NICKEL LATERITE AND THE THREE MINERAL ACIDS

By

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ABSTRACT

Recent literature reports laterite processes based on sulphate, chloride and nitrate chemistry. This paper presents a study of the mass/energy balances associated with processing limonite and saprolite via each of these three different routes, based on information published for each route. The mass/energy balances are analyzed and the variable operating costs potentially associated with each are calculated from the reagent and utility consumptions predicted by the mass/energy balances. The calculated reagent/utility costs are compared and discussed.

INTRODUCTION

About sixty percent of the world's current nickel production comes from sulphide sources[1], but laterite deposits account for about sixty percent of the world's total nickel resources.[2] As world demand increases and currently exploited sulphide sources of nickel become depleted, if no major new sources of sulphide nickel appear it is inevitable that more of the world's nickel will have to be extracted from laterite deposits. Pyrometallurgy is an established technology for producing ferronickel or nickel matte from laterite ores containing about two percent nickel or higher, 10-15 percent Mg and low iron (13-20 percent), i.e. principally the saprolite fraction of the laterite.[3] The Caron Process is another established technology that extracts nickel and cobalt from laterite, again mainly from saprolite.[3] A more recent technology is high pressure acid leaching (HPAL) in which nickel is extracted from laterite ore using sulphuric acid at high temperature and pressure, this time mainly from the higher iron lower magnesium content limonite fraction. There is no one commercial process that can treat the whole laterite orebody.

Laterite ores originate from the weathering of ultramafic rocks (e.g. olivine and pyroxene).[4] The more-weathered upper layer of a typical laterite profile is referred to as the limonite zone, below that is a transition zone called the nontronite or clay zone, below that is a less-weathered zone called the saprolite zone and below the saprolite zone is the un-weathered bedrock. The limonite zone contains primarily the mineral goethite or other hydrated iron oxides, containing nickel in the lattice of the iron minerals. The primary constituent of the saprolite zone is hydrated magnesium silicates with nickel and cobalt replacing some of the magnesium.[4] Saprolitic and transition laterites containing about 1.5 or more percent nickel would be considered appropriate candidates for smelting or the Caron Process. Lower grade laterites have typically been seen as candidates for hydrometallurgical processing.

Hydrometallurgical processing of laterite begins with an acid leach of some kind. The dominant acid so far has been sulphuric acid, but work has been published on processes using hydrochloric acid or nitric acid.[3,5] Sulphuric acid, hydrochloric acid and nitric acid being the three major mineral acids, the question arose of whether or not processes using these acids have intrinsic advantages, depending on the ore treated and the acid used. This paper presents a study examining hydrometallurgical circuits in which these three acids are used to extract nickel and cobalt from laterite. Two laterite ores and two moisture levels were chosen for this study, i.e. limonite and saprolite, at 5 and 20 percent moisture. Process modelling was used to generate mass/energy balances for each ore, for published circuits using sulphuric acid, hydrochloric acid or nitric acid.

FEED

For convenience and to use totally unencumbered examples of limonite and saprolite, yet still remain realistic, a limonite ore and a saprolite ore were arbitrarily chosen from an internet search that found published information on a laterite project in the Philippines[6] Table 1 lists the basic analytical information that was published and Table 2 lists two mineral assemblages that back-calculate to the published assay data.

Table 1 – Limonite and saprolite assays, mass %

Ore type	Ni	Co	Fe	Al	Mg	SiO$_2$
Limonite	1.08	0.11	42.47	2.55	1.46	7.39
Saprolite	1.21	0.03	11.84	0.48	15.24	39.03

The various minor impurities generally found in ores, such as calcium, manganese, sodium and potassium, were omitted from the two feeds in this exercise to avoid complexity, as the objective was to broadly compare the three process routes under conditions reported in the open literature and the deportment of impurities has not been published for the chloride and the nitrate options. Potassium, in particular, can be present in significant (>1%) amounts, as can manganese, and their presence can have an appreciable impact on the overall economics and operating philosophy. In the sulphate circuit, they are simply acid consumers, whereas in the chloride and nitrate circuits, there is potential for by-product revenue. Naturally, the deportment of impurities would be a topic for detailed study should any of these routes ever be evaluated for a real application, but this study ignores their impact.

Table 2 – Limonite and saprolite minerals, mass %

Mineral	Limonite	Saprolite
Ni(OH)$_2$	1.71	1.91
Co(OH)$_2$	0.17	0.05
Mg$_3$Si$_2$O$_5$(OH)$_4$	2.77	38.9
Mg$_4$Si$_6$O$_{15}$(OH)$_2$•4H$_2$O	4.59	31.5
Fe$_2$O$_3$	4.05	0
Fe(OH)$_3$	75.81	22.7
Al(OH)$_3$	7.37	1.39
SiO$_2$	3.48	3.60
Total mass	100.00	100.00

PROCESSES

The three process options selected for this study are all processes that have been presented at this conference in the past - established HPAL for sulphuric acid, a process being developed by Neomet Technologies[7] using hydrochloric acid and a process being developed by Direct Nickel[8] using nitric acid. To simplify the exercise slightly, the final product chosen for all three processes was a mixed nickel/cobalt oxide/hydroxide, which would be processed further elsewhere. The processing rate chosen was 50 000 tonnes per year of nickel in the ore and the moisture content of the ore was set at five and twenty percent to examine the impact of the moisture in the ore on each process.

Sulphate circuit

The HPAL circuit illustrated in Figure 1 was assumed for the circuit using sulphuric acid. In this circuit, the incoming feed is pressurized and pre-heated sequentially by direct contact with steam flashed from the pressure let-down stages after the autoclave. The temperature of the leach is held at 250°C by indirectly heating the pre-heated and pressurized slurry. Concentrated sulphuric acid is injected into the autoclave.

Table 3 lists the stoichiometry used to represent the leach reactions in the autoclave. All these reactions were assumed to reach 99 percent conversion. The reactions using sulphuric acid are shown with only one proton from the sulphuric acid being utilized because sulphuric acid does not dissociate further at the high temperature in the autoclave. The bisulphate ions dissociate further when the leached slurry cools down after the leach. This is included in the background equilibrium aqueous chemistry in Aspen Plus, the software used in this work.

For simplicity, this model assumes that no alunite is formed in the leach, although both it and Al-Mg double salts are known to form.
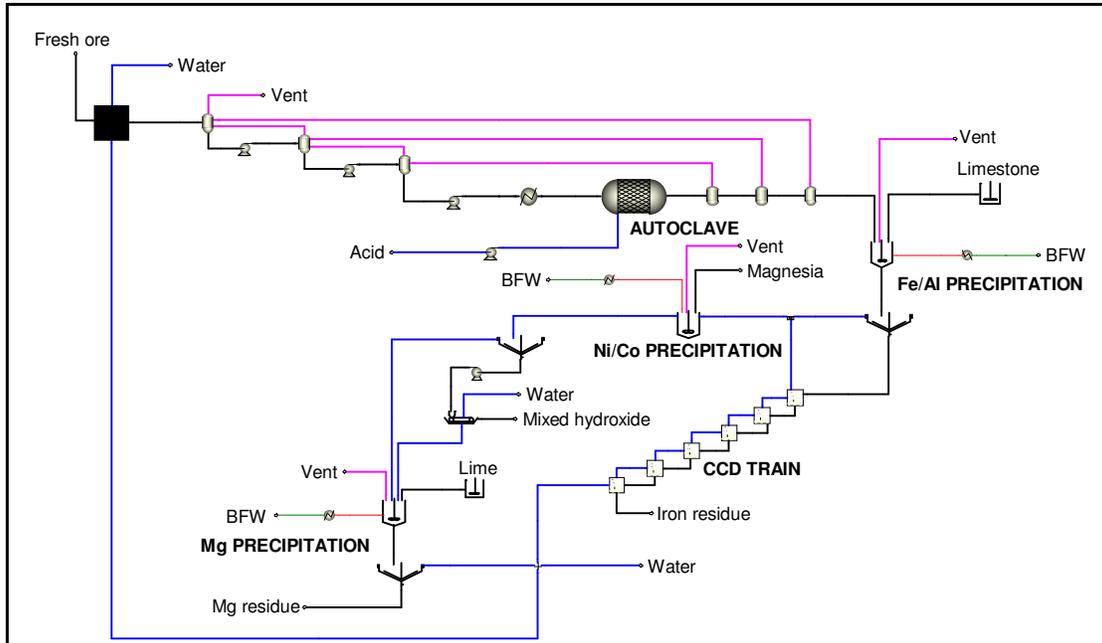
Figure 1 – Sulphate circuit

