

ENVIRONMENTAL EVALUATION OF MAKING NICKEL SULPHATE

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ABSTRACT

Nickel sulphate, conventionally made from pure nickel metal, is a major input in the manufacture of lithium ion batteries. This paper presents a study of the manufacture of nickel sulphate for the manufacture of lithium ion batteries via a number of routes, examining the environmental aspects, i.e. water consumption and the carbon emissions, associated with a number of processing options.

The routes selected for processing limonite to intermediate products are:

- HPAL, making MHP;
- Caron, making BNC;
- Goro, making NiO;
- RKEF, making NPI.

The routes selected for producing nickel sulphate hexahydrate from the intermediate products are:

- MHP leaching, Co SX-EW, Ni EW and redissolution, crystallization of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$;
- MHP leaching, Co SX-precipitation, Ni EW and redissolution, crystallization of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$;
- MHP leaching, Co SX-precipitation, crystallization of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
- Selective acid leaching (SAL) of MHP, purification, crystallization of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$;
- Dissolution of NiO and recrystallisation of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$;
- Dissolution of BNC and recrystallisation of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$;
- Oxidative leaching of NPI with iron rejection, Co SX-precipitation, Ni EW and redissolution, crystallization of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$;

Calculated CO₂ and water footprints are presented for each route examined. The route found to have the lowest CO₂ footprint overall is the HPAL primary circuit coupled with the SAL route to NiSO₄. The HPAL-SAL and the Goro-NiO routes have very nearly the same overall water footprint. The Caron route was found to have substantially higher CO₂ and water footprints than HPAL and Goro. The RKEF circuit has a CO₂ footprint almost triple that of the Caron circuit.

Keywords: Nickel sulphate, Batteries, Economics, Emissions, CO₂, Water

INTRODUCTION

The current environmental climate and accompanying pressure for reduced emissions of carbon dioxide to the atmosphere have generated strong interest in a movement away from fossil fuels for transportation and electricity generation. Currently, non-fossil sources of electricity are hydro-electric, nuclear, solar and wind energy. Electricity can only be generated from wind and solar when the sun is shining or the wind is blowing, which is often not when the electricity is needed. (For electric vehicles the generation and use of electricity are necessarily separated.) This gives rise to a need to store electricity when it is generated, so that it can be used when it is needed, which has given rise to the current wave of development in battery technology.

The dominant battery technology at present is that of the lithium-ion battery. These batteries use lithium, nickel, cobalt and manganese in the active cathode material. While cobalt is, and will most probably remain, a vital part of lithium-ion battery technology (particularly for laptop computers), many lithium-ion batteries, such as the 622 NMC type, actually contain appreciably more nickel than cobalt. The form in which nickel is used in the manufacture of the active cathode material for lithium-ion batteries is high-purity nickel sulphate hexahydrate. A convenient source might be pure nickel metal or oxide, dissolved in sulphuric acid, the solution further purified if necessary and nickel sulphate hexahydrate then crystallised. Nickel metal and oxide are made from sulphide ores and from oxide ores, in various ways. Other potential sources of nickel are mixed hydroxide precipitate (MHP), as produced from laterite, ferronickel and even nickel pig iron (NPI).

An environmental concern that is also growing is the availability of clean water. The extraction of metals, particularly via hydrometallurgy, requires large amounts of water and conservation of fresh water is a topic of increasing importance. The environmental pull towards minimising CO₂ emissions and water consumption leads to the idea that there may (or may not) be some routes to nickel sulphate hexahydrate that are environmentally preferable to others. This paper presents the results of a study examining the production of nickel sulphate hexahydrate by various routes, in the context of CO₂ emission and water consumption.

PRODUCTION ROUTES

Nickel is produced in various forms from sulphide and oxide ores by a number of routes. For this study, the feed selected was a typical limonitic laterite. The composition of the laterite used in this exercise is listed in Table 1.

Table 1 – Laterite composition, mass %

Free H ₂ O	30.0	K ₂ O	0.01
NiO	1.09	Na ₂ O	0.12
CoO	0.18	MnO	1.06
Fe ₂ O ₃	43.8	MgO	1.07
Cr ₂ O ₃	2.35	CaO	0.04
Al ₂ O ₃	3.93	SiO ₂	5.44
FeO	1.11	Bound H ₂ O	9.82

The following primary routes were chosen:

- HPAL technology, making mixed Ni-Co hydroxide precipitate (MHP) as an intermediate product;
- The Goro process, making pure nickel oxide;
- A Caron-type process, making basic nickel carbonate (BNC);
- RKEF (rotary kiln-electric furnace) technology, making nickel pig iron (NPI).

The following processes were selected for making nickel sulphate hexahydrate:

- From MHP via nickel metal, also making cobalt metal;
- From MHP via nickel metal, making cobalt carbonate;

- From MHP, not making nickel metal;
- From MHP via SAL (Selective Acid Leach) technology;
- From nickel oxide or basic nickel carbonate;
- From nickel pig iron via nickel metal.

LATERITE PROCESSING

HPAL

Figure 1 illustrates the HPAL circuit modelled⁽¹⁾. A conventional sulphur-burning acid plant provides the high-pressure steam, concentrated sulphuric acid and electricity required by the rest of the circuit.

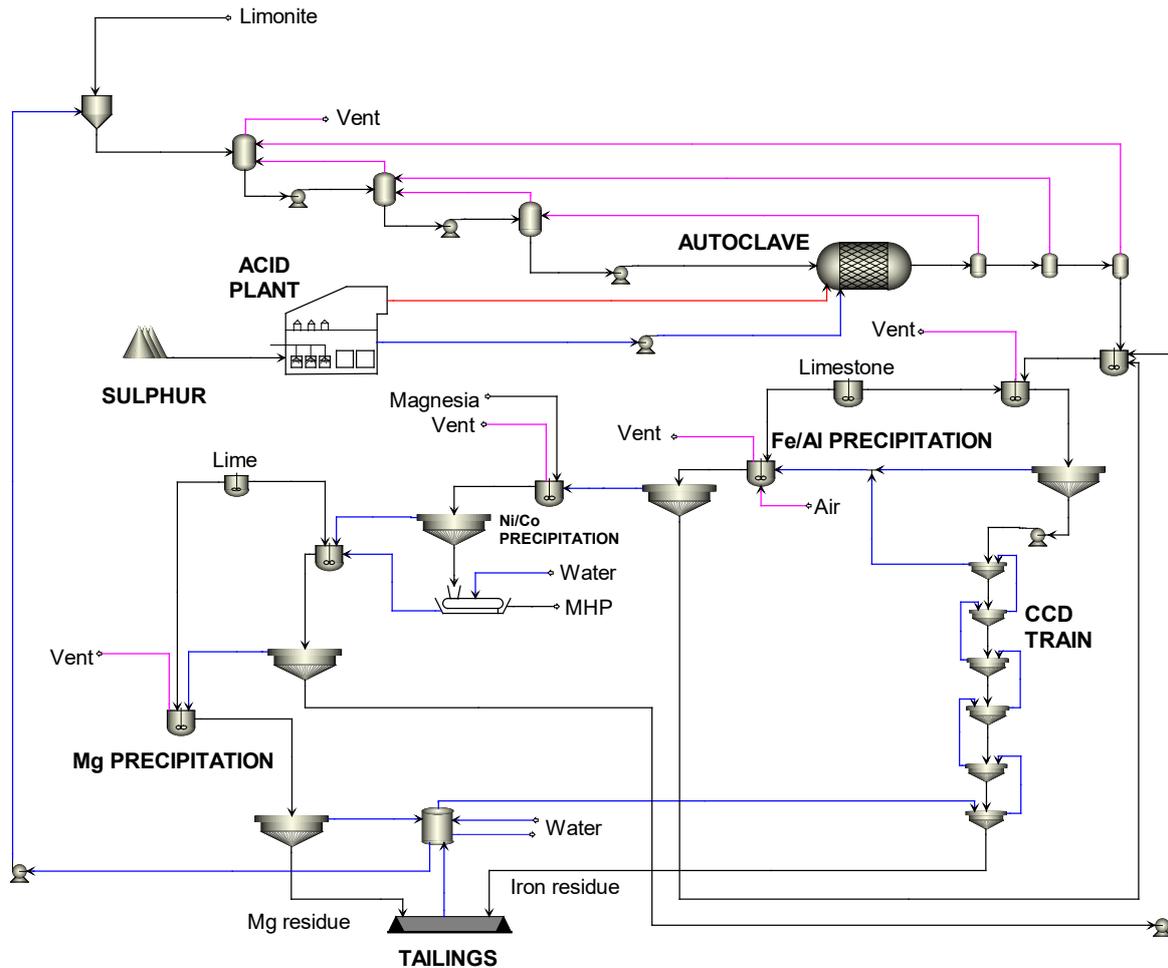


Figure 1 – HPAL circuit

Incoming limonite is slurried with recycled water and pumped through a pre-heating sequence in which it is heated by direct contact with steam flashed from the leached slurry, at three increments of pressure. The pre-heated slurry is pumped into the autoclave, where it is heated further with steam from the acid plant and leached with sulphuric acid.

