crystallisation
Scrubbing
Co Extraction
Preloading
Co Crystallisation
312
310
605
702
315
Base
311
NiSO4·6H2O
Scrub Solution
MgSO4
CoSO4·7H2O

FIGURE 3

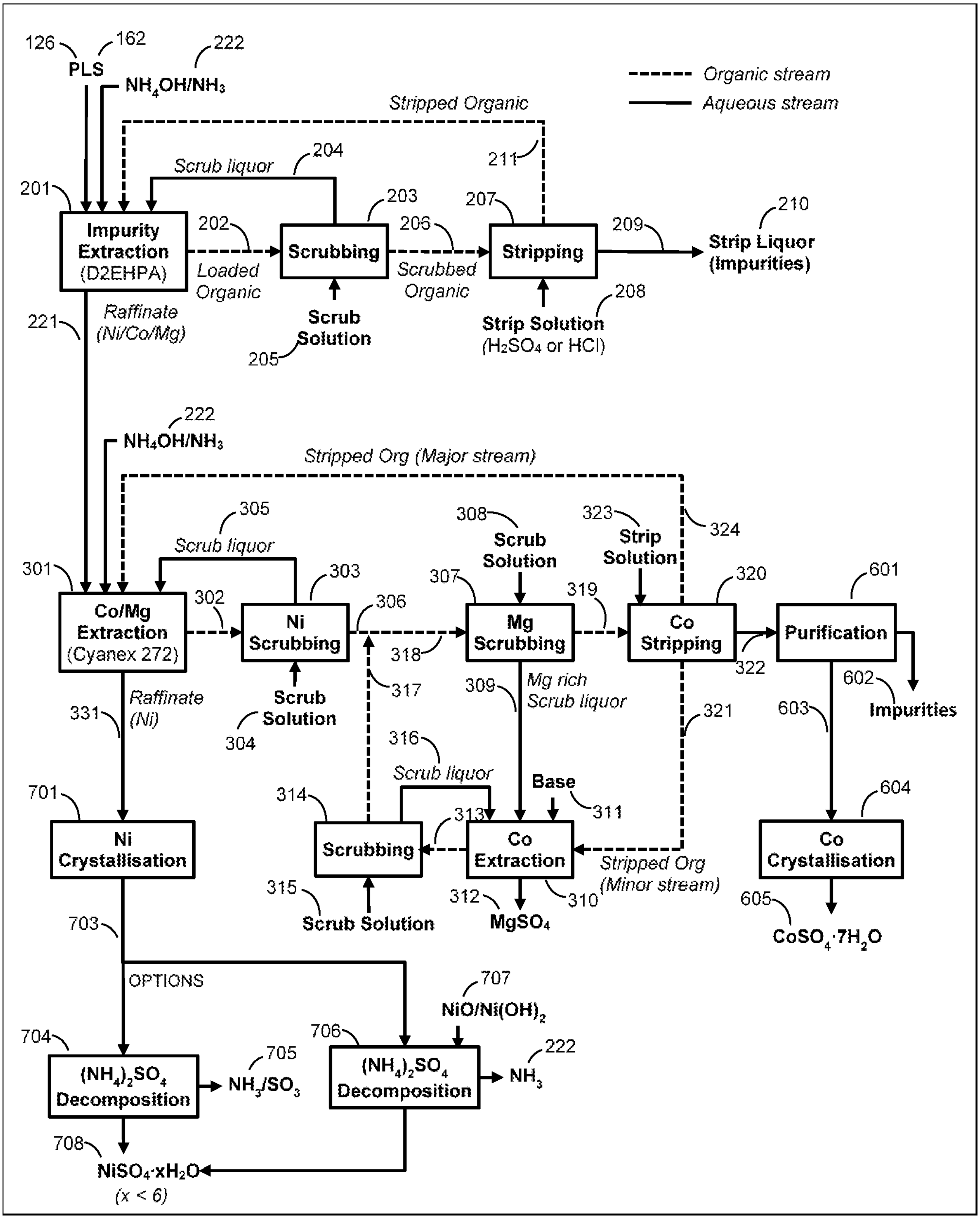

126
162
PLS
222
NH4OH/NH3
Organic stream
Aqueous stream
Stripped Organic
Scrub liquor
204
211
201
203
207
Impurity Extraction (D2EHPA)
202
Scrubbing
206
Stripping
209
210
Strip Liquor (Impurities)
Loaded Organic
Scrubbed Organic
221
Raffinate (Ni/Co/Mg)
Scrub Solution
205
208
Strip Solution (H2SO4 or HCl)
222
NH4OH/NH3
Stripped Org (Major stream)
305
Scrub liquor
308
Scrub Solution
323
Strip Solution
324
301
303
307
319
320
601
Co/Mg Extraction (Cyanex 272)
302
Ni Scrubbing
306
Mg Scrubbing
Co Stripping
Purification
318
322
317
Scrub Solution
304
331
Raffinate (Ni)
309
Mg rich Scrub liquor
321
602
Impurities
603
316
Scrub liquor
Base
311
701
314
313
604
Ni Crystallisation
Scrubbing
Co Extraction
Stripped Org (Minor stream)
Co Crystallisation
315
Scrub Solution
312
MgSO4
310
605
CoSO4·7H2O
703
OPTIONS
707
NiO/Ni(OH)2
704
706
705
222
(NH4)2SO4 Decomposition
NH3/SO3
(NH4)2SO4 Decomposition
NH3
708
NiSO4·xH2O
(x < 6)