Table 3 – Sulphate leach stoichiometry

$$Ni(OH)_2 + 2H_2SO_4 \rightarrow Ni^{2+} + 2HSO_4^- + 2H_2O$$
$$Co(OH)_2 + 2H_2SO_4 \rightarrow Co^{2+} + 2HSO_4^- + 2H_2O$$
$$Mg_3Si_2O_5(OH)_4 + 6H_2SO_4 \rightarrow 3Mg^{2+} + 6HSO_4^- + 5H_2O + 2SiO_2$$
$$Mg_4Si_6O_{15}(OH)_2 \bullet 4H_2O + 8H_2SO_4 \rightarrow 4Mg^{2+} + 8HSO_4^- + 11H_2O + 6SiO_2$$
$$Fe_2O_3 + 6H_2SO_4 \rightarrow 2Fe^{3+} + 6HSO_4^- + 3H_2O$$
$$Fe(OH)_3 + 3H_2SO_4 \rightarrow Fe^{3+} + 3HSO_4^- + 3H_2O$$
$$Al_2O_3 + 6H_2SO_4 \rightarrow 2Al^{3+} + 6HSO_4^- + 3H_2O$$
$$Al(OH)_3 + 3H_2SO_4 \rightarrow Al^{3+} + 3HSO_4^- + 3H_2O$$
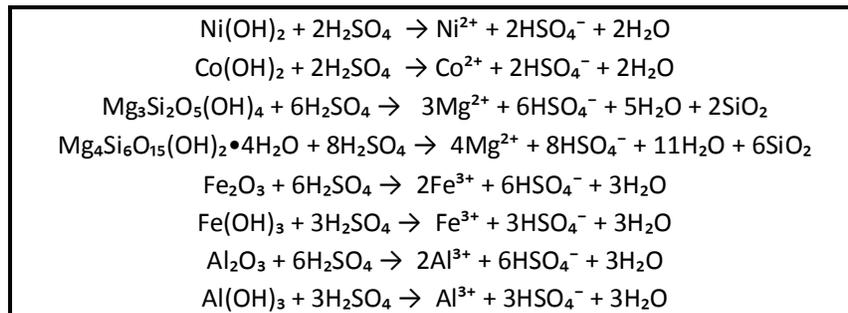
The hot slurry is sequentially depressurised and the steam released is recycled to pre-heat the incoming feed. The depressurised slurry is neutralized with limestone to precipitate the dissolved iron and aluminium. In this model no primary neutralization is done out with saprolite, as has been included in some flowsheets to reduce the acid consumption per unit of nickel dissolved, because this exercise looks at the two laterite types separately.

The neutralized solution is separated from the slurry in a primary thickener, the thickened slurry is washed with water in a six-stage counter-current decantation train, the supernatant from that joins the overflow from the primary thickener and the combined solution is treated with magnesium oxide to precipitate a mixed nickel/cobalt hydroxide.

The resulting slurry is thickened and the thickened slurry is filtered and washed with water. The washed filter cake (about 50 percent solids), containing the nickel and cobalt as a mixed hydroxide, leaves the circuit.

The filtrate and the overflow from the nickel/cobalt hydroxide thickener are combined and treated with lime to precipitate magnesium and the resulting slurry is thickened, the underflow leaving the circuit as a residue and the supernatant being recycled as wash solution to the counter-current decantation train. Table 4 shows the stoichiometry used to represent the various precipitation steps in the sulphate circuit.

Table 4 – Precipitation stoichiometry, sulphate option

Iron precipitation
$H_2SO_4 + CaCO_3 + 2H_2O \rightarrow CaSO_4 \bullet 2H_2O + H_2O + CO_2$
$Fe_2(SO_4)_3 + 3CaCO_3 + H_2O \rightarrow 3CaSO_4 + 2FeOOH + 3CO_2$
Base metal precipitation
$NiSO_4 + MgO + H_2O \rightarrow Ni(OH)_2 + MgSO_4$
$CoSO_4 + MgO + H_2O \rightarrow Co(OH)_2 + MgSO_4$
$CuSO_4 + MgO + H_2O \rightarrow Cu(OH)_2 + MgSO_4$
Magnesium precipitation
$MgSO_4 + CaO + 3H_2O \rightarrow Mg(OH)_2 + CaSO_4 \bullet 2H_2O$

Chloride circuit

The chloride circuit assumed for this exercise is the Neomet process[7], as illustrated in Figure 2. This circuit begins with leaching the feed with strong hydrochloric acid, thickening and filtering the leached slurry, recycling some of the thickener overflow to the leach as the method of moving the feed solids into the leach reactor train and managing the solids content in the leach, washing the residue with water and discarding the washed residue. Table 5 lists the stoichiometry used to represent the leach stage of the chloride circuit. All the reactions were assumed to proceed to 99 percent conversion.
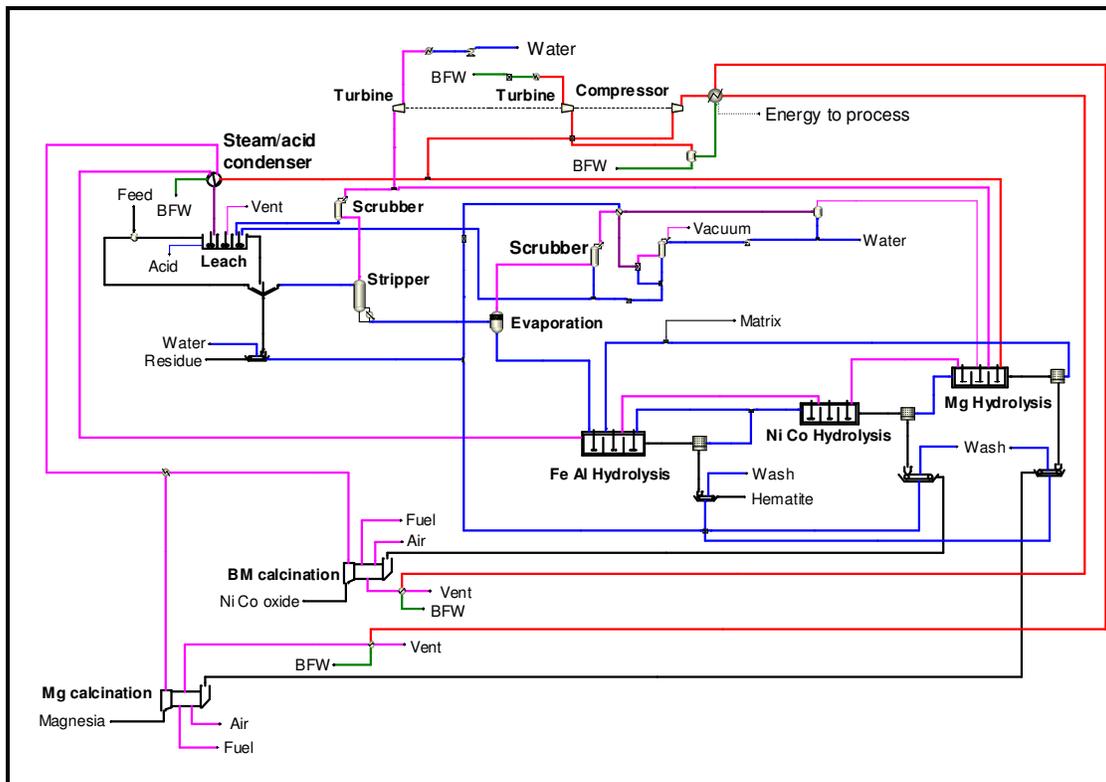
Figure 2 – Chloride circuit