The leached slurry is depressurised in three flash steps, the resulting steam being used to pre-heat the incoming slurry. The depressurised slurry is contacted with recycled hydroxides to consume some of its residual acid, then neutralised in the first of two steps with limestone to consume the remaining free acid and precipitate dissolved ferric iron and aluminium. The slurry from the first neutralisation step is passed through a counter-current decantation train in which the solids are washed with recycled water. The washed solids are transferred to a tailings dam. The solution goes to a second neutralisation with limestone, and air is passed through the slurry to oxidise and precipitate any ferrous iron, which is returned to the step ahead of the first contact with limestone. The solution from the second contact with limestone is reacted with magnesia to precipitate the nickel

and cobalt as a mixed hydroxide precipitate (MHP) that is recovered by thickening and filtration, then washed with water. The remaining solution is contacted with lime in two steps, the first to scavenge any residual nickel and cobalt, that precipitate returning to the step ahead of the first neutralisation with limestone. The second liming step precipitates the remaining magnesium and manganese as hydroxides that are recovered by thickening and sent to the tailings dam. The solution remaining after the second liming step is combined with water returning from the tailings dam, make-up water is added and the whole is recycled as process water.

Goro

The Goro circuit⁽²⁾ is illustrated in Figure 2. As for the HPAL circuit, a sulphur-burning acid plant supplies the sulphuric acid, steam and electricity required by the rest of the circuit. Incoming limonite is slurried with recycled water, pre-heated and leached with sulphuric acid at high temperature and pressure, as in the HPAL circuit. The leached and depressurised slurry ex the autoclave is passed through a counter-current decantation train in which the solids are washed with recycled water. The solution from the counter-current decantation train is neutralised in two steps to remove the residual free acid and impurities (Fe, Al, Si, Cr), first with limestone to remove the bulk of the impurities, then with lime to remove the residual amounts not removed with limestone. The precipitate from the first step is partly recycled and the balance joins the underflow from the counter-current decantation train. The precipitate from the second neutralisation step is recycled to the first neutralisation step for re-dissolution and recovery of co-precipitated nickel. The neutralised solution is passed through an ion exchange step in which copper is removed. The remaining solution is passed to a pulsed-column solvent extraction sequence in which nickel, cobalt and zinc are recovered selectively. The raffinate is combined with the residues from upstream and barren solution from the precipitation of cobalt and neutralised in two steps, first with limestone and then with lime, to precipitate the manganese and magnesium remaining in that solution. The resulting slurry is thickened and the supernatant is recycled as process water, supplemented with fresh water if necessary or with any surplus discharged. The thickened slurry goes to the tailings dam, where it consolidates. The water released as the solids consolidate is returned to the effluent treatment section.

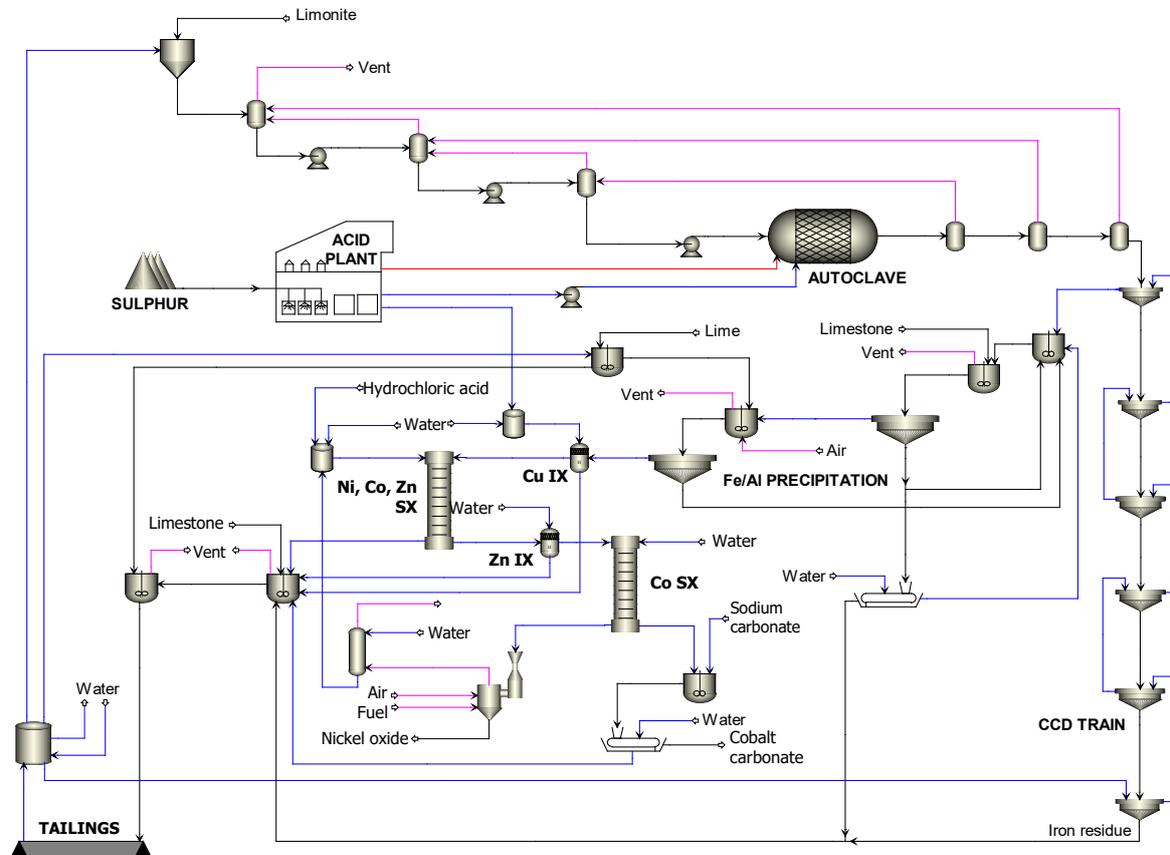


Figure 2 – Goro circuit

In the Ni-Co solvent extraction stage, the loaded solvent is stripped with strong hydrochloric acid. The resulting strip solution is passed through an ion exchange step to remove zinc, then to a second pulsed-column solvent extraction sequence in which the cobalt is selectively extracted and stripped

from the loaded solvent with water. Sodium carbonate is used to precipitate cobalt carbonate from the loaded strip solution. The cobalt carbonate is washed with water, then leaves the circuit.

The raffinate from the second solvent extraction step is converted to nickel oxide, steam and HCl in a pyrohydrolysis step at high temperature. The nickel oxide leaves the circuit and the HCl is captured in a water scrubber, then recycled.

Caron

The circuit illustrated in Figure 3 is based on the Caron process as originally installed by QNI⁽³⁾. The incoming limonite is dried using hot gas from the roaster, in which the dried limonite is heated to about 800°C under a reducing atmosphere. This reduces the nickel and about 70 percent of the cobalt to the metallic state, along with part of the iron. The hot gas from the roaster contains carbon monoxide and air is added to burn that to carbon dioxide, then the hot gas is used as the heat source for drying the incoming limonite, supplemented with natural gas and air as required by the overall energy balance.

