

# NICKELLIFEROUS PYRRHOTITE – ANOTHER SOURCE OF NICKEL IF IT CAN BE EXTRACTED ECONOMICALLY

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## ABSTRACT

This paper presents the results of process modeling studies on the extraction of nickel from nickelliferous pyrrhotite. A numerically rigorous mass/energy balance was prepared for each of four circuits – two using fairly conventional sulphate chemistry and two using novel chloride chemistry. The various reagent and utility consumptions were extracted from the mass/energy balances and used in conjunction with estimated unit prices to calculate the variable portion of the operating cost associated with each circuit. The results of the exercise are compared and discussed. The main conclusion is that the novel chloride technology appears to be significantly superior to the sulphate circuits examined. Once the chloride technology has been proven, the variable cost of impounding nickelliferous pyrrhotite could become greater than the variable cost of processing it.

## 1. INTRODUCTION

Although most of the unmined nickel in the world is in laterites, sulphides nevertheless account for about sixty percent of the world's total nickel production (Davidson, 2006). Of the 1378 kt of nickel produced in 2008 (INSG, 2009), about 800 kt came from sulphide deposits. Typically, the nickel in sulphide deposits occurs as pentlandite, some of which is too finely disseminated in pyrrhotite for economic flotation to produce a concentrate that is suitable for smelting and in Canada about twenty percent of the total sulphide nickel mined is rejected as a pyrrhotite fraction containing 0.6 to 0.8 percent nickel (Agar, 1991). For 2008, that translates to about 200 kt per year of sulphide nickel mined, partially processed and then dumped as nickelliferous pyrrhotite. Recovering that nickel would add substantially to the global supply of nickel. However, the challenge would be to recover it cost effectively. Furthermore, rejection of this pyrrhotite phase generates reactive tailings which incur an appreciable cost in that they have to be disposed of appropriately in dedicated and secure impoundment areas, which will need to be monitored in perpetuity.

This paper presents and examines the results of four process modelling studies in which nickel is extracted from nickelliferous pyrrhotite, two based on conventional sulphate chemistry and the other two on novel concentrated chloride chemistry.

The generic composition shown in Table 1 was used to represent nickelliferous pyrrhotite in this exercise. In this simplified representation, NiS represents the nickel in the pyrrhotite, the MgO represents acid-consuming gangue and silica represents inert gangue.

**Table 1 – Model pyrrhotite composition, mass %**

NiS	1.2
Fe <sub>7</sub> S <sub>8</sub>	68.3
MgO	6.1
SiO <sub>2</sub>	24.3

## 2. CIRCUITS EVALUATED

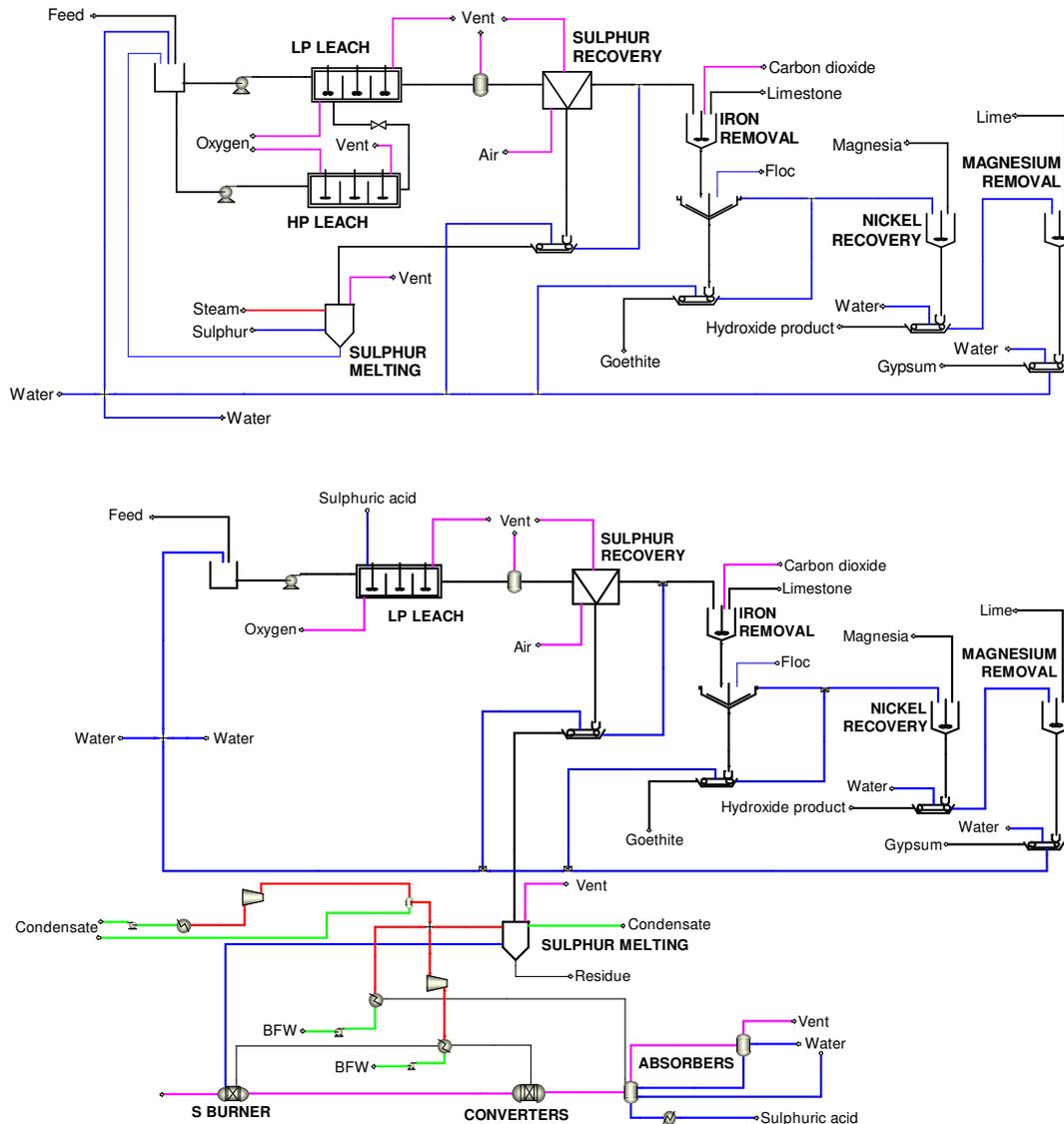
Nickel can be produced as metal or as an intermediate product such as precipitated sulphide or hydroxide. For this exercise, a nickel hydroxide or oxide intermediate product was arbitrarily selected in order to have a common product for easier comparison. Once produced, the intermediate product would be processed elsewhere in the same way, regardless of its origin.

### 2.1 SULPHATE

Two sulphate-based circuits were examined in this study, one producing elemental sulphur and the other sulphuric acid. The two circuits are illustrated in Figure 1. (The dashed lines represent energy flows.) The circuit producing elemental sulphur contains high-pressure and low-pressure oxidative leaching, precipitation of residual iron, precipitation of nickel hydroxide, precipitation of magnesium hydroxide and recycling of the remaining water. The high-pressure leach treats a portion of the feed to generate the sulphate required in the low pressure leach. In the circuit producing sulphuric acid, the high pressure leach is not required because the sulphate is supplied from some of the acid produced.