The leach filtrate is concentrated by evaporation, first in a stripper to remove much of the free acid and then by boiling till the atmospheric boiling point of the concentrated solution is 140°C. The acid in the vapour from the stripper is recovered in a scrubber and returned to the leach. The vapour from the boiling step is scrubbed to capture the acid, which returns to the leach, and the remaining steam is used to concentrate the wash filtrate from the leach.

The concentrated solution is mixed with a circulating solvent matrix, contacted with steam and heated to 180°C, causing the ferric and aluminium chloride to decompose to solid ferric/aluminium oxide (hematite/alumina) and gaseous wet hydrogen chloride. The resulting slurry of hematite and alumina in the molten matrix is filtered at temperature and the filter cake is washed using a

proprietary method that uses substantially less water than is used in conventional washing of filter cakes. The washed filter cake leaves the circuit as pure hematite. The wash filtrates are combined and recycled to the evaporation section.

Table 5 – Chloride leach stoichiometry

$$Ni(OH)_2 + 2HCl \rightarrow Ni^{2+} + 2Cl^- + 2H_2O$$
$$Co(OH)_2 + 2HCl \rightarrow Co^{2+} + 2Cl^- + 2H_2O$$
$$Mg_3Si_2O_5(OH)_4 + 6HCl \rightarrow 3Mg^{2+} + 6Cl^- + 5H_2O + 2SiO_2$$
$$Mg_4Si_6O_{15}(OH)_2 \bullet 4H_2O + 8HCl \rightarrow 4Mg^{2+} + 8Cl^- + 11H_2O + 6SiO_2$$
$$Fe_2O_3 + 6HCl \rightarrow 2Fe^{3+} + 6Cl^- + 3H_2O$$
$$Fe(OH)_3 + 3HCl \rightarrow Fe^{3+} + 3Cl^- + 3H_2O$$
$$Al(OH)_3 + 3HCl \rightarrow Al^{3+} + 3Cl^- + 3H_2O$$
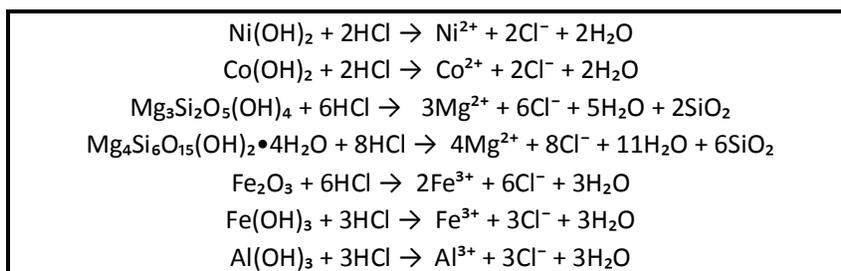
The hot primary filtrate is split, part returning to the iron hydrolysis stage to build up the level of base metals, and a bleed proceeding to the nickel/cobalt hydrolysis step, where it is heated further and contacted again with steam to convert the nickel and cobalt to solid basic hydroxychlorides, releasing the associated chloride ions as gaseous hydrogen chloride. The nickel and cobalt hydroxychlorides are filtered at temperature from the matrix and washed in the same way as the hematite/alumina solids. The hot filtrate is heated further and contacted with the incoming steam, causing the magnesium chloride to decompose to gaseous hydrochloric acid and solid magnesium hydroxychloride that is recovered by filtration at temperature and washed, in the same way as the hematite/alumina.

The base metal hydroxychlorides are calcined to a mixed nickel/cobalt oxide that leaves the circuit as the main product. The magnesium hydroxychloride is calcined to magnesium oxide that leaves the circuit. In both of these steps the chloride is released as gaseous hydrochloric acid that is recycled.

Table 6 shows the stoichiometry used in the process model to represent the various hydrolysis reactions.

Table 6 – Chloride hydrolysis stoichiometry

$$2FeCl_3 + 3H_2O \rightarrow Fe_2O_3 + 6HCl\uparrow$$
$$2AlCl_3 + 3H_2O \rightarrow Al_2O_3 + 6HCl\uparrow$$
$$3NiCl_2 + HO \rightarrow Ni_3(OH)_5Cl + 5HCl\uparrow$$
$$3CoCl_2 + HO \rightarrow Co_3(OH)_5Cl + 5HCl\uparrow$$
$$MgCl_2 + H_2O \rightarrow MgOHCl + HCl\uparrow$$
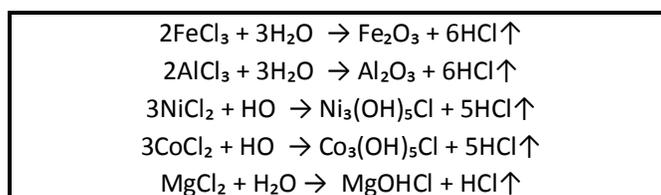
The gaseous mixture of hydrochloric acid and steam from the hydrolysis sequence is condensed in a heat exchanger, boiling water to raise steam at atmospheric pressure. The condensed acid returns to the leach. Some of the steam goes to the hydrolysis train and the balance is split, part being expanded through a turbine and then condensed, the condensate becoming boiler feed water for recycle. The mechanical power from the expansion turbine drives a compressor in which the other part of the atmospheric steam is compressed. The ratio of steam expanded to steam compressed is adjusted to make the compressor deliver steam at a saturation temperature high enough for it to be used as a heat source for the evaporation step in the main circuit.

The amount of steam going to the magnesium hydrolysis step is manipulated to give 35 mass percent HCl in the steam/acid leaving the iron hydrolysis step. The order of steam used for this is first the steam from the stripper/scrubber combination in the evaporation section, and if there is not enough of that steam, some of the steam raised in the steam/acid condensation step ahead of the leach is also sent to the hydrolysis sequence. Any steam from the stripper/scrubber combination not sent to the hydrolysis sequence is expanded through a turbine and condensed. The mechanical power generated is added to the power input to the compressor.

The energy input to the circuit not covered by the energy recycled as condensing compressed steam is supplied from an external source. The process model assumes natural gas, heating value 55.6 MJ/kg, as the heating utility.