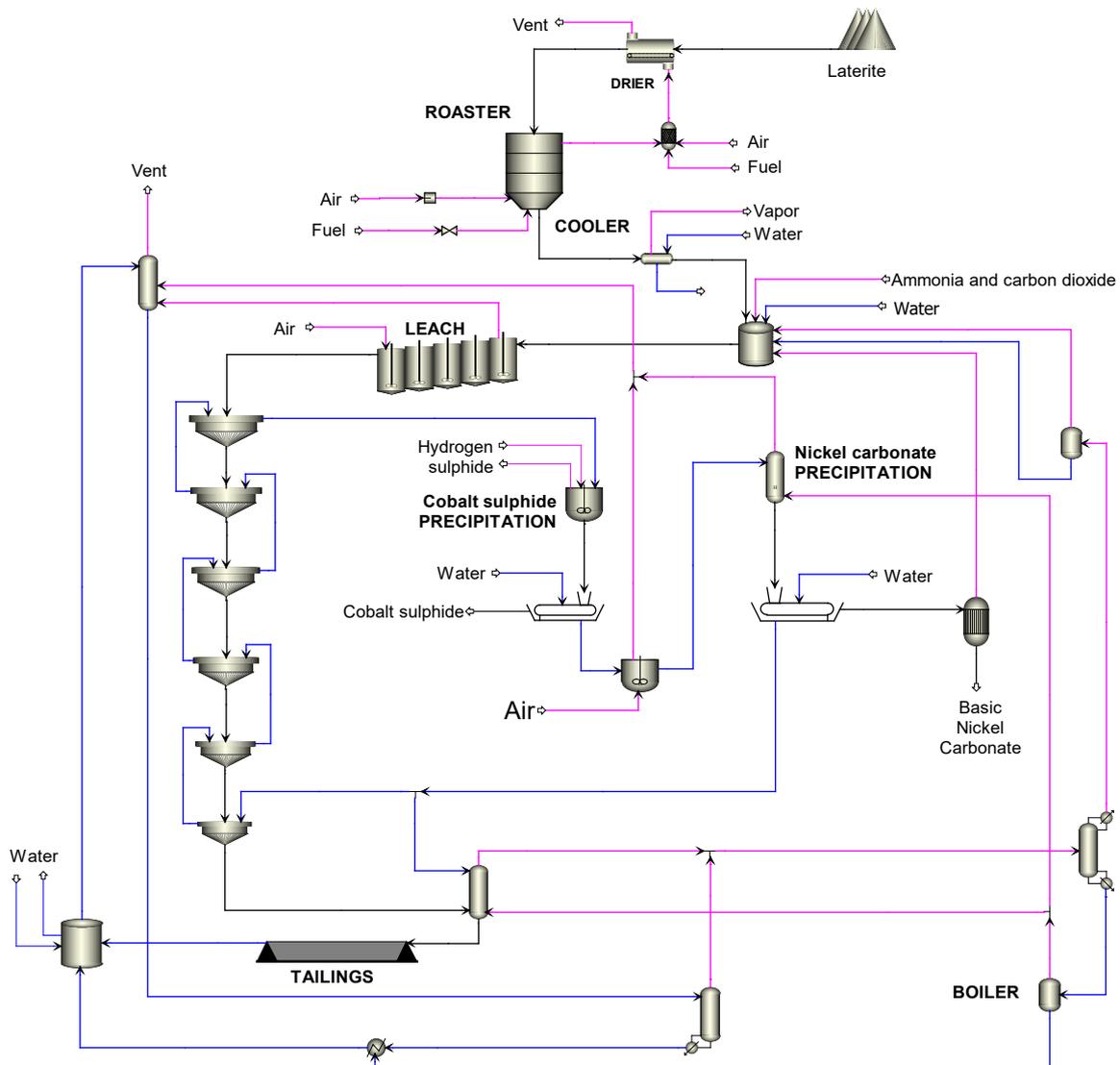


Figure 3 – Caron-type circuit

The hot reduced calcine is cooled in a rotating tube that is externally cooled with water, then leached with air and a recycled solution of aqueous ammonia and ammonium carbonate, causing the metallic nickel and cobalt to dissolve as ammine complexes. The metallic iron is converted into insoluble ferric oxide. The leached slurry is thickened and washed with recycled barren solution in a counter-current decantation train. The supernatant from the counter-current decantation train is contacted with hydrogen sulphide, precipitating the cobalt and some of the nickel as a mixed sulphide that, after recovery by filtration and washing with water, leaves the circuit. The filtrate is contacted with air to oxidize any residual sulphide in the solution, and the oxidized solution is steam-stripped to convert

the aqueous ammonia and ammonium carbonate to gaseous ammonia and carbon dioxide that are removed with the stripping steam, causing the nickel to be precipitated as a basic nickel carbonate (BNC) that is recovered by filtration, washed with water and leaves the circuit.

The washed underflow slurry from the counter-current decantation train is stripped with steam to convert the dissolved ammonia and ammonium carbonate to gaseous ammonia and carbon dioxide. The stripped underflow slurry leaves the circuit as a slurry of leach residue.

The gaseous phase leaving the leach, the air ex the oxidation of the solution from the precipitation of cobalt sulphide and the steam, ammonia and carbon dioxide from the precipitation of nickel carbonate are scrubbed with water to capture the ammonia and carbon dioxide before the remaining water-saturated air is discharged to the atmosphere. The dilute solution of ammonia and ammonium carbonate from the scrubber is distilled to recover the ammonia and carbon dioxide in a more concentrated gaseous form and to regenerate water that is recycled to the scrubber.

The steam, ammonia and carbon dioxide join the stream distilled from the scrubber bottoms and are separated by distillation into water and a concentrated $\text{NH}_3/\text{CO}_2/\text{H}_2\text{O}$ vapour that returns to the leach. Part of the water is boiled to raise steam for stripping the tailings and the rest joins the water going to the scrubber, along with make-up fresh water.

RKEF

Figure 4 illustrates the process model used for the RKEF circuit^(4,5). The incoming ore is dried using hot gas from the pre-reduction kiln (supplemented by burning natural gas in air), then mixed with coal char and heated to 800°C . The hot pre-reduced mixture is then smelted in an electric furnace. Most of the nickel, much of the iron and some of the cobalt and chromium form nickel pig iron (NPI) that is tapped and recovered. The other constituents are rejected to a slag phase. The carbon monoxide in the hot gas leaving the furnace is burned to carbon dioxide with air and the resulting hot gas is recycled to the drying step.

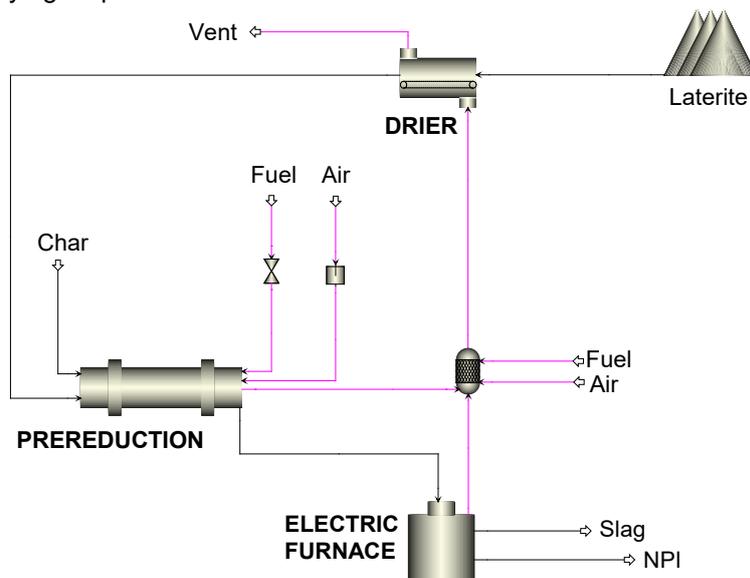


Figure 4 – RKEF circuit

MHP TO NICKEL SULPHATE

The analysis of the mixed hydroxide precipitate is listed in Table 2. Table 3 lists the solid composition calculated from this analysis.

MHP to Co Metal and NiSO_4 via Ni Metal

Figure 5 illustrates a circuit making cobalt metal and nickel sulphate hexahydrate from MHP via nickel metal. The MHP is leached with fresh sulphuric acid and the acid in spent electrolyte from the nickel electrolysis step. The resulting solution is filtered to remove any residual insoluble material, which is washed with water and then removed from the circuit. The filtrate goes to the loading section of a

solvent extraction section in which the copper, zinc, cobalt and manganese are removed. The resulting purified solution from this step goes to nickel electrolysis, from which the spent electrolyte returns to the MHP leach.