FIGURE 4

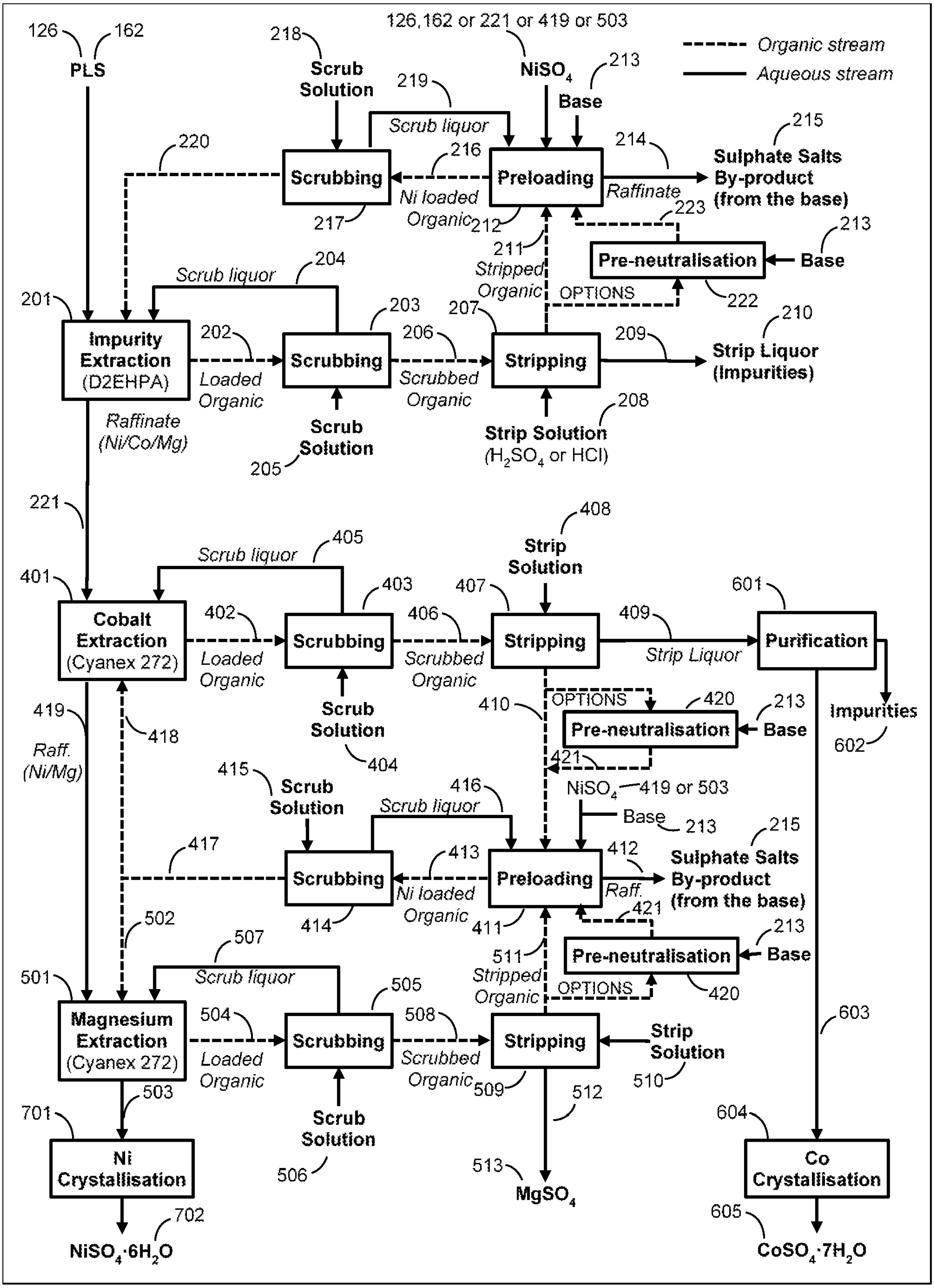

126
162
PLS
218
Scrub Solution
219
Scrub liquor
126,162 or 221 or 419 or 503
NiSO$_4$
213
Base
Organic stream
Aqueous stream
220
Scrubbing
216
Preloading
214
215
Sulphate Salts By-product (from the base)
Ni loaded Organic
Raffinate
217
212
223
211
Stripped Organic
Pre-neutralisation
213
Base
204
Scrub liquor
OPTIONS
222
201
203
207
210
Impurity Extraction (D2EHPA)
202
Scrubbing
206
Stripping
209
Strip Liquor (Impurities)
Loaded Organic
Scrubbed Organic
208
Raffinate (Ni/Co/Mg)
Scrub Solution
Strip Solution (H$_2$SO$_4$ or HCl)
205
221
408
Strip Solution
405
Scrub liquor
401
403
407
601
Cobalt Extraction (Cyanex 272)
402
Scrubbing
406
Stripping
409
Purification
Loaded Organic
Scrubbed Organic
Strip Liquor
419
410
OPTIONS
420
213
Impurities
418
Scrub Solution
Pre-neutralisation
Base
Raff. (Ni/Mg)
602
404
421
415
Scrub Solution
416
NiSO$_4$
419 or 503
Scrub liquor
Base
213
417
412
215
413
Sulphate Salts By-product (from the base)
Scrubbing
Preloading
Ni loaded Organic
Raff.
414
411
421
502
213
507
511
Pre-neutralisation
Base
Scrub liquor
Stripped Organic
505
OPTIONS
420
501
504
508
603
Magnesium Extraction (Cyanex 272)
Scrubbing
Stripping
Strip Solution
Loaded Organic
Scrubbed Organic
509
510
503
512
701
604
Scrub Solution
Ni Crystallisation
513
Co Crystallisation
506
MgSO$_4$
702
605
NiSO$_4$·6H$_2$O
CoSO$_4$·7H$_2$O