Nitrate circuit

The nitrate circuit chosen for this exercise is the Direct Nickel process[8], illustrated in Figure 3. The incoming laterite is leached in regenerated nitric acid, the leached residue is separated and washed with water in a counter-current decantation train and the washed residue leaves the circuit. Table 7 shows the stoichiometry used to represent the nitrate leach. All the reactions were assumed to achieve 99 percent conversion.
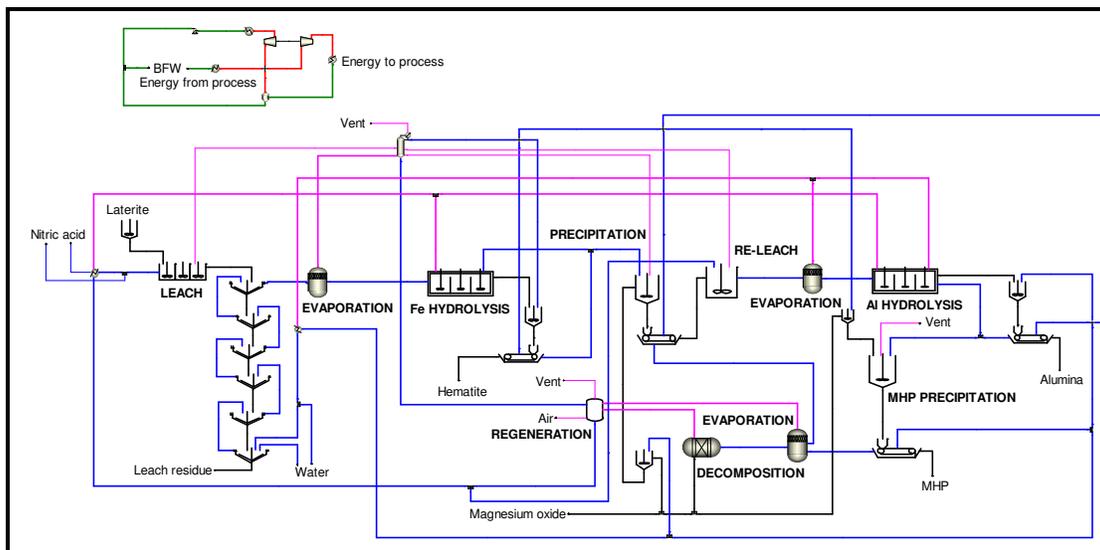
Figure 3 – Nitrate circuit

Table 7 – Nitrate leach stoichiometry

$$Ni(OH)_2 + 2HNO_3 \rightarrow Ni^{2+} + 2NO_3^- + 2H_2O$$
$$Co(OH)_2 + 2HNO_3 \rightarrow Co^{2+} + 2NO_3^- + 2H_2O$$
$$Mg_3Si_2O_5(OH)_4 + 6HNO_3 \rightarrow 3Mg^{2+} + 6NO_3^- + 5H_2O + 2SiO_2$$
$$Mg_4Si_6O_{15}(OH)_2 \bullet 4H_2O + 8HNO_3 \rightarrow 4Mg^{2+} + 8NO_3^- + 11H_2O + 6SiO_2$$
$$Fe_2O_3 + 6HNO_3 \rightarrow 2Fe^{3+} + 6NO_3^- + 3H_2O$$
$$Fe(OH)_3 + 3HNO_3 \rightarrow Fe^{3+} + 3NO_3^- + 3H_2O$$
$$Al_2O_3 + 6HNO_3 \rightarrow 2Fe^{3+} + 6NO_3^- + 3H_2O$$
$$Al(OH)_3 + 3HNO_3 \rightarrow Fe^{3+} + 3NO_3^- + 3H_2O$$
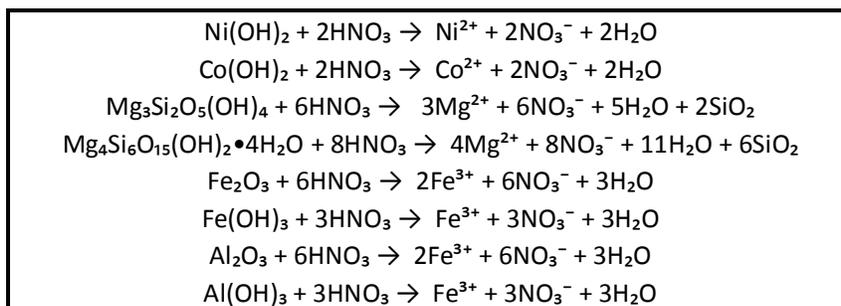
The supernatant from the counter-current decantation train is concentrated by evaporation to an atmospheric boiling point of 140°C, the steam and free nitric acid evaporated going to a scrubber to capture the acid for recycle. The concentrated solution is heated to 180°C and excess steam is added, causing the ferric nitrate to hydrolyse to solid hematite and gaseous nitric acid. Table 8 shows the stoichiometry used to represent the hydrolysis chemistry. The residual steam and the gaseous nitric acid are recycled to the leach.

Table 8 – Nitrate hydrolysis stoichiometry

$$2Fe(NO_3)_3 + 3H_2O \rightarrow Fe_2O_3 + 6HNO_3$$
$$2Al(NO_3)_3 + 3H_2O \rightarrow Al_2O_3 + 6HNO_3$$
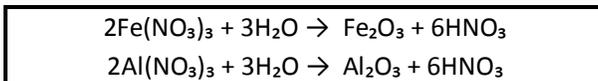
The slurry from the hydrolysis reactor is quenched into water and the hematite is recovered by filtration and washed with water. The washed hematite leaves the circuit. Part of the combined filtrate returns to the iron hydrolysis reactor to control the solids content of the slurry in that reactor and the balance is neutralized with recycled slaked magnesium oxide to precipitate aluminium and the base metals. Table 9 shows the stoichiometry used to represent the precipitation chemistry.

The precipitated slurry is filtered and the filter cake is re-dissolved in recycled nitric acid. The resulting solution is re-concentrated by evaporation. The steam evolved is split, part going to the counter-current decantation train where it is condensed and added to the wash water and the balance going to the aluminium hydrolysis step, in which the concentrated solution from the

evaporation step is heated to 190°C to hydrolyse the aluminium nitrate to solid aluminium oxide and gaseous nitric acid. The excess steam and the gaseous nitric acid from this step are recycled. The hot slurry from the aluminium hydrolysis reactor is quenched into water, the aluminium oxide is separated from the diluted slurry by filtration and the filter cake is washed with water. The washed filter cake leaves the circuit and the combined filtrate is split, part recycling to the aluminium hydrolysis reactor to control the solids level in the reactor and the balance being contacted with recycled magnesium oxide to precipitate the base metals as a mixed nickel/cobalt hydroxide that is filtered out, washed with water and leaves the circuit as the product.

Table 9 – Nitrate precipitation stoichiometry

$$2Al(NO_3)_3 + 3Mg(OH)_2 \rightarrow 3Mg(NO_3)_2 + 2Al(OH)_3$$
$$Co(NO_3)_2 + Mg(OH)_2 \rightarrow Mg(NO_3)_2 + Co(OH)_2$$
$$Ni(NO_3)_2 + Mg(OH)_2 \rightarrow Mg(NO_3)_2 + Ni(OH)_2$$
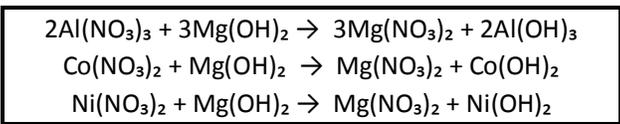
The filtrate from the base metal recovery stage, essentially a solution of magnesium chloride, is again concentrated by evaporation, such that the resulting fluid is a molten salt hydrate, essentially magnesium nitrate dihydrate. This molten salt hydrate is heated to 500°C, causing it to decompose to solid magnesium oxide, steam and gaseous O_2, NO and NO_2. Table 10 shows the stoichiometry used to represent the thermal decomposition of magnesium chloride. The magnesium oxide is partly recycled to the two precipitation steps and the excess leaves the circuit.