Table 2 – MHP analysis, mass %

Ni	40.87	Al	0.2
Co	3.53	Fe	0.5
Cu	0.1	Si	1.4
Mn	5.1	S	4.1
Zn	0.6	C	0.6
Ca	0.05		
Mg	2.4	Free H ₂ O	63

Table 3 – Calculated MHP composition, dry basis, mass %

NiSO ₄ •3Ni(OH) ₂	31.4	Fe(OH) ₃	1.0
Ni(OH) ₂	37.7	Zn(OH) ₂	0.9
CoSO ₄ •3Co(OH) ₂	3.3	SiO ₂	3.0
Co(OH) ₂	2.8	CaSO ₄ •2H ₂ O	0.2
Mn(OH) ₂	8.2	MgCO ₃	4.3
Cu ₂ (OH) ₂ CO ₃	0.2	MgSO ₄ •H ₂ O	6.3
Al ₂ O ₃ •3H ₂ O	0.5		

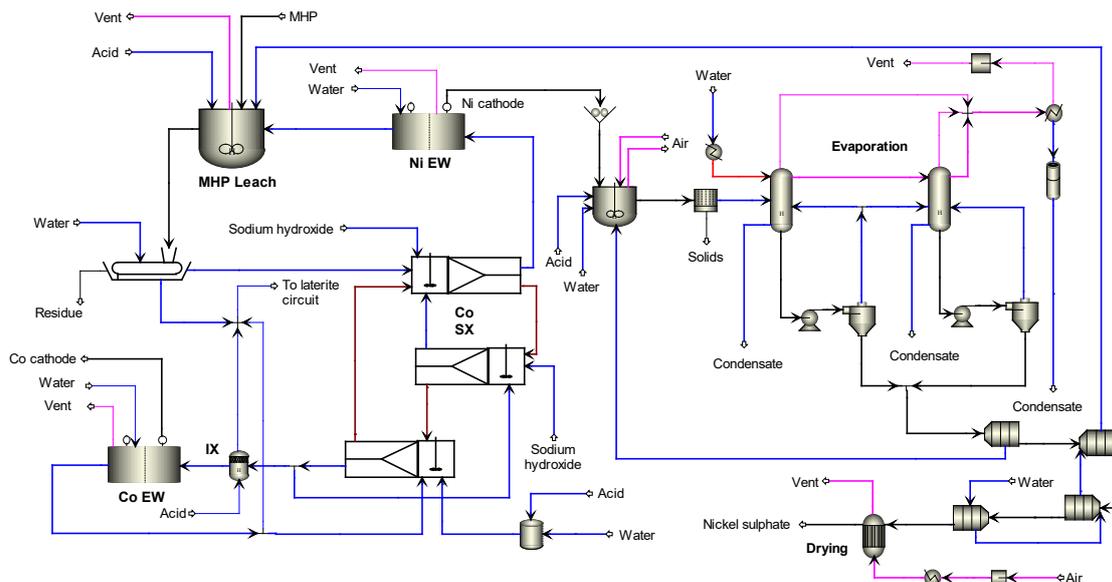


Figure 5 – MHP to Co metal and NiSO₄ via Ni metal

The cobalt-loaded organic phase is scrubbed with a portion of the loaded strip liquor to remove co-extracted nickel. The scrubbed organic phase is stripped with spent electrolyte from the subsequent cobalt electrolysis step, supplemented with fresh acid and water. Copper, manganese and zinc are removed from the strip liquor by ion exchange, then cobalt is recovered by electrolysis. The spent electrolyte is recycled, minus a small bleed, to the stripping stage of the cobalt solvent extraction sequence.

The cathode nickel is re-dissolved in sulphuric acid and recycled aqueous nickel sulphate, with air to oxidise the nickel metal and water added to give a solution just under-saturated in nickel sulphate. The solution is filtered to remove residual solids, then evaporated in a double-effect evaporator to produce nickel sulphate hexahydrate in a slurry containing about 25 percent solids by mass. That slurry is centrifuged to give a solid cake containing 90 percent solids by mass and the centrate is returned to the metal dissolution step. The solids from the centrifuge are washed with water in three

more centrifugation steps in series, with some of the nickel sulphate hexahydrate being re-dissolved. The wash centrate is recycled to the MHP leach and the washed nickel sulphate hexahydrate is dried in air at low temperature and exits the circuit as the desired product.

The sodium added as sodium hydroxide in the loading and stripping stages of the cobalt solvent extraction section circulates as supporting electrolyte and bleeds out in the wash filtrate after the MHP leach and with the wash solution ex the Zn IX step ahead of cobalt electrolysis. The assumption used in this exercise is that this bleed can return to the laterite plant.

MHP to NiSO₄ and CoCO₃ via Ni Metal

This case is similar to the preceding case, except that the scrubbed solvent in the cobalt solvent extraction sequence is stripped with recycled filtrate and make-up sulphuric acid, and the loaded strip liquor is reacted with sodium carbonate to precipitate the cobalt, copper, manganese and zinc as carbonates that are recovered by filtration and leave the circuit. Figure 6 illustrates this variation.

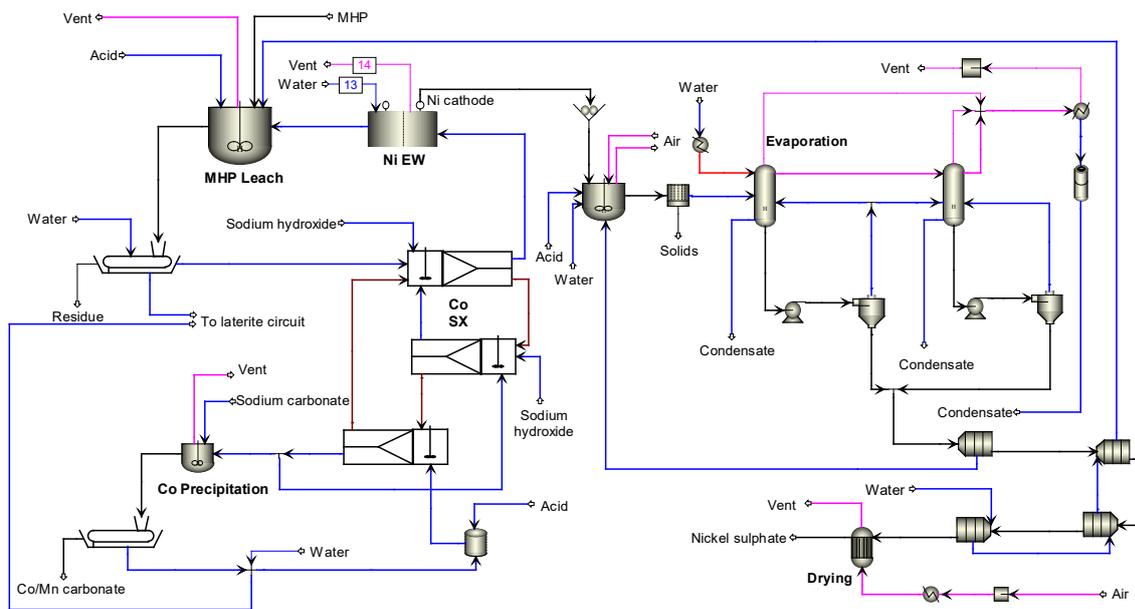


Figure 6 – MHP to CoCO₃ and NiSO₄ via Ni metal

MHP to NiSO₄, Not Via Metal

This circuit is illustrated in Figure 7. It is similar to the circuit in Figure 5, except that the raffinate from the cobalt solvent extraction sequence goes directly to the evaporation sequence.