FIGURE 5

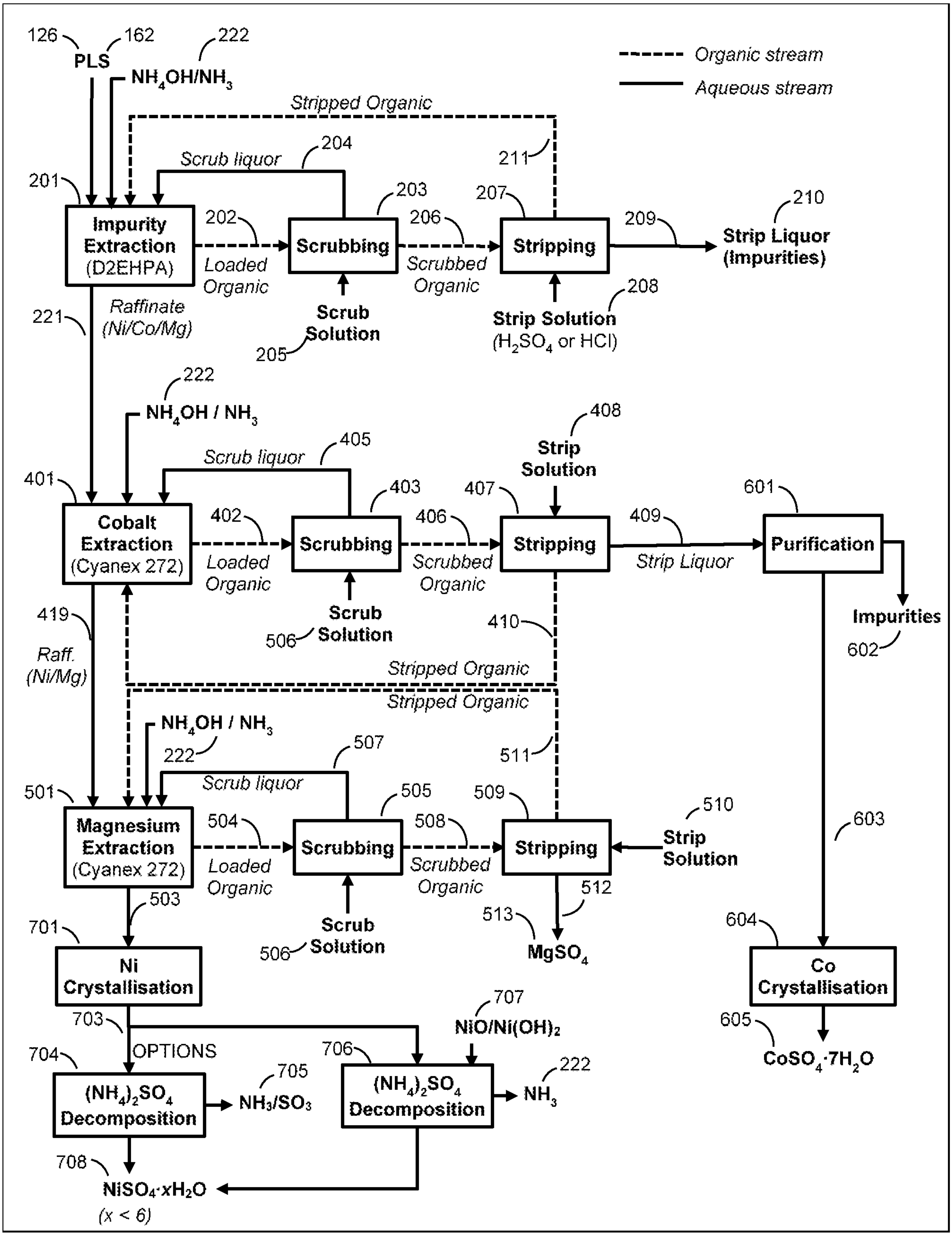

Organic stream
Aqueous stream
126
162
PLS
222
NH4OH/NH3
Stripped Organic
204
Scrub liquor
211
201
Impurity Extraction (D2EHPA)
202
Loaded Organic
203
Scrubbing
206
Scrubbed Organic
207
Stripping
209
210
Strip Liquor (Impurities)
221
Raffinate (Ni/Co/Mg)
Scrub Solution
205
208
Strip Solution (H2SO4 or HCl)
222
NH4OH / NH3
408
Strip Solution
405
Scrub liquor
401
Cobalt Extraction (Cyanex 272)
402
Loaded Organic
403
Scrubbing
406
Scrubbed Organic
407
Stripping
409
Strip Liquor
601
Purification
Impurities
602
419
Raff. (Ni/Mg)
Scrub Solution
506
410
Stripped Organic
Stripped Organic
NH4OH / NH3
222
507
Scrub liquor
511
501
Magnesium Extraction (Cyanex 272)
504
Loaded Organic
505
Scrubbing
508
Scrubbed Organic
509
Stripping
510
Strip Solution
603
503
512
513
MgSO4
Scrub Solution
506
701
Ni Crystallisation
604
Co Crystallisation
605
CoSO4·7H2O
703
OPTIONS
707
NiO/Ni(OH)2
704
(NH4)2SO4 Decomposition
705
NH3/SO3
706
(NH4)2SO4 Decomposition
222
NH3
708
NiSO4·xH2O
(x < 6)

FIGURE 6

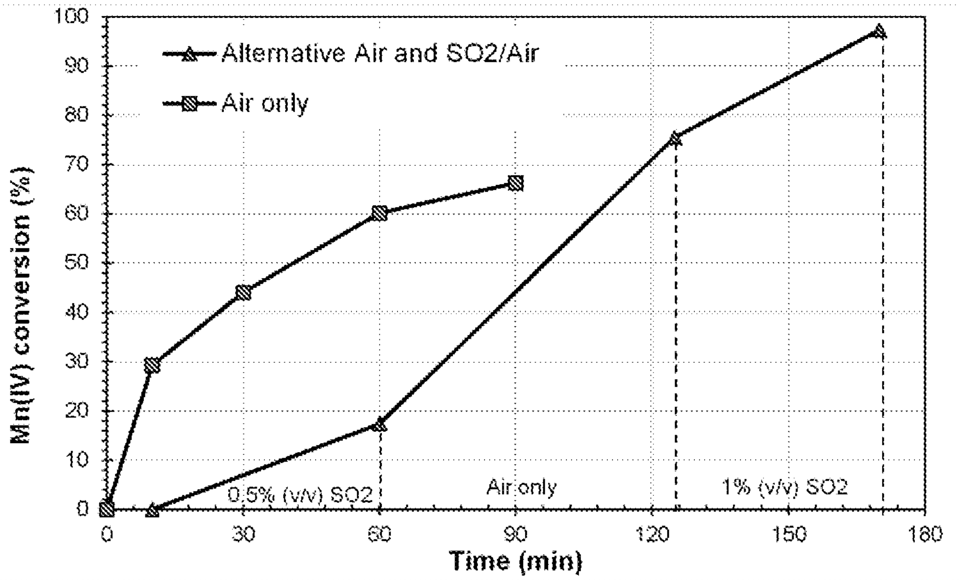
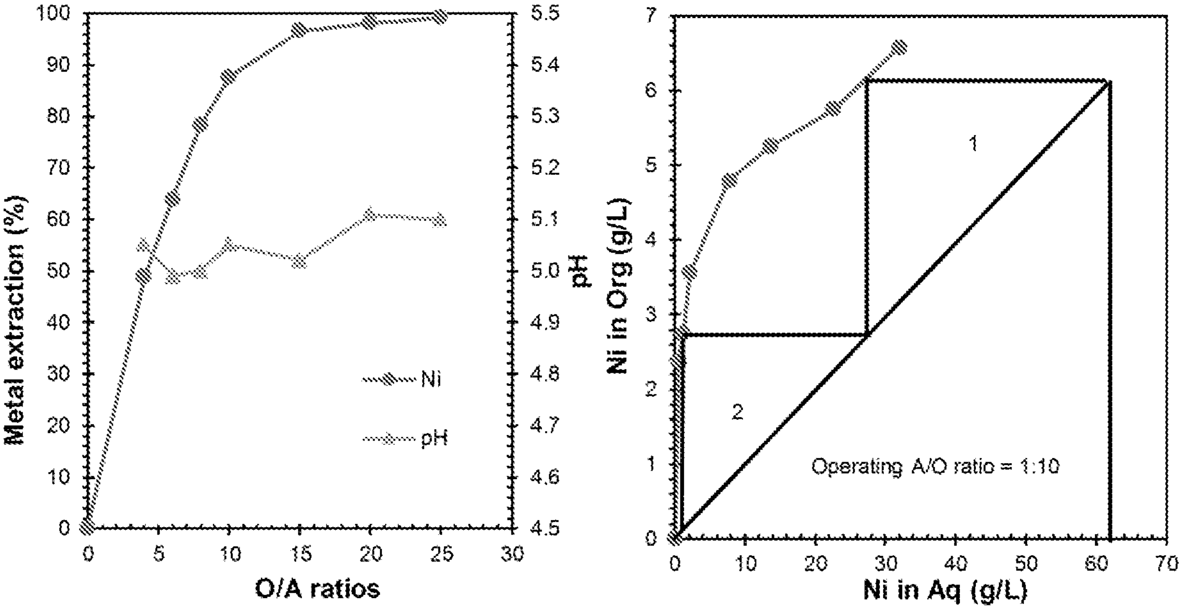