Table 10 – Magnesium nitrate decomposition

$$Mg(NO_3)_2 \bullet 2H_2O \rightarrow MgO + NO_2 + NO + O_2 + 2H_2O$$
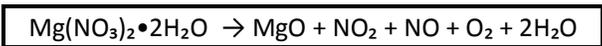
The NO and NO_2 used in the model represent the NO_x referred to in the literature published on the Direct Nickel process[8]. The NO_x is converted back to nitric acid using the method patented by Drinkard[9], in which NO reacts with HNO_3 in the presence of dissolved trivalent nitrogen, then the solution is oxidized to nitric acid with air. The gas from the thermal decomposition step and the steam from the preceding evaporation step are contacted with the aqueous nitric acid scrubbed from the steam from the evaporation step after the leach, and air is added. The NO_x is completely oxidized, giving aqueous nitric acid (60% HNO_3) that returns to the leach and the re-dissolution step after the first precipitation step. Table 11 shows the reaction sequence as described in the patent filed by Drinkard and the overall stoichiometry used to represent this step in the process model.

Table 11 – Nitric acid regeneration

Reaction sequence
$NO + O_2 \rightarrow 2NO_2$
$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$
$4NO + 2HNO_3 \rightarrow 2N_2O_3 + H_2O$
$N_2O_3 + O_2 + H_2O \rightarrow 2HNO_3$
Overall stoichiometry
$NO + O_2 \rightarrow 2NO_2$
$4NO_2 + H_2O + O_2 \rightarrow 4HNO_3$

The steam and gaseous nitric acid leaving the iron and aluminium hydrolysis stages, plus the steam, acid and nitrogen oxides leaving the evaporation and decomposition stages, carry latent heat that can be recycled. The atmospheric boiling point of the solution leaving the leach train is over 110°C. Injecting the steam and gaseous nitric acid from the two hydrolysis stages releases that heat of condensation at the temperature of the leach, thus it can be used to raise steam at 100°C and atmospheric pressure. The heat of reaction of the leach also contributes to the energy that can be captured as atmospheric pressure steam. The steam from the evaporation step ahead of the magnesium nitrate decomposition step, plus the steam and nitrogen oxides from the decomposition step, are cooled to 110°C in the acid regeneration stage of the process, raising more steam at 100°C and atmospheric pressure.

The atmospheric pressure steam raised from the cooling steps described in the preceding paragraph is not shown in Figure 3. The process model uses the energy balances over those steps

to calculate the amount of steam raised, and applies it in the heat exchanger shown above the label "Energy from process" in the separate little circuit at the top left of Figure 3. The waste heat from the process is used to raise steam at atmospheric pressure from boiler feed water, then the steam is split, part being expanded through a turbine and condensed, the power from the expansion turbine driving a compressor that raises the pressure of the balance of the steam such that its saturation temperature is high enough for it to be used as a heat source in the evaporation section. The heat exchanger labelled "Energy to process" represents that. The high temperature condensate is flashed to atmospheric pressure and the steam released joins the atmospheric steam raised from the process waste heat. The two condensate streams become boiler feed water for recycle.

The energy input to the circuit not covered by the energy recycled as condensing compressed steam is supplied from an external source. The process model assumed natural gas, heating value 55.6 MJ/kg, as the heating utility.

RESULTS

The mass/energy balances emanating from the three process models described above were used to calculate the reagent and utility consumption for the circuits and feeds used in this exercise, and the consumption results were used along with assumed unit costs to calculate variable operating costs. The full balances generated are available from the presenter, should anybody wish to peruse them. The unit costs for the various reagents and utilities were extracted from the output of other work and would need to be refined if any of these circuits were to be considered for real-life application.

Sulphate circuit

Table 12 lists the reagent and utility consumption numbers calculated by the process models of the sulphate circuit. Table 13 lists the reagent and utility costs calculated for the four feeds to this circuit, assuming the unit costs shown in parentheses in the first column on the left.

Table 12 – Reagent and utility consumption, sulphate circuit, per kg Ni&Co

Reagent/utility	Limonite		Saprolite	
	5% H_2O	20% H_2O	5% H_2O	20% H_2O
H_2SO_4, kg	15	15	36	36
$CaCO_3$, kg	12	12	11	11
MgO, kg	0.62	0.62	0.66	0.66
CaO, kg	2.9	2.9	23	23
Water, kg	101	91	240	230
Energy, MJ	86	86	27	27
Power, MJ	1.2	1.2	1.2	1.2

Table 13 – Variable costs, sulphate circuit, $/lb Ni&Co

Reagent/utility	Limonite		Saprolite	
	5% H_2O	20% H_2O	5% H_2O	20% H_2O
H_2SO_4 ($100/t)	1.16	1.16	2.75	2.75
$CaCO_3$ ($50/t)	0.02	0.02	0.02	0.02
MgO ($300/t)	0.08	0.08	0.09	0.09
CaO ($100/t)	0.16	0.16	1.31	1.31
Water ($1/t)	0.002	0.002	0.005	0.005
Energy ($4/GJ)	0.44	0.44	0.14	0.14
Power ($13/GJ)	0.02	0.02	0.02	0.02
Variable cost	1.89	1.89	4.33	4.33

As would be expected, the total variable cost is dominated by the costs of sulphuric acid and lime. Also as expected, the variable costs for the two saprolite feeds are substantially higher than those

for the two limonite feeds. That is because the saprolite contains substantially more magnesium than the limonite, so the saprolite requires more acid in the leach and more lime in the final magnesium precipitation step.

Power, in this model, is the electrical energy required to drive the pumps feeding the autoclave.

If magnesium can be impounded or discarded as a magnesium sulphate solution, the calcium oxide would not be needed, which would reduce the variable costs in Table 13 by the costs listed for calcium oxide. The savings would be slightly offset by a higher consumption of fresh water, but the lower unit cost of water would make that a small adjustment.

Chloride circuit

Table 14 lists the reagent and utility consumption numbers for the four feeds to the chloride circuit. Table 15 lists the associated variable costs. The numbers in parentheses in the left hand column are the assumed unit costs. In the chloride circuit the variable costs are dominated by the cost of energy. In this circuit, steam and hydrochloric acid leave the iron hydrolysis stage at 180°C and atmospheric pressure. The heat balance over the leach is such that most of the latent heat of condensation needs to be removed from the recycled steam/acid, either ahead of the leach or by means of a cooling system in the leach train, to operate the leach at about 110°C. That allows the latent heat of condensation in the recycled steam/acid to be used to raise steam at atmospheric pressure and 100°C, thereby recovering a substantial part of the energy consumed in the circuit. Expansion through a turbine of part of the steam thus raised, and using the mechanical power generated to compress the remainder of the steam to a sufficiently high saturation temperature allows it to be used to recycle some of the latent heat of condensation from the steam/acid leaving the hydrolysis section. This energy recycle reduces the consumption of natural gas, and therefore the calculated variable costs.

Table 14 – Reagent and utility consumption, chloride circuit, per kg Ni&Co

Reagent/utility	Limonite		Saprolite	
	5% H_2O	20% H_2O	5% H_2O	20% H_2O
HCl, kg	0.10	0.18	0.06	0.06
Make-up matrix, kg	0.02	0.04	0.04	0.04
Process water, kg	37	38	82	99
Boiler feed ,kg	0	0	29	22
Natural gas, no energy recycle, kg	12	12	10	11
Natural gas, with energy recycle, kg	8	9	5	6
Power, MJ	3	5	6	6

Table 15 – Variable costs, chloride circuit, $/lb Ni&Co

Reagent/utility	Limonite		Saprolite	
	5% H_2O	20% H_2O	5% H_2O	20% H_2O
HCl ($700/t)	0.03	0.03	0.02	0.02
Matrix ($1000/t)	0.01	0.02	0.02	0.02
Water ($1/m³)	0.02	0.02	0.02	0.02
Boiler feed ($2/m³)	0	0	0.00	0.02
Power ($13.33/GJ)	0.00	0.00	0.00	0.00
Natural gas, no energy recycle ($4/GJ)	1.20	1.26	1.03	1.09
Natural gas, with energy recycle ($4/GJ)	0.79	0.89	0.66	0.71
Variable cost, no energy recycle	1.25	1.61	1.13	1.08
Variable cost, with energy recycle	0.85	0.98	0.76	0.82

Table 16 lists the heat transfer duties calculated by the process model for the evaporation and hydrolysis sections of the chloride circuit, as well as the energy recycle calculated for the steam expansion/compression combination.