In the circuit producing elemental sulphur, the slurry leaving the high-pressure leach goes to the low-pressure leach. In both circuits, the slurry leaving the low-pressure leach passes through a step in which the elemental sulphur is recovered (flotation was assumed for simplicity, but there are other methods such as hot filtration or dissolution in an organic solvent) and the remaining slurry is neutralized with limestone to precipitate residual ferric iron. The model assumes that all the ferrous iron is oxidized to ferric iron in the low-pressure leach, but if some ferrous iron were to remain it could be oxidized in this neutralization step. After removal of the precipitated iron along with any inert gangue, the remaining solution is contacted with magnesium oxide to precipitate nickel hydroxide, which is removed, washed and despatched. Magnesium is precipitated from the remaining solution using lime, leaving (gypsum-saturated) process water for recycle. The resulting magnesium hydroxide and gypsum are removed, washed and impounded.

In the circuit producing sulphuric acid, the sulphur is melted and filtered, then burned to sulphur dioxide that is converted to sulphur trioxide and absorbed into concentrated sulphuric acid. The energy released is captured as steam and used to melt the sulphur from the leach. The remaining steam is expanded through a turbine to generate power.



**Figure 1 – Sulphate circuits**

The sulphate chemistry is illustrated by the stoichiometry shown in Table 2. The objective of the high-pressure leach is to generate the sulphate required in the low-pressure leach and the objective of the low-pressure leach is to solubilise all of the nickel while rejecting most of the iron as precipitated goethite ( $\text{FeOOH}$ ). That is achieved by limiting the amount of sulphate allowed into the low-pressure leach, which in turn sets the split of the incoming pyrrhotite between the high- and low-pressure leaches, in the circuit making elemental sulphur. In the circuit making sulphuric acid, it is achieved by manipulating the amount of acid added to the leach.

In the elemental sulphur circuit, whether the sulphate leaves the high pressure leach as ferric sulphate or as sulphuric acid does not affect the overall stoichiometry - both ways, the sulphate ends up as nickel and magnesium sulphate, along with residual ferric/ferrous sulphate.

These two sulphate circuits are deliberately optimistic in this exercise – the underlying objective of the exercise was to determine whether or not the chloride chemistry could lead to significantly lower operating costs, and being optimistic with the sulphate circuits made the comparison harder on the chloride circuits.

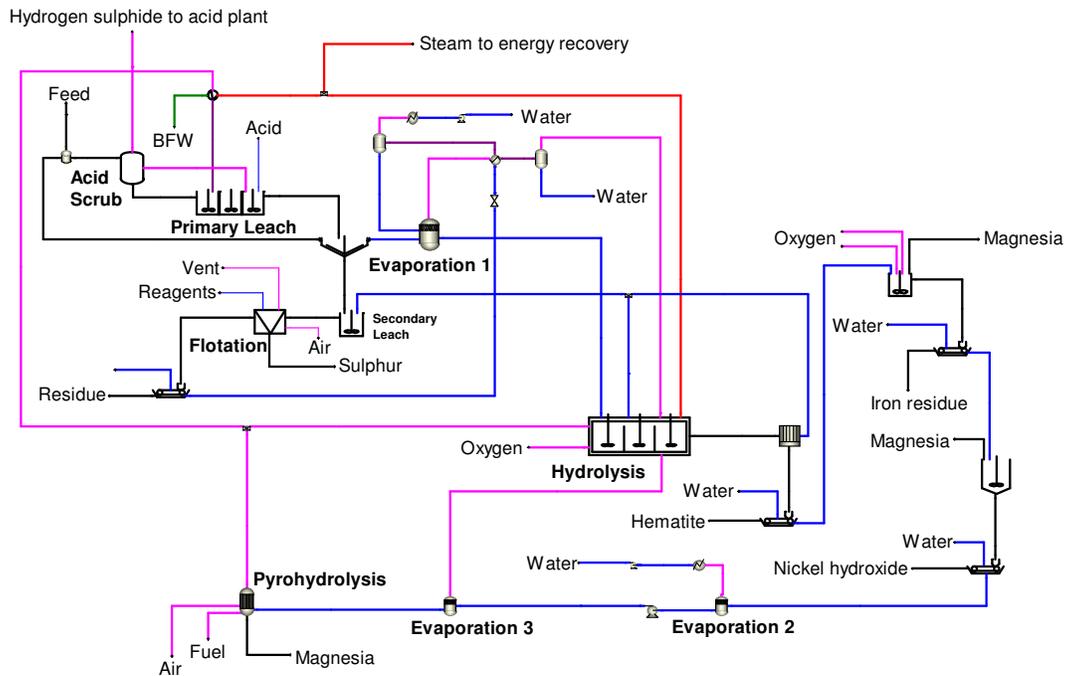
**Table 2 – Sulphate circuit stoichiometry**

<b>High pressure leach</b>
$\text{NiS} + 2\text{O}_2 \rightarrow \text{Ni}^{2+} + \text{SO}_4^{2-}$ $2\text{Fe}_7\text{S}_8 + 34\frac{1}{2}\text{O}_2 + 36\text{H}_2\text{O} \rightarrow 7\text{Fe}_2\text{O}_3 + 16\text{SO}_4^{2-} + 24\text{H}_3\text{O}^+$ $2\text{Fe}_7\text{S}_8 + 34\frac{1}{2}\text{O}_2 + \rightarrow 10\frac{2}{3}\text{Fe}^{3+} + 16\text{SO}_4^{2-} + 1\frac{1}{3}\text{Fe}_2\text{O}_3$ $\text{MgO} + 2\text{H}_3\text{O}^+ \rightarrow \text{Mg}^{2+} + 3\text{H}_2\text{O}$
<b>Low pressure leach (Ferric sulphate and oxygen)</b>
$\text{NiS} + 2\text{Fe}^{3+} \rightarrow \text{Ni}^{2+} + 2\text{Fe}^{2+} + \text{S}$ $\text{Fe}_7\text{S}_8 + 14\text{Fe}^{3+} \rightarrow 21\text{Fe}^{2+} + 8\text{S}$ $2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 2\text{H}_3\text{O}^+ \rightarrow 2\text{FeOOH} + \text{H}_2\text{O}$ $\text{MgO} + 2\text{H}_3\text{O}^+ \rightarrow \text{Mg}^{2+} + 3\text{H}_2\text{O}$
<b>Low pressure leach (Sulphuric acid and oxygen)</b>
$\text{Fe}_7\text{S}_8 + 14\text{H}_3\text{O}^+ + 3\frac{1}{2}\text{O}_2 \rightarrow 7\text{Fe}^{2+} + 8\text{S} + 21\text{H}_2\text{O}$ $2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 2\text{H}_3\text{O}^+ \rightarrow 2\text{Fe}^{3+} + 3\text{H}_2\text{O}$ $\text{NiS} + 2\text{Fe}^{3+} \rightarrow \text{Ni}^{2+} + 2\text{Fe}^{2+} + \text{S}$ $2\text{Fe}^{3+} + 10\text{H}_2\text{O} \rightarrow 2\text{FeOOH} + 3\text{H}_3\text{O}^+$ $\text{MgO} + 2\text{H}_3\text{O}^+ \rightarrow \text{Mg}^{2+} + 3\text{H}_2\text{O}$
<b>Residual iron precipitation</b>
$2\text{H}_3\text{O}^+ + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{CO}_2 + 3\text{H}_2\text{O}$ $2\text{Fe}^{3+} + 3\text{CaCO}_3 + \text{H}_2\text{O} \rightarrow 2\text{FeOOH} + 3\text{Ca}^{2+} + 3\text{CO}_2$ $\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \leftrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
<b>Nickel precipitation</b>
$2\text{H}_3\text{O}^+ + \text{MgO} \rightarrow \text{Mg}^{2+} + 3\text{H}_2\text{O}$ $\text{Ni}^{2+} + \text{MgO} + \text{H}_2\text{O} \rightarrow \text{Ni}(\text{OH})_2 + \text{Mg}^{2+}$
<b>Magnesium precipitation</b>
$\text{Mg}^{2+} + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 + \text{Ca}^{2+}$ $\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \leftrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