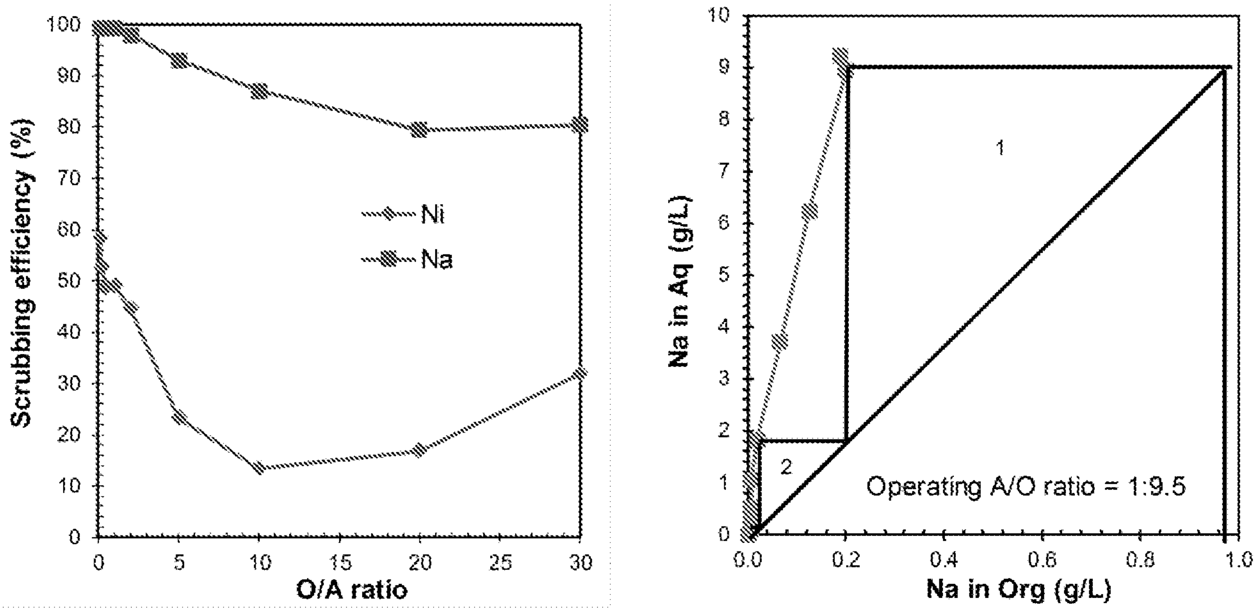
FIGURE 7



(a)

(b)

FIGURE 8



(a) (b)