According to the calculations, the nickel/cobalt hydrolysis step requires no external energy supply. That is because the sensible heat in the steam from the hotter magnesium hydrolysis step supplies the energy needed to hydrolyse the base metals.

The overall energy demand of the chloride circuit is higher for the limonite than it is for the saprolite. One explanation of this is that the limonite contains more iron than the saprolite, and since the iron is trivalent it consumes one and a half moles of hydrochloric acid per mole of iron dissolved in the leach. The overall result is that the limonite, consuming more acid in the leach, requires more acid to be recycled and hence consumes more energy. The increased magnesium in the saprolite does not fully offset the higher acid recycle, compared to the limonite.

Table 16 – Heat transfer duties, chloride circuit, MJ/kg Ni&Co

Section	Limonite		Saprolite	
	5% H_2O	20% H_2O	5% H_2O	20% H_2O
Evaporation	101	118	46	62
Fe&Al hydrolysis	173	173	86	86
Ni& Co hydrolysis	0	0	0	0
Mg hydrolysis	17	17	61	61
Total energy load	291	308	193	209
Energy recycled	101	93	92	95
Energy recycle	35%	30%	48%	45%

Nitrate circuit

Table 17 lists the reagent and utility consumption numbers for the nitrate circuit, as calculated by the process models for each feed. Table 18 lists the calculated variable costs. As before, the numbers in parentheses are the unit costs assumed for this exercise.

Table 17 – Reagent and utility consumption, nitrate circuit, per kg Ni&Co

Reagent/utility	Limonite		Saprolite	
	5% H_2O	20% H_2O	5% H_2O	20% H_2O
Energy to evaporation, MJ	562	562	912	910
Energy to Fe hydrolysis, MJ	455	455	454	454
Energy to Al hydrolysis, MJ	34	34	14	14
Energy to $MgCl_2$ decomposition, MJ	119	119	327	327
Replenishment nitric acid, g HNO_3	0.03	0.03	0.03	0.03
Cooling water make-up, kg	410	431	765	785

Table 18 - Variable costs, nitrate circuit, $/lb Ni&Co

Reagent/utility	Limonite		Saprolite	
	5% H_2O	20% H_2O	5% H_2O	20% H_2O
Natural gas, no energy recycle ($4/GJ)	2.13	2.13	3.10	3.10
Natural gas, with energy recycle ($4/GJ)	1.82	1.89	2.93	2.96
Nitric acid ($1000/t HNO_3)	0.01	0.01	0.01	0.01
Cooling water make-up ($1/t)	0.02	0.02	0.04	0.04
Projected variable cost, no energy recycle	2.16	2.16	3.17	3.16
Projected variable cost, with energy recycle	1.85	1.89	3.00	3.02

As in the chloride circuit, in the nitrate circuit the variable cost is dominated by the cost of energy. In the nitrate circuit the energy load is spread between the evaporation, hydrolysis and magnesium nitrate decomposition sections. Table 19 lists the calculated heat transfer duties for the different sections of the circuit. The bottom three rows of this table are the total energy load for the circuit,

i.e. the total amount of heat transferred as calculated by the model, the energy recycled via the generation and expansion/compression of steam and the percentage energy recycle.

Table 19 – Heat transfer, nitrate circuit, MJ/lb Ni&Co

Section	Limonite		Saprolite	
	5% H_2O	20% H_2O	5% H_2O	20% H_2O
Evaporation	255	255	414	414
Fe hydrolysis	207	207	206	206
Al hydrolysis	15	15	6	6
$MgCl_2$ decomposition	54	54	149	149
Total energy load	531	531	776	775
Energy recycled	78	69	43	34
Energy recycle	15%	13%	6%	4%

The energy calculated for evaporation in the nitrate circuit is appreciably greater than the energy for evaporation in the chloride circuit (compare Table 16 to Table 19). Part of the reason for this is that, in the nitrate circuit, the hot slurry from the iron hydrolysis step and the hot slurry from the aluminium hydrolysis step are quenched and diluted into water before being filtered, and the two filter cakes are washed with water. In the chloride circuit, the slurries ex hydrolysis are filtered without dilution and the filter cakes are washed using a proprietary method that uses substantially less water than is used in conventional washing of filter cakes. That significantly reduces the amount of water entering the circuit and thus requiring evaporation. If the nitrate circuit can adopt these two innovations, the amount of water entering the circuit and requiring evaporation would be reduced significantly, which would reduce the amount and therefore the cost of the energy needed in the nitrate circuit.

Running the models of the nitrate circuit with these assumptions gave the results listed in Table 20. If these two changes are possible, they would benefit the nitrate process substantially.

Table 20 – Variable costs comparison, nitrate circuit, %/lb Ni&Co

Case	Limonite		Saprolite	
	5% H_2O	20% H_2O	5% H_2O	20% H_2O
Modified circuit	1.06	1.14	1.60	1.65
Current circuit	1.85	1.89	3.00	3.02
Reduction	43%	40%	47%	45%

DISCUSSION

The sulphate circuit represents the established technology for processing laterite ore. The chloride and nitrate circuits are not in commercial operation and are therefore new technologies, as yet unproven commercially. This exercise focuses on the mass/energy balances emanating from process models representing the sulphate, chloride and nitrate circuits, calculating the amounts of the various reagents and utilities used by each circuit and using assumed unit costs to convert those quantities into variable costs. Table 21 lists the calculated reagent/utility costs for the three circuits, for limonite and saprolite feed at the two moisture levels chosen for this study, for no energy recycle and with energy recycle, using the unit costs shown in the breakdowns for the individual circuits. The case of the modified nitrate circuit with energy recycle is also listed. The unit costs used were gathered at the end of 2011, for a Canadian location. For different specific projects, the unit cost numbers would change. Fixed operating and capital cost calculations could certainly affect the ranking of these three circuits, but that has been left out of this exercise.

In the case of the laterite feed, the trade-off between the somewhat higher reagent/utility costs for the sulphate circuit may be that technical risk would be lower for that circuit. The sulphate circuit is unaffected by the moisture level in the incoming limonite because the feed is adjusted to 30 percent solids ahead of the autoclave section using water recycled within the circuit, so the autoclave train, which is where energy is used, sees the same feed no matter what the moisture in the incoming laterite. Any excess water leaves as waste water. For saprolite feed to the sulphate circuit, the calculated variable cost is substantially higher than for limonite because of the higher consumption of sulphuric acid and lime caused by the magnesium in the feed.