## 2.2 CHLORIDE

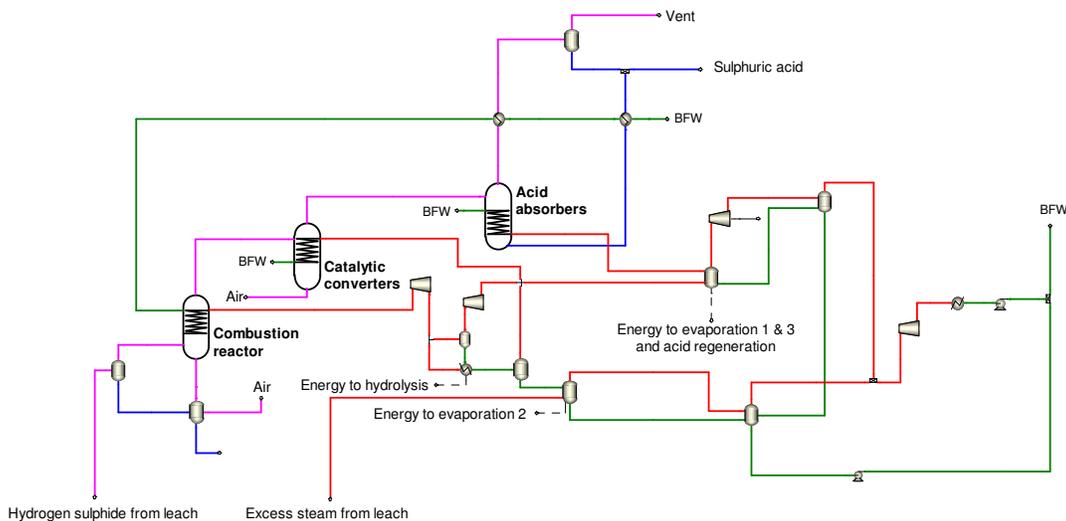
Two circuits based on chloride chemistry were examined. The hydrometallurgical part of the first chloride circuit examined is illustrated in Figure 2. This is an evolution of a circuit that was presented before (Dry, 2008), and is based on novel technology being developed by NMR360 Inc. for processing a variety of mineral feedstocks, including low-grade sulphide and oxide nickel deposits. In the present configuration, it comprises a non-oxidative primary leach in which the iron sulphide in the pyrrhotite is converted to ferrous chloride and hydrogen sulphide (plus some elemental sulphur), a secondary (oxidising) leach in which recycled ferric chloride is used to dissolve the nickel sulphide, an evaporative concentration stage, an oxidative hydrolysis stage in which ferrous and ferric chloride are converted to solid hematite and gaseous hydrochloric acid, a step in which residual iron is precipitated, precipitation of nickel hydroxide using magnesium oxide, and a pyrohydrolysis stage in which magnesium chloride is converted to magnesium oxide and hydrochloric acid. The hydrogen sulphide from the primary leach is converted to sulphuric acid in a conventional wet-gas acid plant. The hydrochloric acid from the hydrolysis and pyrohydrolysis

steps is recycled and the hematite is pure enough to be sold as iron ore or possibly into the iron pigment market.



**Figure 2 – Chloride circuit 1 (hydrometallurgy section)**

Figure 3 illustrates the wet-gas acid plant in which the hydrogen sulphide from the primary leach is converted to sulphuric acid and the energy released is recovered for use in the hydrometallurgical plant. The hydrogen sulphide is burned in air, the resulting sulphur dioxide is catalytically oxidized to sulphur trioxide that combines with the water produced to form concentrated (typically 93%) sulphuric acid.



**Figure 3– Chloride circuit (acid plant and energy recovery)**

The energy released by the combustion reaction is captured as high-pressure (56.6 Bar absolute) steam that is expanded to 31 Bar absolute through a turbine, generating power. Part of the 31 Bar steam is condensed to supply the energy needed by the hydrolysis stage of the chloride circuit and the rest is expanded to 12 Bar absolute, generating more power. The heat of reaction from the catalytic oxidation of sulphur dioxide and the formation of concentrated sulphuric acid is also

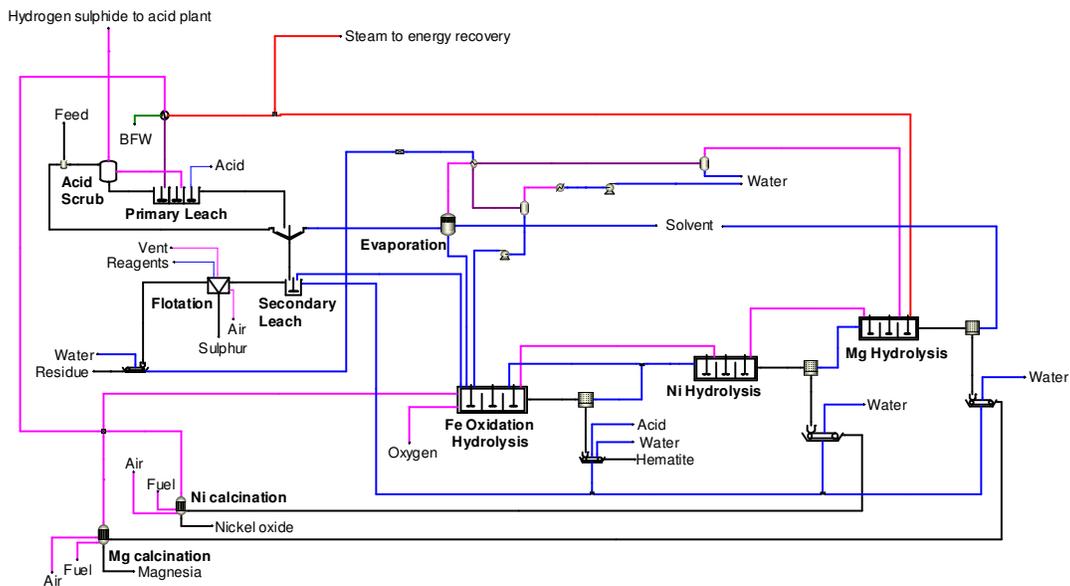
captured as medium-pressure steam (12 Bar absolute). Part of the 12 Bar steam is condensed to supply the energy needed in the evaporation stage and the rest is expanded twice more, to 0.6 Bar absolute then to 0.05 Bar absolute, to extract as much power as possible. The 0.05 Bar steam is condensed and the condensate recycled as boiler feed water.

The chemistry of the first chloride circuit is illustrated by the stoichiometry shown in Table 3. While the chemistry is conceptually simple the operating conditions are novel, in that the circuit makes use of high temperatures in places and atmospheric pressure throughout. It uses a high background concentration of chloride to substantially enhance the activity of hydrochloric acid in the primary leach, achieving virtually complete conversion of the pyrrhotite and a low level of residual acid. For the oxidative hydrolysis step to be carried out at atmospheric pressure, the normal boiling point of the solution must be high enough (about 175°C or hotter) for the endothermic hydrolysis of ferric chloride to occur, necessitating an evaporation step between the leach and the oxidative hydrolysis steps. That, plus the endothermic nature of the hydrolysis reaction, makes the overall energy balance important. The hydrolysis reaction that converts ferric chloride to gaseous hydrogen chloride and solid hematite also requires excess steam to purge away the HCl, otherwise the reaction does not proceed sufficiently. The amount of excess steam required is such that the steam and HCl leaving the hydrolysis stage is equivalent to 30 to 40 percent HCl, were it to be condensed.