FIGURE 9

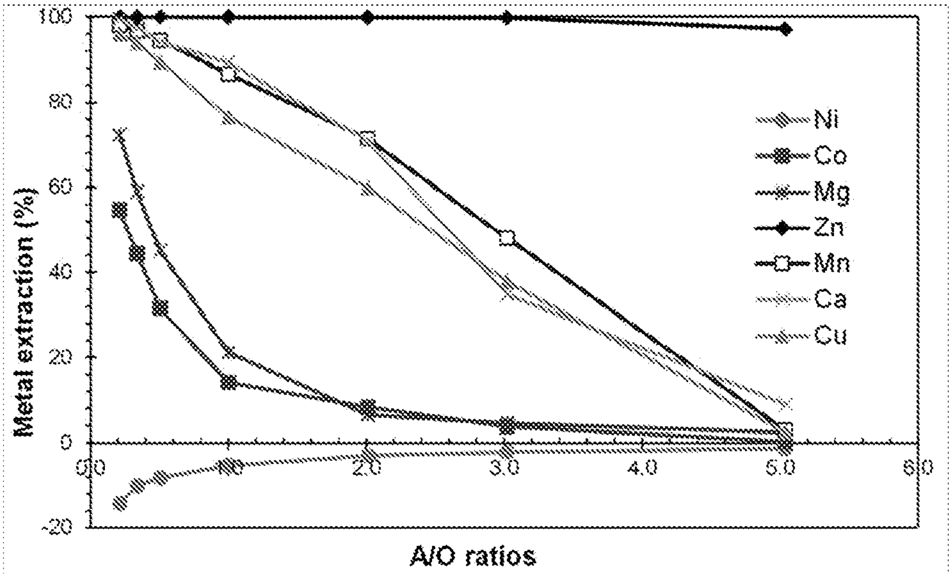
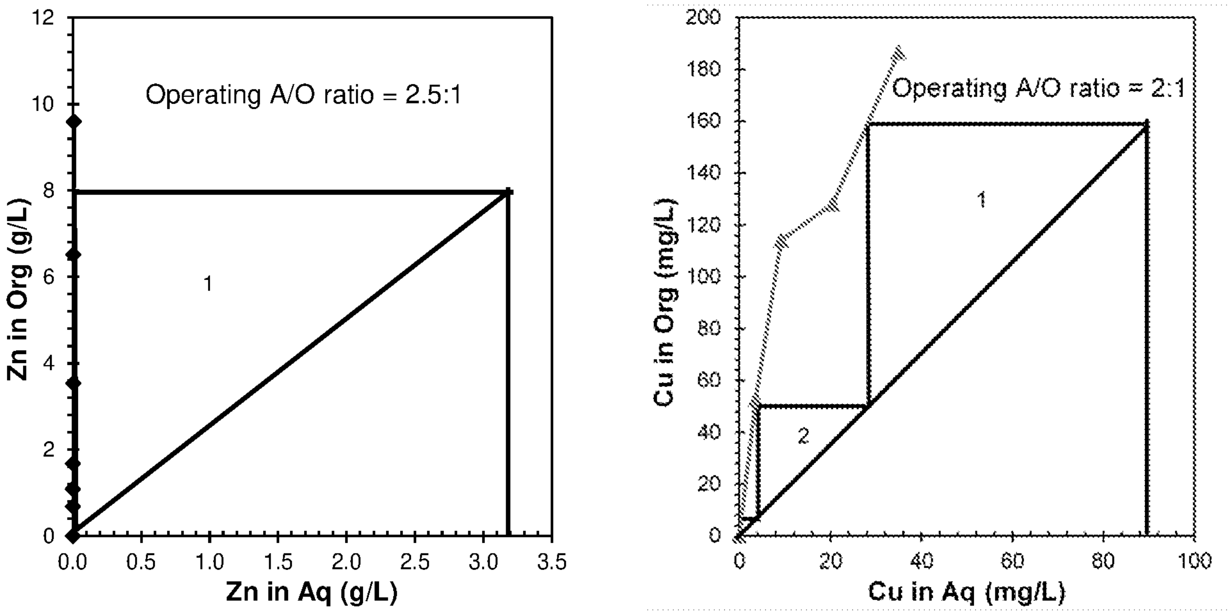
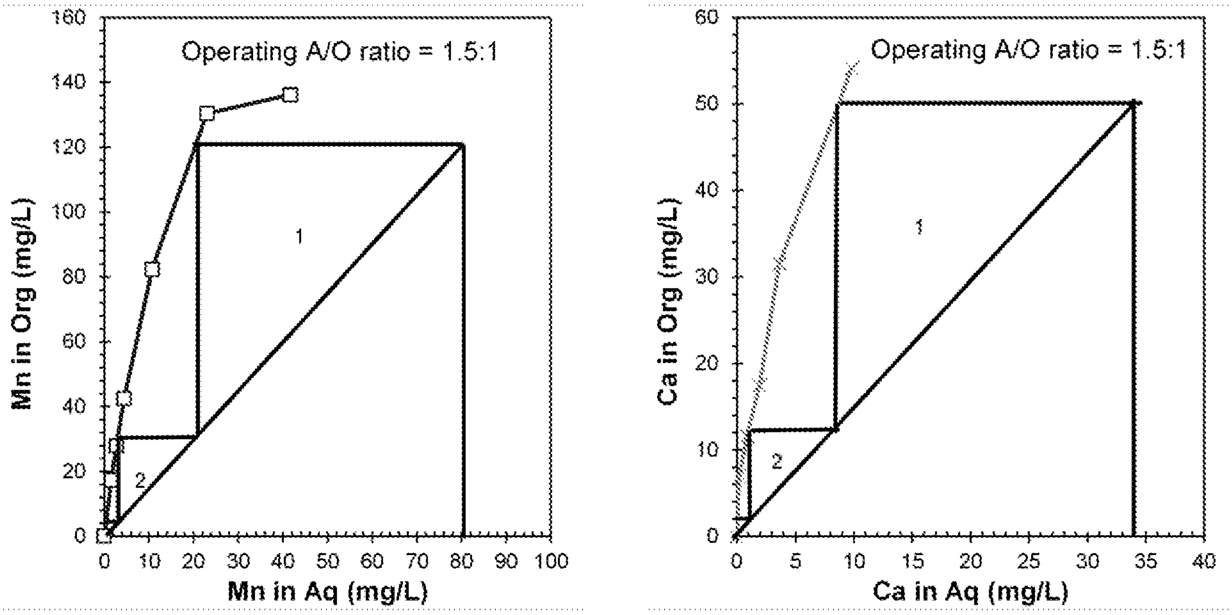


FIGURE 10



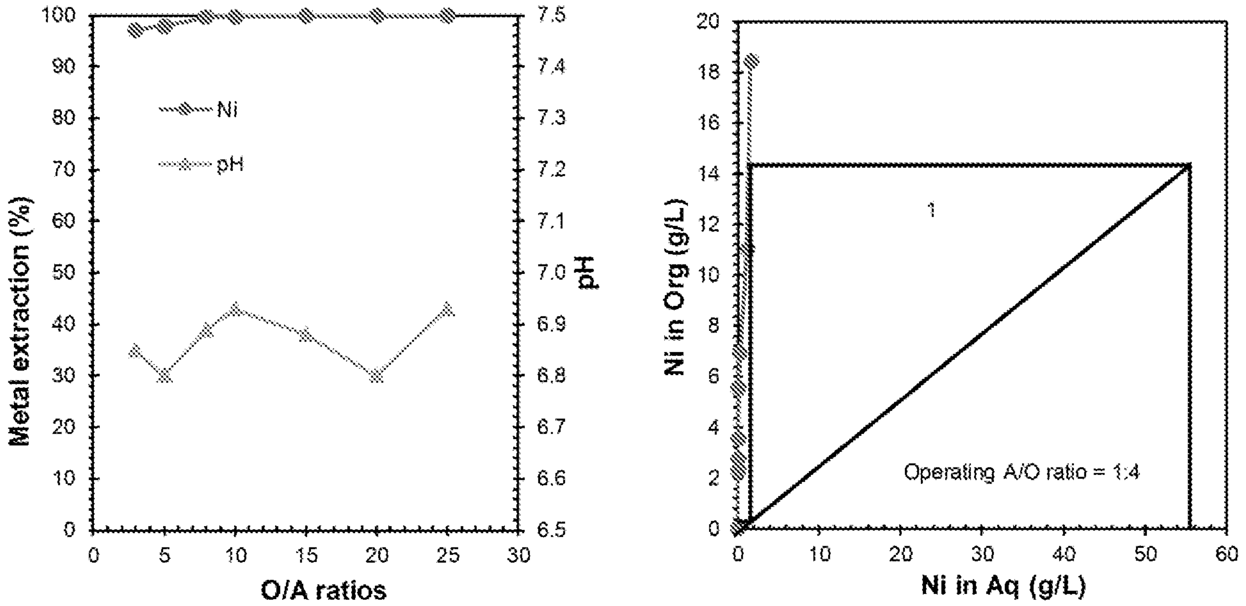
(a) (b)