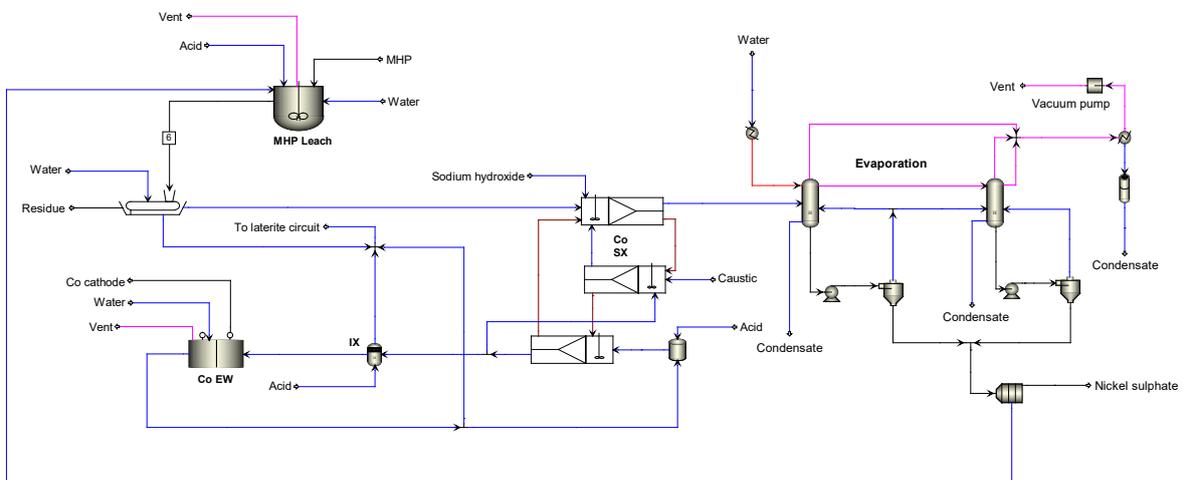


Figure 7 – MHP to NiSO₄, not via metal

This circuit cannot produce pure nickel sulphate. In the loading stage of the solvent extraction sequence, the cobalt, copper, manganese, zinc and also most of the calcium and magnesium in the feed solution have to be extracted into the organic phase to leave a pure solution of nickel sulphate. The cations extracted are replaced with protons from the organic extractant, lowering the pH and stopping the extraction. These protons have to be neutralised, which is done using sodium hydroxide, to enable complete extraction of the cobalt, copper, manganese and zinc into the organic phase. The sodium from this sodium hydroxide remains in the aqueous phase. Each mole of cobalt, copper, manganese and zinc is replaced with two moles of sodium, thus the feed to the evaporation sequence becomes a solution containing sodium sulphate as well as the nickel sulphate. Evaporating this solution gives rise to the crystallisation of a sodium-nickel double sulphate, thereby excessively contaminating the nickel sulphate with sodium. (Battery-grade nickel sulphate must generally contain less than 20 parts per million by mass of sodium.) Re-dissolution and recrystallization of the mixed nickel sulphate and sodium-nickel double sulphate results in the removal of the single salt, leaving only the double salt. Since the double salt would have to be discarded, this route was dropped from further consideration.

MHP to NiSO₄ and CoCO₃ via Ni Metal and MVR Evaporation

The evaporation step in the crystallisation of nickel sulphate hexahydrate could be done using multi-effect evaporation or it could use MVR (mechanical vapour recompression). Multi-effect evaporation requires a steam source, and that steam would be raised in a boiler fired by a hydrocarbon fuel (oil, coal, natural gas). MVR uses steam re-compression to recycle the latent heat, consuming mechanical energy that would generally come from an electric motor or a steam turbine. Both multi-effect and MVR evaporation therefore have carbon footprints, either from combustion of the fuel used to raise steam or from the electricity needed to power the recompression of steam. That raises a sub-question in the overall study, i.e. whether or not one type of evaporation is better than the other, in the overall context of CO₂ emission and water consumption.

To examine this sub-question, the circuit in Figure 6, which uses double-effect evaporation, was also modelled using MVR evaporation, as shown in Figure 8. The only difference between this and the other circuit is the mode of evaporation – MVR instead of double-effect. In the MVR option, some of the condensate is re-injected into the steam ex each compression stage to de-superheat it.

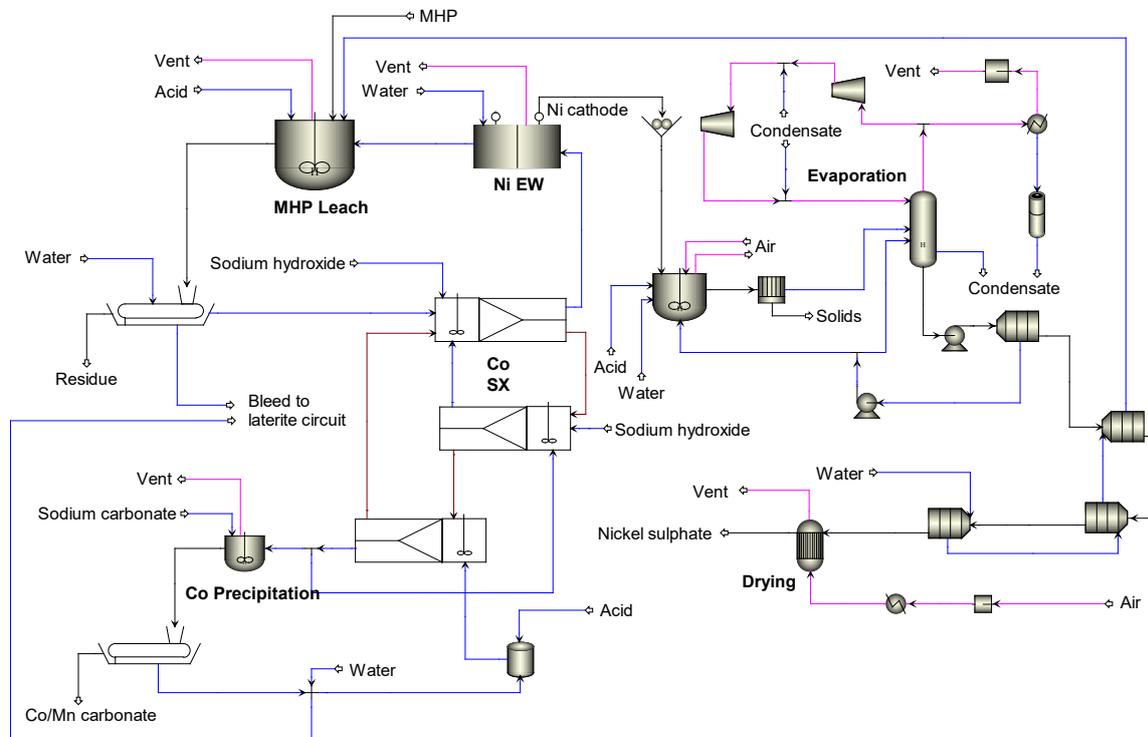


Figure 8 – MVP to CoCO₃ and NiSO₄ via Ni metal and MVR evaporation

SAL Circuit

The SAL (Selective Acid Leach) circuit has evolved since it was last discussed in the open literature⁽⁶⁾, but the developers are not yet ready to disclose it in its latest form. Figure 9 illustrates the circuit modelled. The incoming MHP is oxidised and leached under conditions that convert cobalt and manganese from the divalent to the trivalent state, rendering them insoluble in dilute sulphuric acid. The nickel is selectively leached, leaving the manganese and cobalt in the solid phase. The resulting slurry is thickened and filtered, the filter cake is washed with water and removed as a cobalt-manganese concentrate also containing some nickel. The thickener overflow and filtrate are combined and contacted with a reductant to remove any remaining traces of the oxidant.

The SAL section has two components, one in which the selective leaching of nickel is done, and one in which nickel is separated from magnesium and calcium, which are rejected to the aqueous stream called Effluent. Minor impurities (Cu, Zn) are rejected as solids to the stream called Residue.

The reduced solution is purified and the purified solution is evaporated under vacuum (the model assumes mechanical vapor recompression, but it could as well have been a conventional multi-effect system), crystallising nickel sulphate hexahydrate. The slurry of nickel sulphate hexahydrate from the evaporative crystallisation loop is centrifuged and the centrate is split, part going back to the evaporation loop and the balance returning to the SAL section as a bleed to control trace impurities in the evaporation loop. The crystallised nickel sulphate hexahydrate is washed with water (which dissolves some nickel sulphate in the final wash centrifuge, where the water is added) in three more centrifuge steps in series. The wash centrate is recycled to the SAL section. The washed nickel sulphate hexahydrate is dried with low-temperature air and exits the circuit.