Table 21 – Variable cost comparison, $/lb Ni&Co

Process	Limonite		Saprolite	
	5% H₂O	20% H₂O	5% H₂O	20% H₂O
Sulphate, baseline	1.89	1.89	4.33	4.33
Nitrate, no energy recycle	2.16	2.16	3.17	3.16
Nitrate, with energy recycle	1.85	1.89	3.00	3.02
Chloride, no energy recycle	1.25	1.61	1.13	1.08
Modified nitrate, with energy recycle	1.06	1.14	1.60	1.65
Chloride, with energy recycle	0.85	0.98	0.76	0.82

In the chloride circuit, higher moisture in the feed does slightly increase the calculated variable cost because all the water entering with the feed is evaporated. The calculated reagent/utility cost is appreciably lower for the saprolite feed than for the limonite feed. The reason for that is that the limonite consumes more acid in the leach than the saprolite does, because of the higher iron content in the limonite. The higher magnesium content of the saprolite only partially offsets the reduction in acid consumption due to its lower iron content. For the feeds selected for this exercise, the limonite consumes 916 kg of HCl per tonne of dry ore, compared to 698 kg of HCl per tonne of dry saprolite. The increased amount of iron thus requires an increased circulation of ferric chloride to the hydrolysis section and a higher circulation of acid back to the leach, plus more evaporation and condensation of water. Since the hydrolysis reactions are endothermic, the higher acid consumption in the leach, giving a higher hydrolysis duty, increases the energy consumption of the chloride circuit.

The hydrolysis of magnesium requires more energy in the case of saprolite than limonite because the saprolite contains more magnesium than the limonite, but the difference is not enough to offset the effect of the higher acid consumption in the leach, for limonite relative to saprolite, in the chloride circuit.

According to the process models, the energy consumption in the nitrate circuit is higher than in the chloride circuit. One reason for that would be because of the higher evaporation load in the nitrate circuit. If the nitrate circuit can be modified to not quench the hot hematite slurry and alumina slurry into water, and to wash these filter cakes using less water, the overall energy consumption of the nitrate circuit would be reduced considerably.

Another reason for the higher energy consumption in the nitrate circuit, relative to the chloride circuit, is that the thermal decomposition of magnesium nitrate is more endothermic than the hydrolysis and calcination of magnesium chloride. Figure 4 shows heats of reaction versus temperature, calculated using data taken from the FACT database[10]. The solid lines are for the chloride reactions and the dashed lines are for the nitrate reactions.
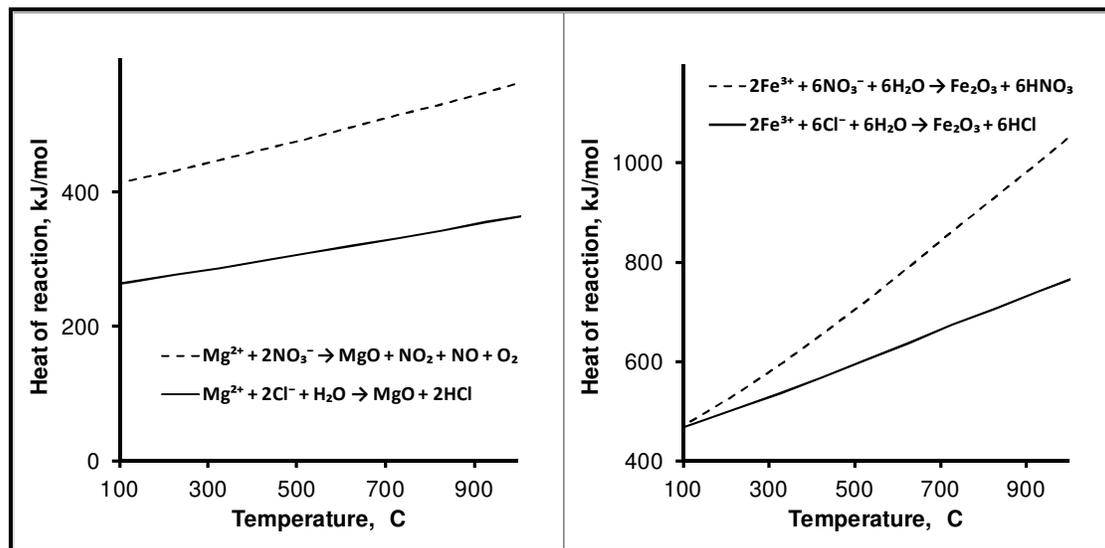
Figure 4 – Heats of reaction

The first graph in Figure 4 shows that the energy required to thermally decompose magnesium nitrate is substantially more than the energy required to hydrolyse magnesium chloride. The second graph shows that hydrolysis of ferric nitrate requires more energy than hydrolysis of ferric chloride. While this may be simplistic, it does begin to explain the differences between the energy balances of the nitrate and the chloride circuits.

Another consideration in comparing the energy consumptions of the chloride and nitrate circuits is that in the nitrate circuit magnesium oxide is recycled to precipitate aluminium, nickel and cobalt. The recycled magnesium oxide reverts to magnesium nitrate and that magnesium nitrate is re-decomposed to nitrogen oxides and magnesium oxide. The recycle of magnesium oxide increases the amount of magnesium nitrate decomposed, hence raising the energy demand in that part of the nitrate circuit.

The process models calculate very low losses of chloride and nitrate from the respective circuits. In both circuits, the losses are small amounts in the residues and products. The nitrate models predict a make-up acid of 0.03 kg of nitric acid per tonne of dry feed and the chloride models predict an acid make-up of 0.1 to 0.2 kg of HCl per tonne of dry feed. At those levels the cost of the make-up acid is trivial. However, the Direct Nickel web site[11] lists an overall consumption of 30 kg of nitric acid per tonne of ore. This is orders of magnitude greater than the make-up calculated in this exercise. If the actual make-up of nitric acid is of the order of 30 instead of 0.03 kg per tonne of ore, and assuming the nitric acid cost used in this exercise, that would raise the variable cost by about $1.1 per pound of nickel plus cobalt produced. For limonite, that would make the nitrate circuit more expensive than the sulphate circuit. A crucial part of the nitrate circuit, therefore, is the acid regeneration stage. An overall make-up of 30 kg of HNO_3 per tonne of ore translates to a nitrogen capture of just over 99.8 percent of the NO_x from the thermal decomposition of magnesium nitrate. The process models developed in this exercise assume total conversion of the NO_x from the thermal decomposition of magnesium nitrate, to nitric acid. This would seem to be an aspect of the nitrate circuit that merits the appropriate attention (if it has not already…).

A similar argument can be made about the chloride circuit, of course. A difference between the chloride circuit and the nitrate circuit, though, is that in the chloride circuit hydrochloric acid is not decomposed and reconstituted as is the case in the nitrate circuit. In the chloride circuit the recovery of acid depends on efficient scrubbing of the various vapour streams, which is affected by the amounts of steam condensed with the acid in the scrubbers. More water condensed means better acid capture, but that water has to be re-evaporated, leading to a trade-off between acid loss and energy cost. In this exercise, the acid capture has been assumed to be efficient, as has the reconstitution of nitric acid from the nitrogen oxides. These assumptions would need to be verified, should these circuits ever be considered for any real project.

In reality, other aspects of the three processes would also need to be considered, especially the capital expenditure. Three recent HPAL plants, (Ravensthorpe, Goro and Ambatovy) all came in with expenditures of >$3 billion for plants producing in the order of 50 000 tonnes of nickel. On its website, Direct Nickel quotes $500-600 million for a plant producing 20 000 tonnes of nickel, which extrapolates to $0.8-1.0 billion for a 50 000 tonne plant.[12] Order of magnitude capital cost estimates for a Neomet plant are of the same magnitude as the Direct Nickel estimate. The atmospheric processes appear, at this level of estimate, to have a clear capital advantage over the HPAL option.