FIGURE 11



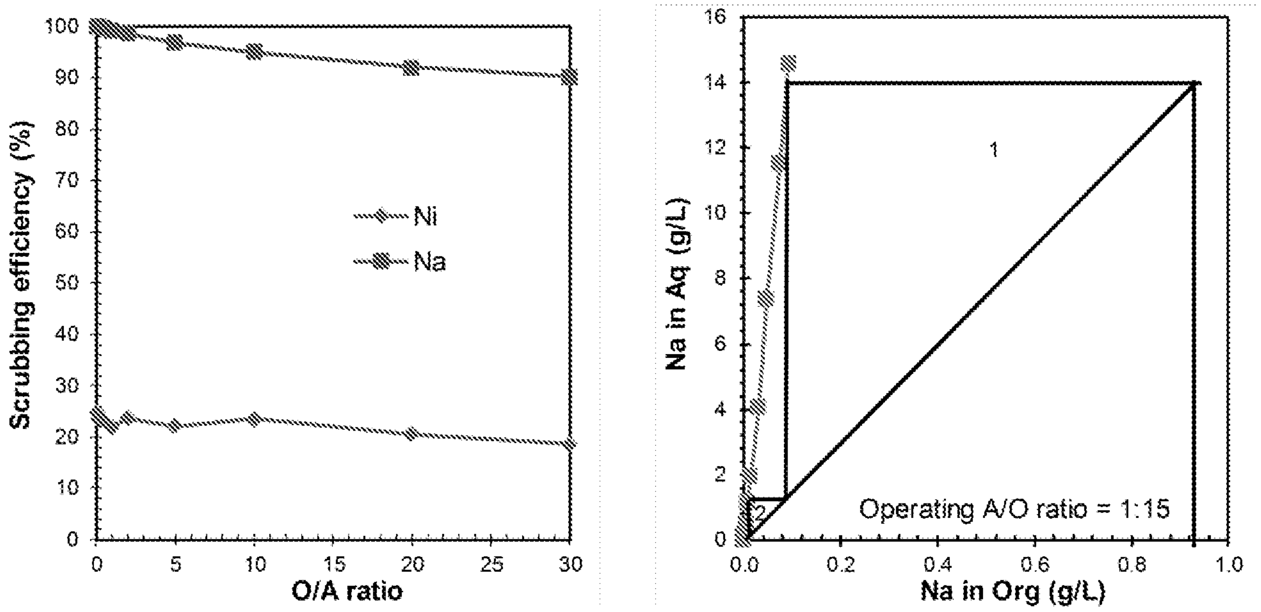
(a) (b)

FIGURE 12



(a) (b)

FIGURE 13



(a) (b)

FIGURE 14

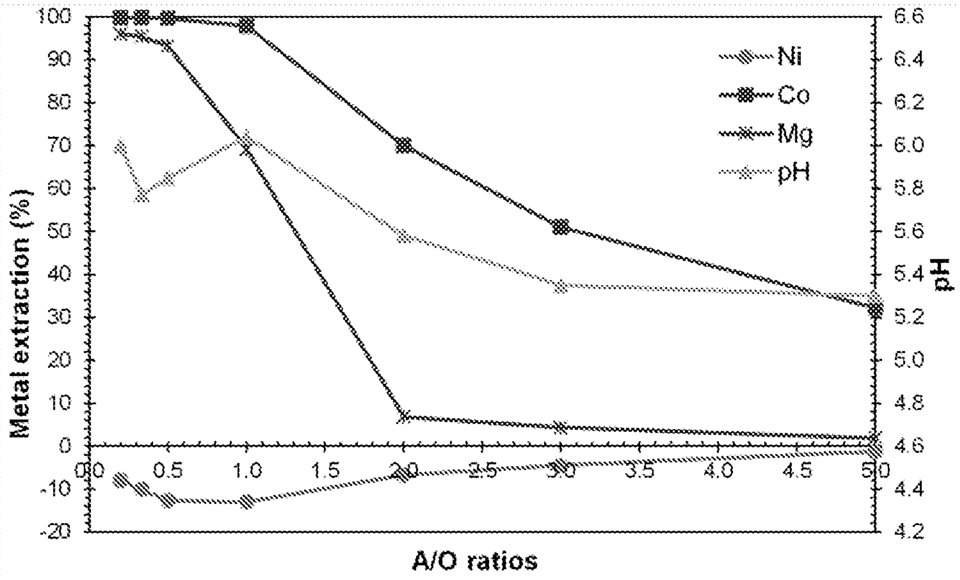
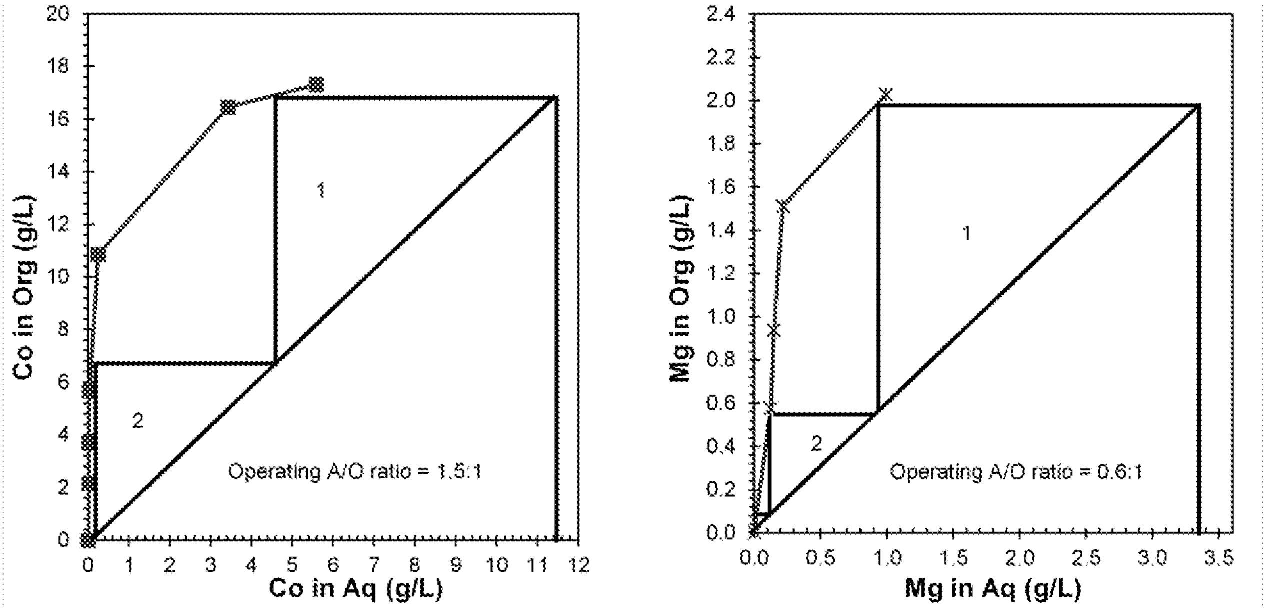
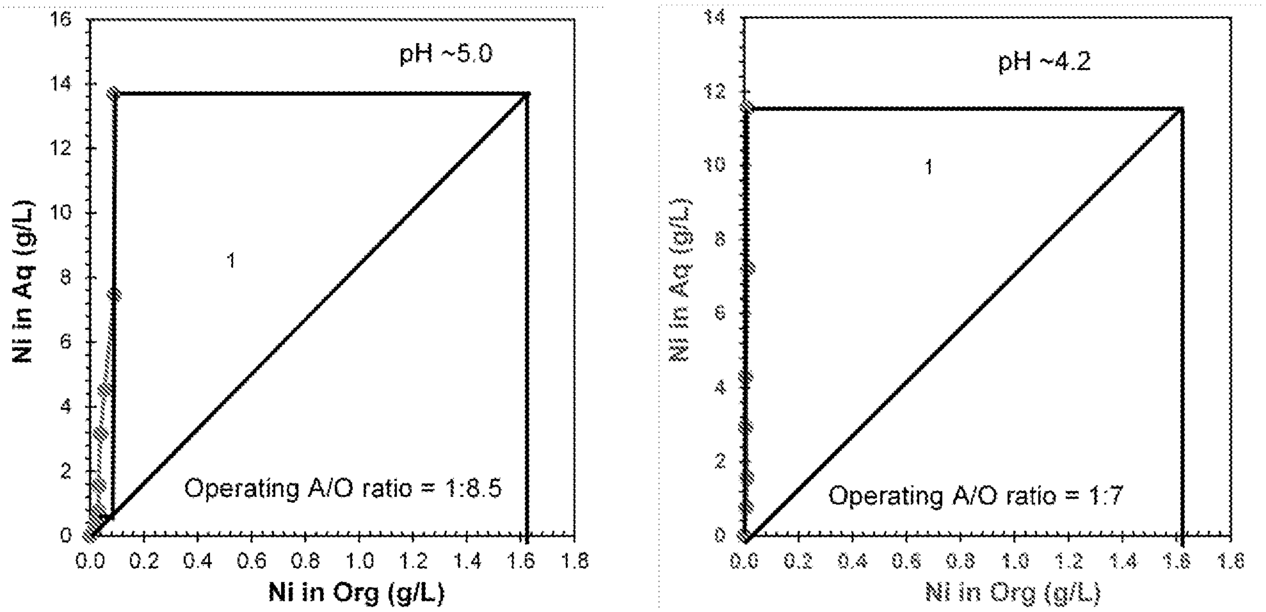