**Table 3 – Chloride circuit 1 stoichiometry**

<b>Primary leach</b>
$\text{Fe}_7\text{S}_8 + 14\text{HCl} \rightarrow 7\text{Fe}^{2+} + 14\text{Cl}^- + 7\text{H}_2\text{S} + \text{S}$ $\text{MgO} + 2\text{HCl} \rightarrow \text{Mg}^{2+} + 2\text{Cl}^- + \text{H}_2\text{O}$
<b>Secondary leach</b>
$\text{Fe}_7\text{S}_8 + 14\text{Fe}^{3+} \rightarrow 21\text{Fe}^{2+} + 8\text{S}$ $\text{NiS} + 2\text{Fe}^{3+} \rightarrow \text{Ni}^{2+} + 2\text{Fe}^{2+} + \text{S}$ $\text{MgO} + 2\text{HCl} \rightarrow \text{Mg}^{2+} + 2\text{Cl}^- + \text{H}_2\text{O}$
<b>Oxidative hydrolysis</b>
$6\text{Fe}^{2+} + 1\frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4\text{Fe}^{3+}$ $2\text{Fe}^{3+} + 3\text{H}_2\text{O} + 6\text{Cl}^- \leftrightarrow \text{Fe}_2\text{O}_3 + 6\text{HCl}$
<b>Iron precipitation</b>
$2\text{H}_3\text{O}^+ + \text{MgO} \rightarrow \text{Mg}^{2+} + 3\text{H}_2\text{O}$ $2\text{Fe}^{3+} + 3\text{MgO} + \text{H}_2\text{O} \rightarrow 2\text{FeOOH} + 3\text{Mg}^{2+}$
<b>Nickel precipitation</b>
$2\text{H}_3\text{O}^+ + \text{MgO} \rightarrow \text{Mg}^{2+} + 3\text{H}_2\text{O}$ $\text{Ni}^{2+} + \text{MgO} + \text{H}_2\text{O} \rightarrow \text{Ni}(\text{OH})_2 + \text{Mg}^{2+}$
<b>Pyrohydrolysis</b>
$\text{Mg}^{2+} + 2\text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{MgO} + 2\text{HCl}$ $\text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2$

Figure 4 illustrates the second chloride circuit examined. This is the latest evolution of the novel technology being developed by NMR360 Inc. The acid plant, energy recovery and primary leach are as they were in the first chloride circuit. The secondary leach is similar, except that it receives ferric chloride from a slightly different point in the circuit. The radical shift in this circuit rests on the discovery of an inert solvent (confidential, patent pending) in which the oxidation of ferrous chloride and the hydrolysis of ferric chloride can be combined into a single unit operation, as well as enabling the base metals (nickel, in this case) to be captured as basic chlorides after complete conversion of the iron to hematite and hydrochloric acid, followed by rejection of magnesium as magnesium hydroxychloride.



**Figure 4 - Chloride circuit 2 (hydrometallurgy section)**

The solution from the primary leach is combined with recycled solvent and heated to 175°C. The steam evolved is used to partially evaporate the solution from the secondary leach (under reduced pressure) and both concentrated solutions are then oxidized with oxygen and hydrolyzed with steam, giving solid hematite and gaseous hydrochloric acid. The acid is combined with the hot gas from the calcination of the basic nickel chloride and the magnesium hydroxychloride and recycled to the primary leach.

The slurry leaving the iron hydrolysis stage is filtered hot and the hematite filter cake is washed twice, first with dilute hydrochloric acid to re-dissolve any co-precipitated basic nickel chloride, then with water. The washed hematite leaves the circuit and the combined wash filtrate goes to the secondary leach. A part of the oxidized solution, containing ferric chloride, is also recycled from the iron oxidation step to provide excess oxidant for the secondary leach. The hot primary filtrate is split, the bulk being recycled to the start of the iron oxidation and hydrolysis stage and a bleed contacted with more steam to convert the nickel chloride to basic nickel chloride and hydrochloric acid. The slurry is again filtered hot and the filter cake is washed with water, that wash filtrate also returning to the secondary leach. The hot filtrate from the nickel hydrolysis stage is heated to about 225°C and contacted with fresh steam to convert the magnesium chloride to magnesium hydroxychloride and hydrochloric acid. The basic nickel chloride and the magnesium hydroxychloride are calcined (separately) to oxides and the steam and hydrogen chloride evolved return to the primary leach. The energy required for these reactions comes from the combustion of natural gas (approximated as methane) in air. The hot flue gas containing the steam and acid is cooled to about 250°C before returning to the leach. The energy from this cooling step is used in the hydrolysis section.

The chemistry of the base metal and magnesium hydrolysis steps is illustrated by the stoichiometry shown in Table 4. The leach chemistry is as for the first chloride circuit.

### 3. RESULTS

Process models (mass/energy balances and vapour-liquid equilibrium calculations) of the circuits examined were constructed using commercially available process simulation software known as AspenPlus. The mechanics of that part of the exercise are omitted from this paper for brevity. The output of the process models covers nickel, iron, magnesium, calcium, sulphur and silica, oxygen, hydrogen, nitrogen and carbon (from the methane used to approximate the natural gas used as fuel). The purpose of the exercise was to calculate the consumptions of the various reagents and energy in the circuits modelled, then translate those numbers into variable costs per unit of nickel in the nickel product and compare the results for the four circuits.

**Table 4 – Divalent metal hydrolysis and calcination**

Nickel and magnesium hydrolysis
$3\text{Ni}^{2+} + 6\text{Cl}^- + 5\text{H}_2\text{O} \rightarrow \text{Ni}_3(\text{OH})_5\text{Cl} + 5\text{HCl}$
$\text{Mg}^{2+} + 2\text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{MgOHCl} + \text{HCl}$
<b>Calcination</b>
$\text{Ni}_3(\text{OH})_5\text{Cl} \rightarrow 3\text{NiO} + \text{HCl} + 2\text{H}_2\text{O}$
$\text{MgOHCl} \rightarrow \text{MgO} + \text{HCl}$
$\text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2$

In Canadian operations producing sulphide nickel concentrates, nickelliferous pyrrhotite and talc are rejected together. It would seem reasonable to suppose that, in appropriate cases, the nickelliferous pyrrhotite might be separated from the talc to reduce the level of acid consuming gangue. The studies presented here included varying the amount of acid consuming gangue (MgO) in the incoming feed, to see what effect this has on the calculated variable costs associated with recovering nickel from nickelliferous pyrrhotite.

At about 0.6 to 0.8 percent by mass, the nickel in nickelliferous pyrrhotite could be considered to be a minor element even though it remains the main element of commercial interest, and the iron and sulphur, being the major elements present, might also be targeted for revenue production. In the study assuming sulphate chemistry, one case assumes that elemental sulphur is produced and sold and the other case assumes that the elemental sulphur can be sensibly converted to sulphuric acid. The iron is rejected as goethite in the sulphate circuits and is not a saleable by-product, but rather something that has to be disposed of.

In the study assuming chloride chemistry, the sulphide sulphur is released as hydrogen sulphide and since the process itself is energy intensive, it is necessary to produce sulphuric acid and energy from the hydrogen sulphide, in order to close the overall energy balance. In the chloride circuits, the iron is rejected as highly pure hematite that is a saleable by-product.