Whilst chloride plants have, and continue to be, operated commercially, there are no commercial large-scale operations using nitric acid. Noranda operated the Brenda Leach Process, employing a high temperature (105-110°C), high-strength chloride ($CaCl_2$, NaCl, HCl) atmospheric leach of copper-molybdenum sulphide concentrates until the mine shut down in the 1990s.[13] Xstrata (Falconbridge) operates a chloride process at its nickel-cobalt refinery in Kristiansand, Norway, which was initially a hydrochloric acid leach, but more recently a chlorine leach.[14,15,16] These and other plants such as those operated by Jinchuan[17], Sumitomo[18] and SLN[19] in a mixed chloride-sulphate medium, demonstrate that chloride-based circuits are perfectly feasible, and that any material-handling issues associated with a chloride environment can be and are being overcome.

Nitrate plants are generally small-scale, such as for silver refining or the production of molybdic oxide. A problem in operating nitrate processes is the tendency for "runaway" reactions, particularly during leaching if there are minerals present that catalyze the decomposition of nitric acid. Balancing that, the issue of materials of construction may well be simpler for a nitrate circuit than for a chloride circuit.

There are also the minor elements, notably calcium, sodium, potassium and manganese, which have not been considered in this exercise. In sulphate circuits, these are easily handled, generally reporting to a magnesium sulphate effluent, although manganese can co-precipitate with the MHP.

In chloride circuits, all of these elements report through to the magnesium hydrolysis stage. Calcium is easily controlled via sulphate addition, and both potassium and sodium can be selectively crystallized from the magnesium hydrolysis filtrate, whereas manganese is conveniently oxidized to MnO_2.

In nitrate circuits, these impurities will behave similarly to their behavior in the chloride circuit, except that manganese will partially deport to the MHP product. Calcium nitrate would deport to the MgO product, representing a loss of nitrate and degrading the MgO purity, if calcium cannot be controlled by sulphate addition. Potassium and sodium could be problematic, as they decompose at a lower temperature than magnesium nitrate to the nitrite (a factor made use of in gunpowder), and could also represent a loss of nitrogen to the MgO product.

Finally, there is the issue of ferric nitrate, present in the leach solution in large quantities. Previous testwork has been reported showing that copper could be hydrolysed from silver nitrate solutions at 180 °C.[20] Although not reported at that time, ferric nitrate was found to be unpredictable in its behaviour, which is consistent with its description in its MSDS that it can explode when heated.[21] This is not to say that it will do so, just that there is the potential as with many nitrate solutions, and therefore that there might be risks associated with the use of nitrates which are not present with chloride or sulphate.

CONCLUSION

From the numbers emanating from the process models developed for this study, it would seem that both the chloride and the nitrate circuits examined have appreciably lower variable operating costs than the sulphate circuit. The reason is that the chloride and the nitrate circuits regenerate and recycle the acid used in the leach, while the sulphate circuit does not. The largest component of the variable cost in the nitrate and chloride circuits is energy. In this exercise natural gas was assumed as a heating utility, at a cost of $4/GJ. Since this is the dominant variable cost, the economics of any real project using either chloride or nitrate chemistry would be sensitive to the cost of energy.

The numbers generated in this exercise give the chloride process a somewhat lower variable cost than the nitrate process, because the chloride process has a lower evaporation load and therefore a lower energy demand. However, if the nitrate circuit can be modified to use less water, its energy cost would be reduced significantly.

HPAL technology has reached commercial operation, and therefore the problems associated with its operation are well known and understood. This is not so for the chloride and nitrate processes, which are in the development stage. There may be more comfort with chloride, since there are large-scale commercial operations using most aspects of the process. The key component of the chloride process, hydrolysis, has been extensively tested by Neomet. It has also been scaled up by a factor of five, twice. Similarly, the key aspects of the nitrate process are being piloted in Perth.

Downward pressure on the cost of nickel production is unlikely to diminish. New nickel extraction technology that offers lower costs must be of value to the industry and to society. Both the chloride and the nitrate processes examined in this exercise appear to appreciably reduce the cost of nickel production, at least relative to HPAL technology. One or both of these processes may well unlock laterite nickel that would otherwise remain in the ground.

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REFERENCES

1. Davidson, Vanessa. Nickel Market Overview – The Supply Response. INSG Meeting, October 2006

2. U.S. Geological Survey, Mineral Commodity Summaries, January 2003

3. Kyle, Jim. Nickel Laterite Processing – Where To Next? Alta 2010 Nickel/Cobalt/Copper Conference, Perth, Australia, May 2010

4. Botsis, Nicole. Nickel Laterite Characterization. Alta 2008 Nickel/Cobalt Conference, Perth, Australia, June 2008

5. Cox, D. M. Independent Geological Report on the Nickel Laterite Resource at Agata North Laterite Project Area, http://www.mindoro.com/i/pdf/AGATA_NI43-101_dmc080920.pdf

6. Harris, B. and White, C. Recent Developments in the Chloride Processing of Nickel Laterites. Alta 2011, Perth, Australia, May 2011

7. McCarthy, F. and Brock, G. The Direct Nickel Process, Continued Progress on the Pathway to Commercialization. Alta 2011, Perth, Australia, May 2011

8. Drinkard, Jr. William, US patent 6,264,909 B1. Nitric Acid Production and Recycle, July 24, 2001.

9. Direct Nickel Pty Limited, web site http://www.directnickel.com/progress/economics.htm accessed April 12, 2012.

10. .   Jennings, P.H., Stanley, R.W. and Ames, H.L., "Development of a Process for Purifying Molybdenite Concentrates",. in Proceedings of Second International Symposium on Hydrometallurgy, (D.J.I. Evans, Editor), AIME, New York (1973), p. 868.

11. .   Thornhill, P.G. Wigstol, E. and Van Weert, G., "The Falconbridge Matte Leach Process", Journal of Metals, 23(7), (1971), p. 13.

12. .   Stensholt, E.O., Zachariasen, H. and Lund J.H., "The Falconbridge Chlorine Leach Process", in Nickel Metallurgy, Volume I - Extraction and Refining of Nickel, (E. Ozberk and H. Marcusson, Editors), CIM Montreal, (1986), p. 442.

13. .   Stensholt, E.O., Zachariasen, H., Lund, J.H. and Thornhill, P.G., "Recent Improvements in the Falconbridge Nickel Refinery", in Extractive Metallurgy of Nickel and Cobalt, TMS AIME, Warrendale, (1988), p. 403.

14. .   Yang Yuhua and Meng Xianxuan, "Operating Practice and Technical Developments in Nickel Refining and Cobalt Recovery at Jinchuan Non-Ferrous Metal Company", in Electrometallurgical Plant Practice, (P.L. Claessens and G.B. Harris, Editors), Proceedings of the 20th Annual CIM Hydrometallurgical Meeting, Pergamon Press (1990), p.253.

15. .   Fujimori, M., Ono, N., Itasako, S. and Fukui, I., "Solvent Extraction in Sumitomo's Cobalt Refining Process", Paper presented at Cobalt 80, 10th Annual CIM Hydrometallurgical Meeting, Edmonton, Alberta, (October 26-28, 1980).

16. .   Demarthe, J.M., Gandon, L. and Goujet, M., "Hydrometallurgical Method For Treating Nickel Mattes", Canadian Patent 1 126 201, to Société Métallurgique le Nickel-SLN, (22 June, 1982).

17. .   Bryn Harris, Carl White, George Demopoulos and Levente Becze, Recovery of Metal Oxides and Associated Acid from Process Solutions Using Water as Reagent, Presented at ALTA Copper 2008, Perth, Australia, June 19-20, 2008.

18. Ferric nitrate MSDS, http://isites.harvard.edu/fs/docs/icb.topic869246.files/ironnitrate.htm, accessed April 12, 2012.