FIGURE 15



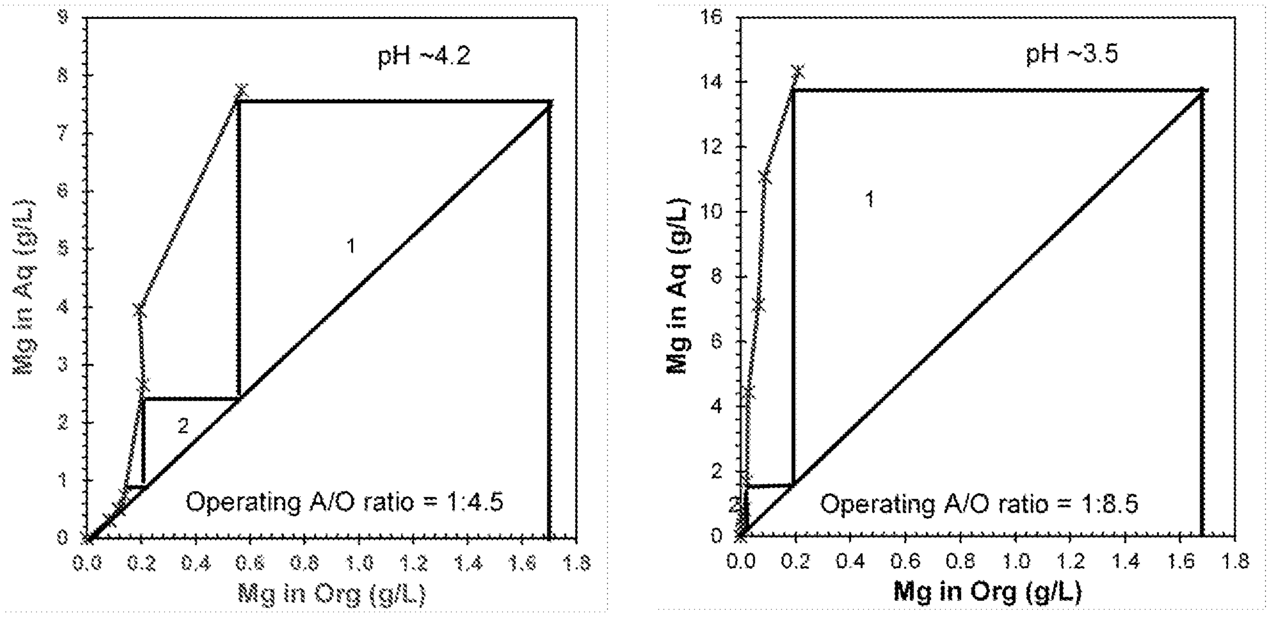
(a) (b)

FIGURE 16



(a) (b)

FIGURE 17



(a) (b)

FIGURE 18

A. CLASSIFICATION OF SUBJECT MATTER

C22B 23/00 (2006.01) C22B 7/04 (2006.01) C22B 3/38 (2006.01) C22B 5/18 (2006.01) B01D 11/04 (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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)

Google Patents, Google, Espacenet and PATENW search using keywords: SEPARATION, NICKEL, COBALT, CRUDE MATERIAL, JAROSITE, AL SALT, FE SALT, PRECIPITATION, REDUCTION, INCRESE pH, PLS, EXTRACTANT, ORGANOPHOSPHORIC ACID, ORGANOPHOSPHONIC, CYANEX, HIGH-PURITY and like terms. Relevant results viewed.