### 3.1. SULPHATE

Table 5 lists the consumptions calculated, as tons per ton of nickel in the hydroxide intermediate, for the two cases examined. Table 6 lists the products and residues generated, again as tons per ton of nickel in the hydroxide intermediate. As might be expected, the differences between these two cases are small because they employ essentially the same chemistry. The biggest difference in reagent consumption that of pure oxygen. In the case making elemental sulphur, the high-pressure leach consumes more oxygen to convert part of the sulphide sulphur to the sulphate needed in the low-pressure leach. In the case making sulphuric acid, that oxygen comes from air consumed in the acid plant.

Table 7 lists the unit costs assumed and the variable costs calculated for the two circuits using sulphate chemistry.

**Table 5 – Consumption, t/t Ni (Sulphate)**

Input	Sulphur	Sulphuric acid
Nickelliferous pyrrhotite	125.3	125.3
Oxygen, tons 100% O <sub>2</sub>	47.0	22.6
Limestone, tons 100% CaCO <sub>3</sub>	14.0	20.0
Magnesia, tons 100% MgO	0.85	0.86
Lime, tons 100% CaO	11.6	11.6
Water, tons	220.8	213.0

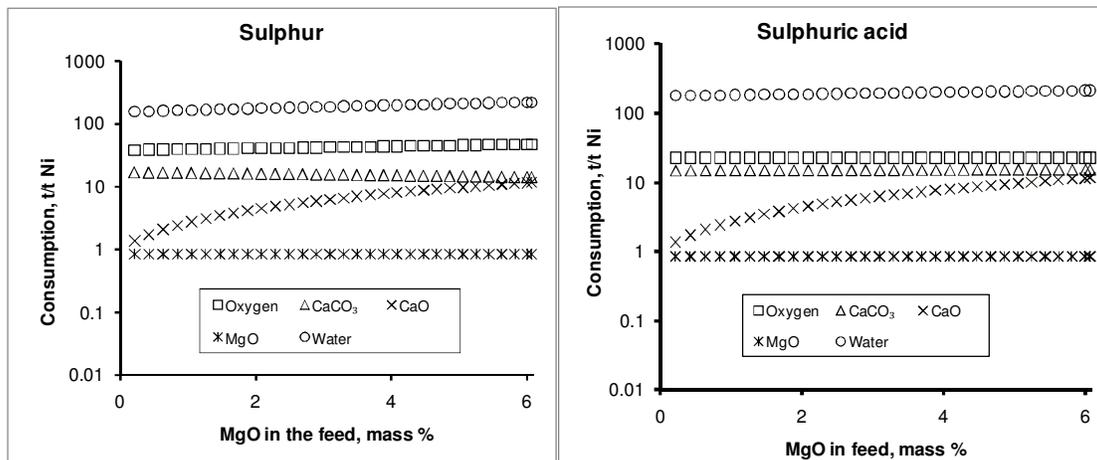
**Table 6 – Production, t/t Ni (Sulphate)**

Product	Sulphur	Sulphuric acid
Iron residue plus gangue	134.3	137.7
Elemental sulphur	23.1	-
Sulphuric acid	-	69.0
Surplus power, MWh/t Ni	-	7.5
Gypsum and Mg residue	48.1	48.0

**Table 7 – Variable costs, \$/lb Ni (Sulphate)**

	Unit cost	Sulphur	Sulphuric acid
Feed pyrrhotite	\$5.00/t	0.28	0.28
Oxygen	\$10.00/t	0.21	0.10
Limestone	\$50.00/t	0.32	0.35
Magnesia	\$150.00/t	0.06	0.06
Lime	\$150.00/t	0.79	0.79
Fresh water	\$0.25/t	0.03	0.02
Residue disposal	\$5.00/t	0.41	0.42
Total calculated variable cost		2.10	2.03

One of the factors influencing the variable cost associated with processing nickelliferous pyrrhotite is the amount of acid consuming gangue in the feed, which could conceivably be reduced – either in the flotation circuit in which the pyrrhotite is generated or perhaps by separate flotation if the feed is recovered from a dump. The technical feasibility of doing that is not addressed in this paper, merely its impact, assuming it to be possible. Figure 5 shows the effect of the MgO content of the feed on the consumptions of reagents and water. As might be expected, the consumption of lime increases as MgO in the feed rises, simply because lime is used to precipitate magnesium.



**Figure 5 – Consumption versus MgO in the feed, t/t Ni (Sulphate)**

Figure 6 shows the variable costs calculated from the consumptions and the unit costs listed in Table 7, against the MgO content of the feed. Again, not surprisingly, the numbers are similar for both cases.

In the case making sulphuric acid, two by-products are generated, namely concentrated sulphuric acid and energy. If the acid cannot be sold or otherwise disposed of, this option would not be viable. Assuming that the acid can be sold, and accepting the unit costs in Table 7, it would appear

that the circuit making sulphuric acid is slightly better in terms of the variable cost and appreciably better when the sale of by-products is considered, than the one making elemental sulphur. Of course, this is only a theoretical exercise – in reality the preferable option would be determined by other factors as well, particularly capital cost and market considerations. Given that caveat, though, making and selling sulphuric acid could add appreciably to the revenue emanating from the processing of nickelliferous pyrrhotite. As the global economy recovers, increasing demand for sulphuric acid from the base metals and fertilizer industries, along with declining sulphur production and potential extra demand for sulphuric acid from new ethanol plants (Graff, 2009) could well generate stable demand, along with reasonable prices, for sulphuric acid and for elemental sulphur. Table 8 lists the calculated extra revenue, should the sulphur, sulphuric acid and surplus power be sold at the prices shown. These numbers may well be too low, but were thought adequate for this work. The revenue to be had from sulphuric acid, in particular, would appear to be significant.

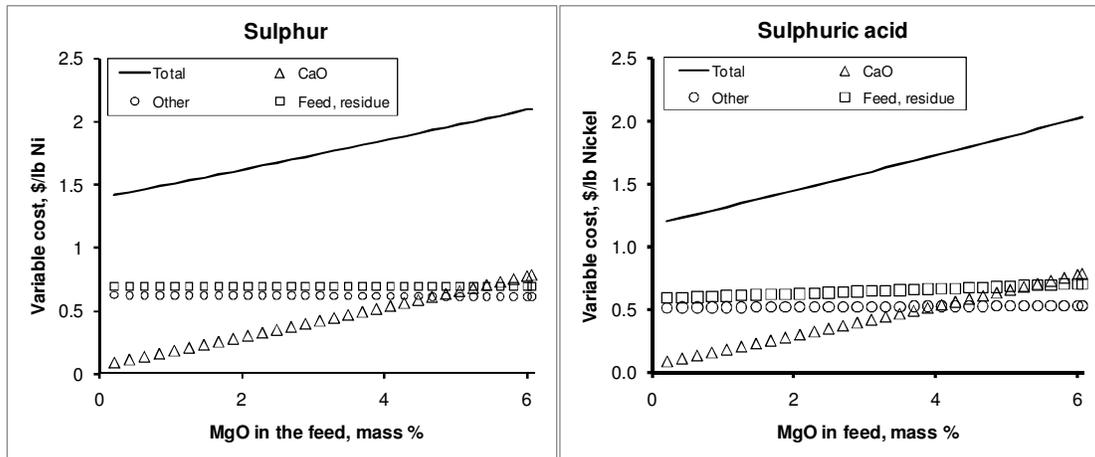


Figure 6 – Variable cost versus MgO in the feed, \$/lb Ni (Sulphate)

Table 8 – Revenues from by-products, \$/lb Ni (Sulphate)

By-product	Selling price	Additional revenue, \$/lb Ni	
		Sulphur	Acid
Elemental sulphur	\$20/t	0.21	-
Sulphuric acid	\$75/t	-	2.35
Surplus power	\$50/MWh	-	0.28

### 3.2. CHLORIDE

**Error! Not a valid bookmark self-reference.** lists the consumption numbers calculated for the chloride circuits and Table 10 lists the overall recovery of nickel and the amounts of residue, hematite, sulphuric acid, elemental sulphur and surplus power produced. The small differences are due to the slightly different nickel recoveries - a small loss of soluble nickel to the iron residue in circuit 1 lowers the overall nickel recovery slightly.