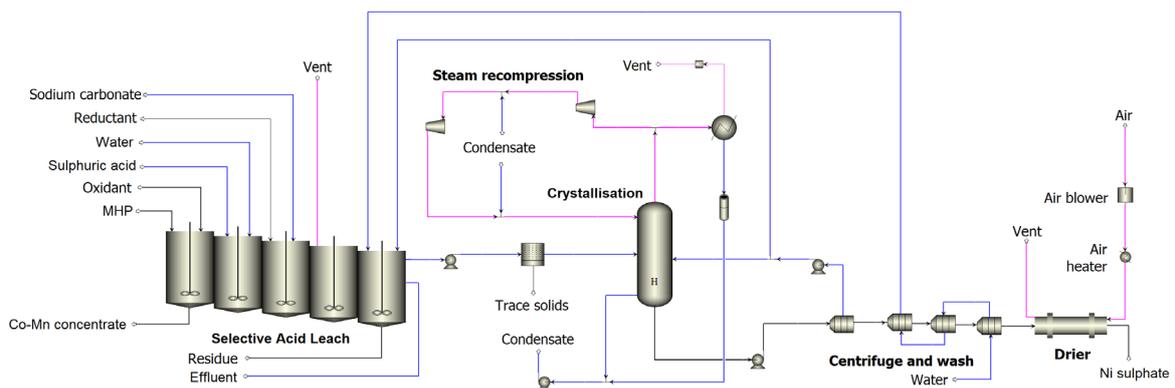


Figure 9 – SAL circuit

NICKEL OXIDE TO NICKEL SULPHATE

The model of the Goro circuit is somewhat simplified and predicts 100% pure nickel oxide, so the composition of nickel oxide used in the circuit making nickel sulphate from the nickel oxide was calculated from a published analysis⁽⁷⁾ of the Goro nickel oxide. The nickel content of the oxide is given as 80.3 percent by mass (pure NiO is 78.6% Ni), thus that particular sample contained metallic as well as oxide nickel. Nevertheless, this being the only published analysis found for Goro nickel oxide, it was used. The composition calculated from the published assay of this nickel oxide is listed in Table 4. The circuit used to model this case is shown in Figure 10.

NiO	86.95	MgO	0.07
CuO	0.04	SiO ₂	0.09
CoO	0.46	PbO	0.02
FeO	0.26	NiSO ₄	0.06
CaO	0.03	Ni	11.95
Al ₂ O ₃	0.07	Total	100.00

Table 4 – Goro nickel oxide, mass %

The incoming nickel oxide is dissolved in sulphuric acid and water, such that the resulting solution is almost-saturated in nickel sulphate. Hydrogen peroxide is added to oxidise most of the iron, half of the manganese and half of the cobalt. The acid addition is manipulated to dissolve all the nickel while not dissolving the oxidised iron, manganese and cobalt. After filtration to remove the oxidised iron, manganese and cobalt in the solids ex the leach, the resulting solution is evaporated under vacuum to give a slurry containing nickel sulphate hexahydrate that is recovered in cyclones and then separated from the bulk of the remaining liquid by centrifuge, the centrate returning to the dissolution step. The solids from the centrifuge are washed with water in three more centrifuge steps in series, with some of the nickel sulphate hexahydrate being re-dissolved. The washed nickel sulphate hexahydrate is dried in air at low temperature, then exits the circuit. The dissolved nickel and divalent impurities (Co, Mn, Fe) in the combined (primary and wash) centrate are precipitated with sodium carbonate (the pH and addition being such that Mg and Ca are not precipitated) and the resulting slurry is filtered. The filter cake is returned to the dissolution step and the filtrate exits the circuit.

BNC TO NICKEL SULPHATE

The circuit converting basic nickel carbonate (BNC) to nickel sulphate hexahydrate is the same as the circuit converting nickel oxide to nickel sulphate hexahydrate, as shown in Figure 10. The only difference is that the incoming nickel feed is BNC instead of NiO. The carbonate in the BNC is converted to carbon dioxide that is vented from the leach step. The BNC was assumed to be $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2$ with the same impurities as the nickel oxide, at the same Ni-to-impurity element ratios.

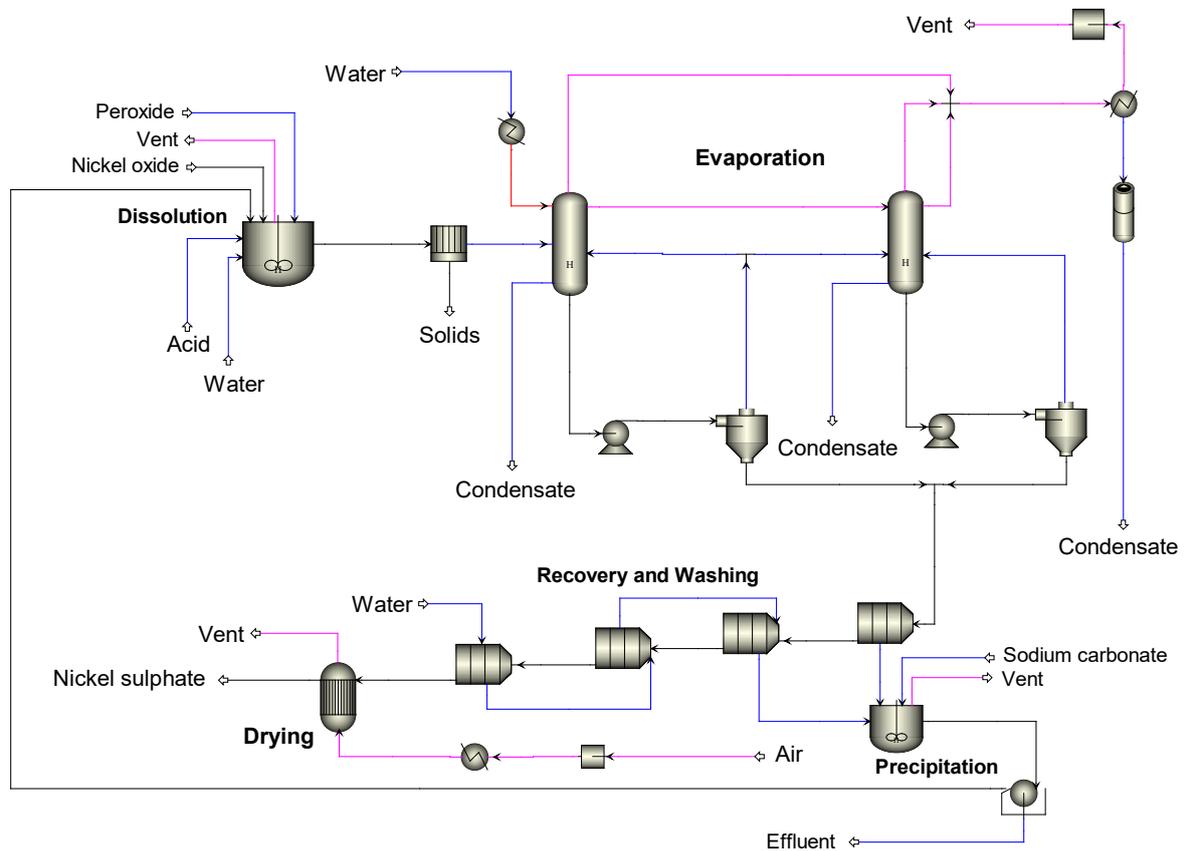


Figure 10 – NiO to NiSO₄

NPI TO NICKEL SULPHATE

The recoveries of nickel, cobalt, iron and chromium to the metal produced in the RKEF circuit were taken from published work⁽⁸⁾ on smelting laterite to nickel pig iron (NPI). Table 5 lists the composition of the NPI and the recoveries of nickel, cobalt, iron and chromium to the NPI.

The circuit modelled is illustrated in Figure 11. Trivalent chromium behaves similarly to trivalent iron in sulphate solutions. Incoming NPI (assumed to be fine enough) is pressure leached with sulphuric acid and air, at 90°C and 10 bar. The amount of acid added is sufficient to dissolve all of the nickel

and cobalt, along with only 5 percent of the iron and chromium. The rest of the iron and chromium are leached and re-precipitated as goethite and chromium hydroxide. The leached slurry is depressurised, exits the leach autoclave and is neutralised with limestone to precipitate the dissolved iron and chromium. The neutralised slurry is filtered and the filter cake is washed with water. The washed filter cake exits the circuit. The filtrate goes to the same cobalt solvent extraction sequence, cobalt carbonate precipitation and nickel electrolysis, re-dissolution and evaporative crystallisation as in the case of MHP to cobalt carbonate and NiSO_4 via nickel metal.