IPC and CPC symbols: C22B23/00, C22B23/04, C22B23/0407, C22B23/0453, C22B23/0476, C22B23/0484, C22B7/04, C22B7/006, C22B3/20, C22B3/26, C22B3/38, C22B3/3846, C22B3/40, C22B3/44, Y02P10/00, Y02P10/20, Y02P10/25, C22B1/00, B01D11/04, C22B5/18. Relevant results viewed.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

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

Date of the actual completion of the international search 30 June 2022	Date of mailing of the international search report 30 June 2022
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	**Authorised officer** Raihan Rumman AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262832443

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	US 5378262 A (MIHAYLOV ET AL.) 03 January 1995	
X	Title, Abstract, Field of Invention, Column 5 lines 28-54, Claims 3, 16, 18, 33, Columns 1-2, Column 5 line 29, column 6 line 14, Examples 1-6, Claim 1, 8, 23, 40, Column 5 lines 14-27, Column 4 lines 34-60, Table 2.	1-4
Y	Title, Abstract, Field of Invention, Column 5 lines 28-54, Claims 3, 16, 18, 33, Columns 1-2, Column 5 line 29, column 6 line 14, Examples 1-6, Claim 1, 8, 23, 40, Column 5 lines 14-27, Column 4 lines 34-60, Table 2.	5-38
Y	WO 2002022896 A1 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 21 March 2002 Whole document. See report.	5-38
A	WO 2013/120131 A1 (BHP BILLITON SSM DEV PTY LTD [AU]) 22 August 2013 Claim 6	1
A	CN 109234526 A (CHINA ENFI ENG CORP) 18 January 2019, English translation retrieved from Google Patents. Abstract, Claims, Paragraphs [0002], [0004], [0012], [0015], [0026], [0044], [0048], [0050], [0054].	1-4
A	EP 3670686 A1 (A.C.N. 630 589 507 PTY LTD.) 24 June 2020 Whole document.	28-33, 35
A	Devi et al., "Separation and recovery of cobalt (II) and nickel (II) from sulphate solutions using sodium salts of D2EHPA, PC 88A and Cyanex 272." Hydrometallurgy, Vol 49.1-2 (1998): Pages 47-61 Whole document.	5-38
A	Park, K.H, et al., "Process for cobalt separation and recovery in the presence of nickel from sulphate solutions by Cyanex 272." Metals and Materials International, Vol 12.5 (2006): Pages 441-446. Whole document.	5-38
A	Sahu, S. K., et al., "Recovery of copper, nickel and cobalt from the leach liquor of a sulphide concentrate by solvent extraction." Minerals engineering, Vol 17.7-8 (2004): Pages 949-951. Whole document.	1-38
A	Reddy, B. R, et al., "Separation and recovery of cadmium (II), cobalt (II) and nickel (II) from sulphate leach liquors of spent Ni–Cd batteries using phosphorus based extractants." Separation and Purification Technology, Vol 50.2 (2006): pages 161-166. Whole document.	1-38
A	CN 109097570 B (Changchun Institute of Applied Chemistry, Chinese Academy of Sciences) 19 June 2020, English translation retrieved from Google Patents. Whole document.	1-38
A	US 4600435 A (AMAX INC [US]) 15 July 1986 Whole document.	1-38
A	JP 2014162982 A (JX NIPPON MINING & METALS CORP) 08 September 2014, English translation retrieved from Google Patents. Whole document.	1-38
	CN 112342393 A (HUNAN BRUNP RECYCLING TECH CO LTD et al.) 09 February 2021, English translation retrieved from Google Patents.	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2022/050459

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Whole document.	1-38
A	CN 108517409 B (Changsha Research Institute of Mining and Metallurgy Co., Ltd.) 29 November 2019, English translation retrieved from Google Patents. Whole document.	1-38

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2022/050459**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
US 5378262 A	03 January 1995	US 5378262 A	03 Jan 1995
		AU 1496695 A	28 Sep 1995
		AU 687981 B2	05 Mar 1998
		BR 9501135 A	24 Oct 1995
		CA 2145054 A1	23 Sep 1995
		CN 1109913 A	11 Oct 1995
		CO 4440445 A1	07 May 1997
		FR 2717826 A1	29 Sep 1995
		FR 2717826 B1	14 Mar 1997
		GT 199500013 A	21 Mar 1995
		JP H0835023 A	06 Feb 1996
		JP 2760956 B2	04 Jun 1998
		OA 10135 A	18 Dec 1996
		PH 31603 A	03 Nov 1998
		US 5447552 A	05 Sep 1995
		ZA 952338 B	15 Dec 1995
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		AU 9346801 A	26 Mar 2002
		AU 9346901 A	26 Mar 2002
		AU 9347001 A	26 Mar 2002
		CA 2421970 A1	21 Mar 2002
		EP 1330555 A1	30 Jul 2003
		US 2004050212 A1	18 Mar 2004
		WO 0222897 A1	21 Mar 2002
		WO 0222898 A1	21 Mar 2002
WO 2013/120131 A1	22 August 2013	WO 2013120131 A1	22 Aug 2013
		AU 2013220925 A1	02 Oct 2014
		AU 2013220925 B2	06 Apr 2017
		CN 104379779 A	25 Feb 2015
		CN 104379779 B	17 Apr 2018
		CO 7141436 A2	12 Dec 2014
		EP 2814992 A1	24 Dec 2014
		US 2015000466 A1	01 Jan 2015
		US 9481919 B2	01 Nov 2016

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

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2022/050459**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
CN 109234526 A	18 January 2019	CN 109234526 A	18 Jan 2019
		CN 109234526 B	03 Nov 2020
EP 3670686 A1	24 June 2020	EP 3670686 A1	24 Jun 2020
		AU 2019400942 A1	24 Jun 2021
		CA 3122118 A1	25 Jun 2020
		CL 2021001648 A1	25 Feb 2022
		CN 113423849 A	21 Sep 2021
		EA 202191664 A1	22 Oct 2021
		EP 3899071 A1	27 Oct 2021
		JP 2022513445 A	08 Feb 2022
		KR 20210113605 A	16 Sep 2021
		SG 11202106070R A	29 Jul 2021
		US 2022017989 A1	20 Jan 2022
		WO 2020124130 A1	25 Jun 2020
CN 109097570 B	19 June 2020	CN 109097570 A	28 Dec 2018
		CN 109097570 B	19 Jun 2020
US 4600435 A	15 July 1986	US 4600435 A	15 Jul 1986
JP 2014162982 A	08 September 2014	JP 2014162982 A	08 Sep 2014
		JP 5706457 B2	22 Apr 2015
CN 112342393 A	09 February 2021	CN 112342393 A	09 Feb 2021
		WO 2022089203 A1	05 May 2022
CN 108517409 B	29 November 2019	CN 108517409 A	11 Sep 2018
		CN 108517409 B	29 Nov 2019

End of Annex

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