Table 9 – Consumption, t/t Ni (Chloride)

Material consumed	Circuit 1	Circuit 2
Nickelliferous pyrrhotite	125	125
Hydrochloric acid, tons 100% HCl	0.64	0.19
Oxygen, tons 100% O <sub>2</sub>	9.9	8.1
Fresh water, tons	410	312
Natural gas, tons	3.5	1.2

The reason for circuit 1 producing so much more excess power than circuit 2 is that in circuit 1 the magnesium enters the pyrohydrolysis step as a brine and the associated water has to be evaporated. In circuit 2 the magnesium is rejected as solid MgOHCl that is calcined to MgO, so much less water needs to be evaporated at that point in the circuit. That is also why circuit 1 consumes almost three times the fuel that circuit 2 consumes. The extra steam raised in circuit 1 ends up in the energy recovery section, and the associated energy from the extra fuel consumed emerges as more surplus power.

**Table 10 - Production, t/t Ni (Chloride)**

Product	Circuit 1	Circuit 2
Nickel recovery to product	99.1%	99.8%
Leach and iron residue	34.0	30.5
Hematite	71.4	73.8
Sulphuric acid, tons 100% H <sub>2</sub> SO <sub>4</sub>	91.3	90.7
Elemental sulphur	4.8	4.8
Surplus power, MWh/t Ni	41.5	26.5

The calculated variable costs, listed in Table 11, are dominated by the contributions for feed, fuel and hydrochloric acid.

**Table 11 – Variable costs, \$/lb Ni (Chloride)**

Item	Unit cost	Circuit 1	Circuit 2
Feed pyrrhotite	\$5.00/t	0.29	0.28
Hydrochloric acid	\$1000/t	0.23	0.09
Oxygen	\$10.00/t	0.04	0.04
Fresh water	\$0.25/t	0.05	0.04
Residue disposal	\$5.00/t	0.08	0.07
Fuel	\$375/t	0.60	0.21
Total calculated variable cost		1.28	0.72

Of the two chloride circuits, the newer one (circuit 2) appears to have a distinct advantage over the older one. The reason is that the inert solvent enables essentially complete oxidation and hydrolysis of the iron chloride in a single pass, as well as hydrolysis of the nickel and magnesium. This causes the newer circuit to evaporate and condense substantially less water than the older circuit, which reduces the fuel demand.

**Error! Not a valid bookmark self-reference.** lists the main losses of chloride as percentages of the fresh hydrochloric acid consumed. These losses arise from incomplete washing of the various solids and losses of HCl to the vapour phase during evaporation, putting chloride into the process water.

**Table 12 – Distribution of chloride losses, %**

Source	Circuit 1	Circuit 2
Leach residue	32	46
Hematite	0	3
Process water	65	51

Even with this loss, which could be reduced by more thorough washing and by changing the configuration in the evaporation section, the variable costs calculated for the chloride circuits are significantly lower than the variable costs calculated for the two sulphate circuits. Assuming that the

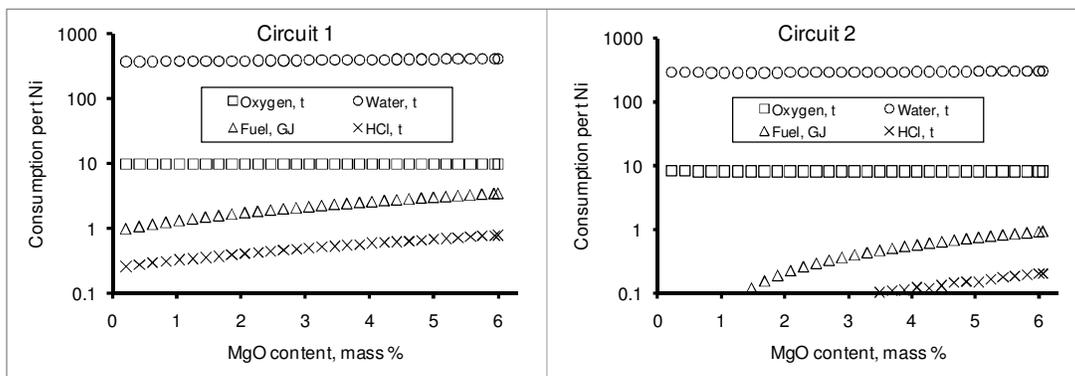
chloride losses to the process water can be eliminated brings the calculated variable cost to \$1.13 for circuit 1 and \$0.67 per pound of nickel, respectively, for circuits 1 and 2.

**Error! Reference source not found.** lists the calculated extra revenue to be had from the by-products of the chloride circuits, for the selling prices shown. In this case the revenue from the by-products might even approach that from nickel (assuming \$5/lb for nickel), effectively doubling the value of the feed material.

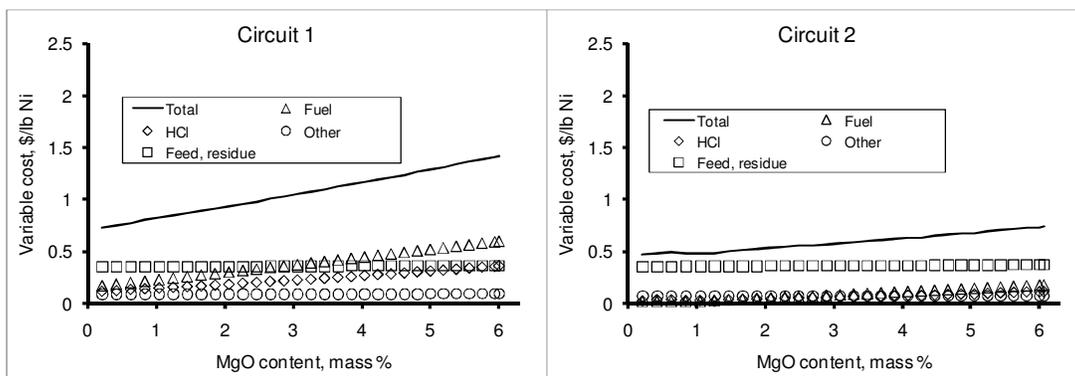
**Table 13 – Revenues from by-products, \$/lb Ni (Chloride)**

By-product	Selling price	Additional revenue \$/t Ni	
		Circuit 1	Circuit 2
Hematite	\$50/t	1.62	1.68
Sulphuric acid	\$75/t	3.11	3.09
Elemental sulphur	\$20/t	0.04	0.04
Surplus power	\$50/MWh	0.94	0.30

Figure 7 shows how the amount of MgO in the feed affects the consumption numbers and Figure 8 shows how the MgO affects the calculated variable costs for the two chloride circuits. It would seem that reducing the level of magnesium oxide in the feed, if this can be done, would reduce the variable cost appreciably.