Table 5 – NPI composition, mass %

Element	Mass %	Recovery, %
Ni	2.9	88
Co	0.1	28
Fe	94	78
Cr	3.0	49

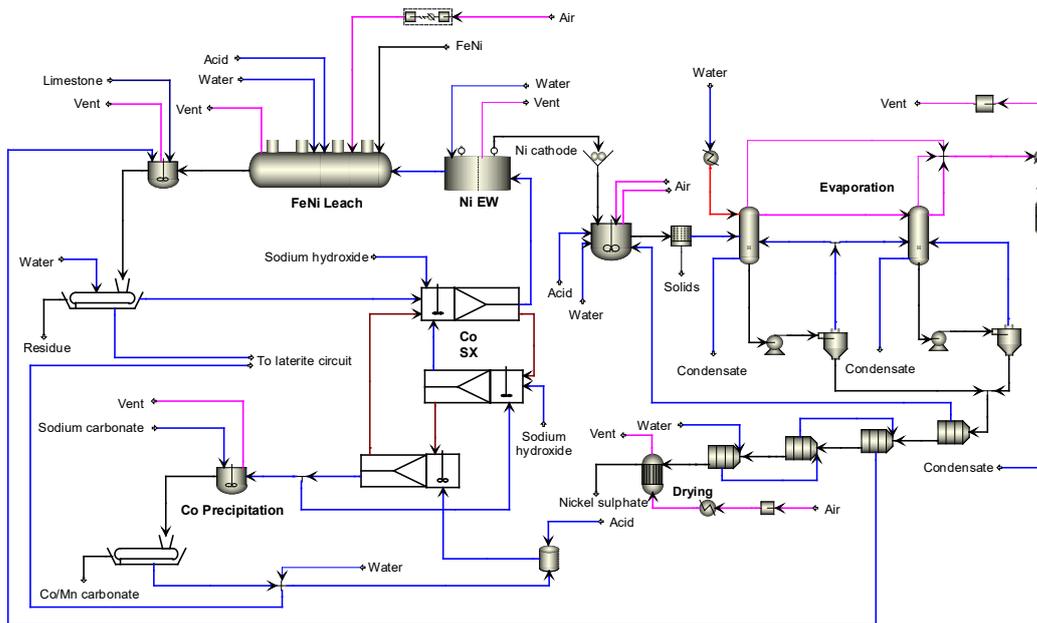


Figure 11 – NPI to NiSO_4

CALCULATION OF CO_2 EMISSIONS

Carbon dioxide emissions emanating directly from a circuit can be extracted from the mass-energy balance for that circuit. Indirect emissions are those not emitted directly, but rather in the manufacture of the reagents and utilities going into the circuit. In this exercise, the utilities having associated CO_2 emissions are electricity and fuel used for heating. Fuel used for heating was taken to be natural gas, approximated as methane. For every mole of methane burned, one mole of CO_2 is emitted. For translating heating input into mass of natural gas, a heating value of 55.6 MJ per kg of natural gas was assumed, hence a CO_2 footprint of 49 kg of CO_2 per GJ of energy from natural gas. Since most electricity is still generated from coal-fired power stations, a value for a modern coal-fired power station, 800 kg of CO_2 per MWh (222 kg/GJ) was used⁽⁹⁾.

The CO_2 emissions associated with manufacturing the various reagents were taken from a tabulation found in the open literature⁽¹⁰⁾. A published value was not found for the CO_2 emission associated with the manufacture of the oxidant, $\text{Na}_2\text{S}_2\text{O}_8$, used in the SAL circuit, so this number had to be estimated. Low-temperature electrolysis of sulphuric acid can be used to make $\text{H}_2\text{S}_2\text{O}_8$ ⁽¹¹⁾ and that can be reacted with sodium hydroxide to make $\text{Na}_2\text{S}_2\text{O}_8$. Table 6 lists the values used.

Table 6 - CO₂ associated with reagent manufacture, kg per kg reagent

Reagent	CO ₂	Calculation for Na ₂ S ₂ O ₈	
Na ₂ CO ₃	0.59	$S_2O_8^{2-} + 2H^+ + 2e^- \rightarrow 2HSO_4^-$	
NaOH	1.46	$2H^+ + 2e^- \rightarrow H_2$	
HCl	0.89	$2HSO_4^- \rightarrow H_2 + S_2O_8^{2-}$	
H ₂ O ₂	2.28	$H_2S_2O_8 + 2NaOH \rightarrow Na_2S_2O_8 + 2H_2O$	
CaCO ₃	0.01	Energy per kg H ₂ S ₂ O ₈	3.68 kWh
CaO	0.15	Latent heat per kg H ₂ O	0.63 kWh
NH ₃	2.11	H ₂ O per kg Na ₂ S ₂ O ₈	0.15 kg
CO ₂	0.82	H ₂ S ₂ O ₈ per kg Na ₂ S ₂ O ₈	0.82 kg
MgO	1.06	NaOH per kg Na ₂ S ₂ O ₈	0.34 kg
Char	2.82	CO ₂ emission per kg Na ₂ S ₂ O ₈	2.97 kg

RESULTS AND DISCUSSION

The process models used in this exercise were generated using commercially available software known as AspenPlus™.

Circuits Processing Limonite

Table 7 lists the amounts of each reagent/utility consumed in the various circuits processing laterite. Viewed through the lens of CO₂ emissions and setting less to be better, the HPAL and Goro circuits would appear to be significantly better than the Caron and RKEF circuits. The negative values calculated for the CO₂ emissions associated with electricity in the HPAL and Goro circuits are so because the process models calculate the electricity produced in the acid plant to be slightly more than the electricity consumed by the rest of the circuit. Since this electricity comes from the burning of sulphur, and the sulphur is captured as sulphuric acid, the acid plant has no (or even a negative) carbon footprint.

Table 7 – Reagent and utility consumption for the circuits processing limonite, per tonne Ni processed

Circuit	HPAL	Caron	Goro	RKEF
Char, as C, tonne	-	-	-	11
Ammonia, as NH ₃ , tonne	-	0.1	-	-
Carbon dioxide, as CO ₂ , tonne	-	0.2	-	-
Elemental sulphur, tonne	11	-	12	-
Hydrochloric acid, as HCl, tonne	-	-	6.0	-
Limestone, as CaCO ₃ , tonne	15	-	13	-
Magnesia, as MgO, tonne	2.5	-	-	-
Lime, as CaO, tonne	4.0	-	3.8	-
Sodium carbonate, as Na ₂ CO ₃ , tonne	-	-	0.3	-
Water, tonne	155	293	158	-
Natural gas, as CH ₄ , tonne	-	16	0.5	7
Hydrogen sulphide, as H ₂ S, tonne	-	0.07	-	-
Electricity, MWh	-0.3	0.2	-0.2	37
CO ₂ from reagent manufacture, tonne	3.4	0.4	6.2	31
Process CO ₂ emissions, tonne	0.0001	16	0.03	60
Utility CO ₂ emissions, tonne	-	27	-	-
Electricity CO ₂ emissions, tonne	-0.3	0.2	-0.2	30
Tonnes CO ₂ per tonne Ni processed	3.1	44	6.0	121

Table 8 and Table 9 list the amounts of water and energy consumed, for the circuits processing limonite. The Goro and HPAL circuits consume substantially less water and energy than the Caron and RKEF circuits.

Table 8 – Water consumption, circuits processing limonite, tonnes per tonne Ni processed

Circuit	HPAL	Caron	Goro	RKEF
Water consumed in the acid plant	33	-	37	-
Water to lime slaking	8	-	10	-
Make-up to process water	63	100	19	-
Water to solids washing	4	3	34	-
Water to IX and SX	-	-	5	-
Water to Na ₂ CO ₃ make-up	-	-	1	-
Water to CoCO ₃ washing	-	-	1	-
Water to HCl regeneration	-	-	6	-
Cooling water make-up	45	191	45	-
Total water consumption	154	293	158	-

Table 9 – Energy consumption, circuits processing limonite, MWh per tonne Ni processed

Circuit	HPAL	Caron	Goro	RKEF
Electricity	1.8	0.2	1.9	37
Natural gas	-	86	0.5	34

In terms of water consumption, the pyrometallurgical RKEF circuit, as modelled, uses no water. In reality, it would most probably need at least some cooling water, but that was not included in the process model used in this exercise. Its massive CO₂ footprint, compared to the other circuits processing limonite, would most probably outweigh any advantage in water consumption.

Circuits Producing NiSO₄

Turning next to the sub-question of whether multi-effect or MVR evaporation is better in terms of CO₂ emission and water consumption, Table 10 lists the reagent and utility consumptions calculated for the three circuits processing MHP. The column headed MHP-1 is for the circuit producing cobalt metal and nickel sulphate via double-effect evaporation, the column headed MHP-2 is for the circuit producing cobalt carbonate and nickel sulphate via double-effect evaporation and the column headed MHP-3 is for the circuit making cobalt carbonate and nickel sulphate via MVR evaporation. The difference in CO₂ footprint between MVR-1 and MVR-2 is due to the extra electricity required for cobalt electrolysis, which outweighs the CO₂ associated with the sodium carbonate used to precipitate cobalt carbonate. Comparing double-effect and MVR evaporation (MHP-2 and MHP-3), the MVR option emits about 0.1 tonne more of CO₂ from electricity than the double-effect option, but also about 0.2 tonnes less from fuel combustion, for an overall benefit of about 0.1 tonnes of CO₂ per tonne of nickel processed. The MVR option also consumes slightly less water than the double-effect option.