**Figure 7 – Consumptions versus MgO in the feed (Chloride)**



**Figure 8 – Variable costs versus MgO in the feed (Chloride)**

**4. EVALUATION**

Variable operating costs are only a part of the economics associated with the potential recovery of nickel from nickelliferous pyrrhotite. The other cost elements are the fixed costs and the capital cost, which have not been determined for a specific example of processing nickelliferous pyrrhotite. However, in previously published work on the processing of low grade laterite (Harris et al., 2009), the cost for consumables and manpower for a laterite facility producing 50 kt/y of nickel was estimated at \$11 million per year. That work assumed a base case feed containing 0.75 mass percent nickel, which is similar terms of nickel to the feed shown in Table 1. Table 14 shows the capital costs from that study, alongside very crudely extrapolated costs for the circuits examined in this work – merely removing the process equipment not required in this exercise.

Using these highly crude estimates of the capital cost for each case studied, a fixed operating cost of \$11 million per year, variable costs as listed in Table 7 and Table 11, by-product credits as listed in Table 8 and **Error! Reference source not found.**, a tax rate of 20 percent, capital spent equally in years one and two, full fixed costs from year two onwards, production starting at 25% in year three, 50% in year 4, 75% in year 5 and 100% thereafter and assuming a design nickel production of 50 kt per year gives the indicative 20-year internal rates of return listed in Table 15. To “compensate” for the highly crude level of the capital cost guesstimate, Table 15 lists the calculated internal rates of return at half the capital costs listed in Table 14, the numbers as listed and twice the capital costs listed.

**Table 14 – Capital cost breakdown, \$ million (based on Harris et al., 2009)**

Process equipment	Laterite	Sulphate		Chloride
		Sulphur	Acid	
Mining Equipment	60	60	60	60
Ore Preparation Storage and Handling	177	177	177	177
Leach	90	90	90	90
Evaporation/Hydrolysis	127			127
Purification	15			
IX/SX	171			
EW	72			
Evaporation	12			12
Sulphur Burner/Acid Plant	162		162	162
Power Plant	270		270	270
Reagents Handling	10	10	10	10
Utilities and Auxiliaries	30	30	30	30
Direct Equipment Costs	1196	367	799	938
<b>Direct Installed Costs (Factor = 2)</b>	<b>2392</b>	<b>734</b>	<b>1598</b>	<b>1876</b>
EPCM (12% Installed Cost)	287	88	192	225
Owner Costs (4% Installed Cost)	96	29	64	75
Spares and Maintenance (5% DEC)	120	37	80	94
Transportation (12% DEC)	287	88	192	225
Chemicals, initial fill (3% DEC)	72	22	48	56
<b>Total Indirect Costs</b>	<b>622</b>	<b>623</b>	<b>624</b>	<b>625</b>
<b>Total capital cost</b>	<b>3014</b>	<b>1357</b>	<b>2222</b>	<b>2501</b>
Contingency (15%)	452	204	333	375
<b>Total Capital Investment</b>	<b>3466</b>	<b>1561</b>	<b>2555</b>	<b>2876</b>

It could also be argued that there is a cost of “doing nothing” in the case of nickelliferous pyrrhotite. Since the pyrrhotite is a reactive material, it would oxidize in a tailings facility, producing ferric sulphate that would need to be neutralized to prevent heavy metal contamination of the ground water. Assuming that limestone could be used for this leads to a requirement of 51.5 tons of CaCO<sub>3</sub> per ton of nickel in the nickelliferous pyrrhotite assumed for this exercise. At \$50 per ton of limestone, that translates to \$1.17/lb for the nickel impounded. This is still below the totals shown in Table 7, on the strength of which “doing nothing” might be considered viable if the sulphate chemistry were the only contender. In the case of the chloride chemistry, however, the variable cost of the second circuit is appreciably below the limestone cost of the “do nothing” scenario. The lower of the two IRR values for each circuit in Table 15 was calculated using the fixed, variable and capital costs and the revenues for that circuit. The higher value was calculated by subtracting the cost of the “do nothing” scenario from the variable costs, the argument being that not needing the limestone represents a cost saving that should be taken into the calculations.

All four circuits appear to be sensitive to the capital cost, but all that really means is that the capital costs would have to be estimated properly if any of these circuits is to be evaluated at all seriously. Even so, notwithstanding the higher capital cost, the chloride circuits, particularly the latest one, appear to be appreciably stronger, financially, than the sulphate circuits.

**Table 15 – Indicative economics**

Circuit	IRR, %		
	Half capex	Full capex	Twice capex
Sulphate circuit making elemental sulphur	16 to 26	9 to 16	3 to 8
Sulphate circuit making sulphuric acid	21 to 28	12 to 16	5 to 8
Chloride circuit 1	32 to 38	20 to 23	10 to 12
Chloride circuit 2	33 to 39	20 to 24	10 to 13

The numbers in Table 14 and Table 15 are by no means accurate estimates for the processing of nickelliferous pyrrhotite. They are good only for roughly ranking the different circuits. Any actual application of processing nickelliferous pyrrhotite would require the appropriate detailed and case-specific study.

## 5. EVIDENCE

The numbers presented so far suggest quite strongly that the chloride circuits are superior to the sulphate circuits examined, at least in terms of the variable operating costs. If the sale of by-products is added to the comparison, the chloride circuits would appear to be appreciably superior. An obvious question, therefore, is what is the technical status of the chloride technology? Leaching, wet-gas acid plants and hydroxide precipitation are all proven technology. HCl gas handling is well-known in the hydrochloric acid industry, therefore the only novel aspects of the circuit are the iron oxidation and hydrolysis. SMS Siemag have described a circuit for treating spent steel pickling liquor on their website ([www.sms-siemag.com](http://www.sms-siemag.com)). The oxidation and hydrolysis stage of the first chloride circuit in this study is very similar to that of SMS Siemag, except that iron oxidation is carried out atmospherically rather than in an autoclave. This enabling step in the chloride circuit, namely the oxidation of ferrous chloride at atmospheric temperature and hydrolysis of the resulting ferric iron, has been demonstrated in laboratory tests at NMR 360 Inc.'s facilities in Montreal, Canada, using spent steel pickling liquor as the feed. The spent pickling liquor contains mostly ferrous chloride, with minor amounts (up to 2 g/L) of vanadium, manganese, copper, zinc, silica and chromium, and is thus reasonably comparable to the ferrous chloride generated by the leaching of nickelliferous pyrrhotite.

Figure 9 shows the results of a batch oxidation test, where spent pickling liquor from a US steel plant was oxidized in the inert solvent. The plateau in the middle of the curve is there because the system was left overnight without oxygen flow and re-started on the following day. The oxygen utilization was low but to date this has not been optimized, the intent being to demonstrate the efficiency of the technique on a continuous basis, for which a continuous mini-plant is being

assembled at NMR 360. The important result from this test is that an overall extent of oxidation of 94 percent was achieved.

Figure 10 shows the same data as Figure 9, but plotted as the rate of oxidation of ferrous iron versus the concentration of ferrous iron. At higher concentrations of ferrous iron, the rate levels off, most probably because it becomes controlled by the rate of oxygen mass transfer. The line labelled Model comes from a very simple rate equation in which the rate is directly proportional to the concentration of ferrous iron at low concentrations and becomes limited by the mass transfer of oxygen at high concentrations of ferrous iron.

The mixing in this test was done using a standard laboratory glass impeller at relatively low rotation speed. This is to be switched to a high-shear gas-dispersing impeller, which should enhance the rate of oxygen mass transfer appreciably.