Table 11 lists the breakdown of water consumption and Table 12 lists the energy consumption, for the circuits processing MHP. The one producing cobalt carbonate and nickel sulphate via MVR evaporation is the best of these three, but the differences are probably too small to be significant.

Table 13 lists the reagent and utility consumptions of the MHP circuit using MVP and the other circuits producing nickel sulphate hexahydrate. It would appear that the circuit with the lowest overall CO₂ footprint is the one converting nickel oxide to nickel sulphate, the next lowest is the one processing BNC, then the SAL circuit. This is hardly surprising, as the circuits processing MHP have to electrowin nickel to separate it from the sodium used to control pH in the solvent extraction of cobalt. Nickel electrolysis is a major consumer of electricity in these circuits, hence their larger CO₂ footprints.

Table 14 and Table 15 present the amounts of water and energy consumed by the MHP circuit using MVR evaporation and the other circuits producing nickel sulphate hexahydrate. The circuit starting with BNC has the lowest water consumption and the one starting with ferronickel has the highest water consumption. The SAL circuit uses slightly more water than the MHP circuit using MVR.

An appreciable consumer of power in all the circuits producing nickel sulphate is moving air through the low-temperature drying of the hexahydrate product. Using air at 45°C to dry the product at about 40°C (to keep it as nickel sulphate hexahydrate) requires a large volume of air. The SAL circuit and the MHP circuit using MVR also require appreciable electricity for the MVR compressors in the evaporation-crystallisation loop, but even so have lower overall CO₂ and water footprints than the same circuits using double-effect evaporation.

The two leading overall routes from limonite to nickel sulphate hexahydrate being the HPAL-SAL and the Goro-NiO options, it is worth also examining the calculated quality of the nickel sulphate product. Table 16 shows the levels of the main impurities, as calculated by the process models. Both routes appear to meet the specifications for battery-grade nickel sulphate.

Table 10 – Reagent and utility consumption, circuits processing MHP to NiSO₄, per tonne Ni processed

Circuit	MHP-1	MHP-2	MHP-3
H ₂ SO ₄ , t	6.4	2.9	2.5
NaOH, t	0.8	0.8	0.8
Na ₂ CO ₃ , t		0.8	0.8
Water, t	21	20	19
Natural gas, as CH ₄ , t	0.09	0.09	0.01
Hydrogen sulphide, as H ₂ S, t			
Electricity, MWh	6.2	5.0	5.3
Ni in product, t	2.2	2.3	2.3
CO ₂ from reagent manufacture, t	0.3	0.7	0.7
Process CO ₂ emissions, t	0.13	0.16	0.16
Utility CO ₂ emissions, t	0.3	0.2	0.0
Electricity CO ₂ emissions, t	2.3	1.8	1.9
Tonnes CO ₂ per tonne Ni processed	2.9	2.8	2.7

Table 11 – Water consumption, circuits processing MHP, tonnes/tonne Ni processed

Circuit	MHP-1	MHP-2	MHP-3
Water for manufacturing H ₂ SO ₄	6.5	5.8	5.8
Water to reagent make-up	5.1	6.1	6.3
Water to solids washing	1.7	1.4	0.4
Process water consumed	3.7	2.7	2.7
Cooling water make-up	4.1	3.9	3.9
Total water consumption, t/t Ni	21	20	19

Table 12 - Energy consumption, circuits processing MHP, MWh per tonne Ni processed

Circuit	MHP-1	MHP-2	MHP-3
Electrolysis	5.4	4.2	4.3
Steam compression	-	-	0.3
Drying (moving air)	0.9	0.8	0.8
Total	6.2	5.0	5.3

Table 13 – Reagent and utility consumption for the circuits producing NiSO₄, per tonne Ni processed

Circuit	MHP-3	SAL	NiO	BNC	FeNi
Sulphuric acid, as H ₂ SO ₄ , tonne	2.5	3.0	2.9	2.7	7.5
Sodium hydroxide, as NaOH, tonne	0.8	-	-	-	0.1
Na ₂ S ₂ O ₄ , tonne	-	0.5	-	-	-
Hydrochloric acid, as HCl, tonne	-	-	-	-	-
Hydrogen peroxide, as H ₂ O ₂ , tonne	-	-	0.2	0.01	-
Limestone, as CaCO ₃ , tonne	-	-	-	-	6.1
Magnesia, as MgO, tonne	-	-	-	-	-
Lime, as CaO, tonne	-	-	-	-	-
Sodium carbonate, as Na ₂ CO ₃ , tonne	0.8	1.5	1.4	1.1	0.1
Water, tonne	19	22	18	18	142
Natural gas, as CH ₄ , tonne	0.1	0.003	0.1	0.1	0.1
Electricity, MWh	5.3	1.7	0.9	0.9	40.1
CO ₂ , reagent manufacture, tonne	0.7	0.7	0.3	0.2	0.1
Process CO ₂ emissions, tonne	0.2	0.4	0.2	0.7	2.6
Utility CO ₂ emissions, tonne	0.02	0.01	0.2	0.2	0.2
Electricity CO ₂ emissions, tonne	1.9	0.4	0.2	0.2	11.5
Tonnes CO ₂ per tonne Ni	2.7	1.5	1.4	1.5	14.5

Table 14 – Water consumption, circuits producing NiSO₄, tonnes/tonne Ni processed

Circuit	MHP-3	SAL	NiO	BNC	FeNi
Water for manufacturing H ₂ SO ₄	5.8	1.6	2.9	2.2	15.1
Water to reagent make-up	6.3	9.7	3.5	2.3	2.0
Water to solids washing	0.4	5.7	4.7	3.7	95.8
Process water consumed	2.7	3.0	4.0	2.7	25.5
Cooling water make-up	3.9	2.4	2.4	1.9	3.9
Total water consumption	19	22	18	13	142

Table 15 – Energy consumption, other circuits producing NiSO₄, MWh per tonne Ni processed

Process	MHP-3	SAL	NiO	FeNi
Electrolysis	4.2	-	-	4.2
Compression	0.3	0.8	-	35.0
Drying (moving air)	0.8	0.8	0.9	0.8
Total	5.3	1.5	0.9	40.1

Table 16 – Impurities in the NiSO₄•6H₂O, ppm

Impurity	Specification	Goro-NiO	HPAL-SAL
Cobalt	<100	1.1	0.4
Copper	<1	0.1	0.03
Sodium	<15	5	0.8
Calcium	<4	0.1	0.0004
Magnesium	<10	0.1	5

CONCLUSION

If the CO₂ and water footprints are the definitive criteria, then it would be reasonable to consider the entire processing route, from limonite to nickel sulphate hexahydrate.

While the circuits converting nickel oxide or basic nickel carbonate to nickel sulphate have lower CO₂ footprints than the SAL circuit, the Goro circuit itself has a higher CO₂ footprint than the HPAL circuit. Making nickel sulphate hexahydrate from limonite via HPAL and MHP (cobalt carbonate and MVR), the overall CO₂ footprint is 5.8 kg per kg of nickel processed. Using HPAL and SAL, the overall CO₂ footprint is 4.6 kg per kg of nickel processed. Making nickel sulphate hexahydrate via the Goro process and converting the nickel oxide to nickel sulphate hexahydrate has a CO₂ footprint of 7.4 kg per kg of nickel processed. The Caron circuit on its own would emit 44 kg of CO₂ per kg of nickel processed, and the RKEF 121 kg CO₂ per kg Ni processed.

In terms of water requirements, the HPAL and GORO circuits appear to be the same. The circuit making nickel sulphate from Goro nickel oxide requires less water than the SAL circuit, but the Goro circuit requires the same amount more water than the HPAL circuit, for an overall difference of zero. Basic nickel carbonate from Caron-type operations would not make sense through the lens of CO₂ emission and water consumption because of the high CO₂ emission and the high consumption of water associated with the Caron circuit.

Similarly, the high CO₂ emission of the RKEF process would most probably remove it from any list of candidate processes for making battery-grade nickel sulphate from laterite.

Overall process complexity, process economics and environmental impacts other than the water and CO₂ footprints were not taken into account in the analysis presented here. Adding these aspects would be relevant and extending this exercise might well be appropriate at some future time.

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