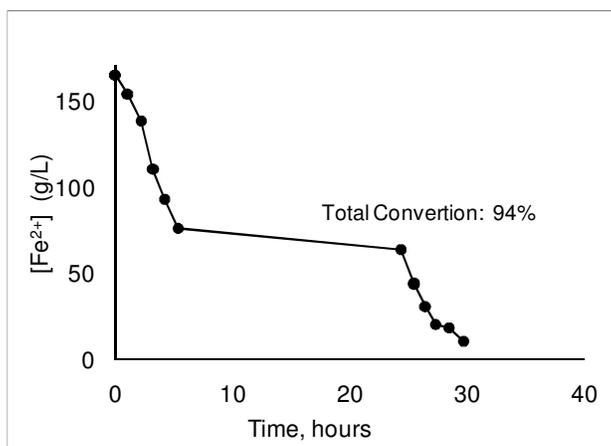


Figure 9 – Batch oxidation in the inert solvent

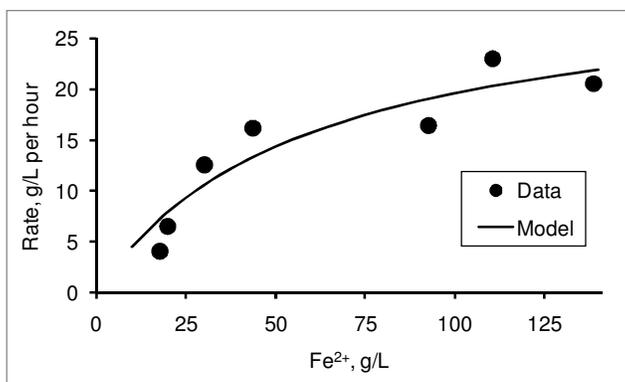


Figure 10 – Rate of oxidation

The hydrolysis of ferric chloride to pure hematite and concentrated hydrochloric acid has been demonstrated in previous laboratory work (Harris et al, 2008). Table 16 shows a typical analysis of black hematite generated recently from spent industrial steel-pickling liquor. The hematite is exceptionally pure, containing very low levels (<0.1%) of chloride, along with only trace amounts of the other elements contained in the feed liquor. When the hematite slurry was filtered, the filter cake had very low residual moisture (over 90% solids content). The XRD spectra in Figure 11 show that it is identical to typical spray dried hematite that is commercially marketed to the pigment industry.

Table 16 - Hematite from industrial spent pickling liquor

Element	Mass %	Element	Mass %
Fe <sub>2</sub> O <sub>3</sub>	99.1	Ni	0.006
S	0.036	Al	0.02

Cl	0.06	Cr	0.007
P	0.03	SiO <sub>2</sub>	0.076
Fe	69.3		

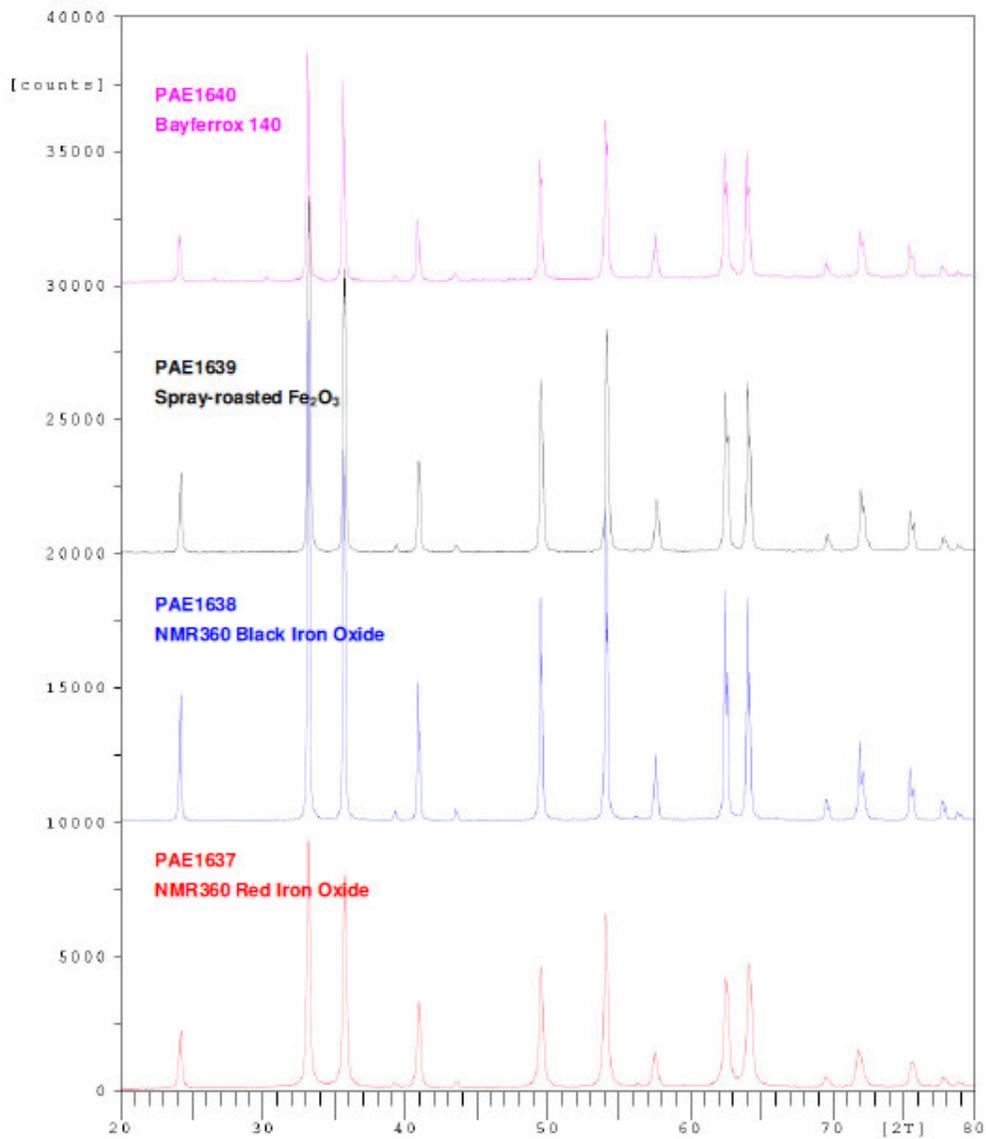


Figure 11 – XRD spectra

## 6. CONCLUSION

The main conclusion emanating from this exercise is that the novel chloride technology being developed by NMR360 Inc. appears to be superior to the sulphate circuits examined, even though the treatment of the sulphate circuits was deliberately optimistic. Once the chloride technology has been proven, impounding nickelliferous pyrrhotite could become more expensive in terms of variable cost than processing it. If these conclusions are correct, nickelliferous pyrrhotite could become a significant source of nickel.

## 7. ACKNOWLEDGEMENTS

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## 8. REFERENCES

1. Davidson, Vanessa. Nickel market Overview – The Supply Response. INSG Meeting, October 2006.
2. INSG statistics, November 2009. <http://www.insg.org/stats.aspx>
3. Agar, G. Flotation of chalcopyrite, pentlandite, pyrrhotite ores. International Journal of Mineral Processing, 33 (1991) 1-19
4. Dry, M.J. Aspects of Modelling a Complex Chloride leach Circuit: Starfield Resources' Ferguson Lake project. Paper published at the 2008 Alta Nickel Copper Conference, Perth, Australia, May 2008.
5. Graff, Gordon. Purchasing.com, December 2009. [http://www.purchasing.com/article/439185-Sulfuric\\_acid\\_demand\\_and\\_prices\\_set\\_to\\_escalate\\_as\\_economy\\_revives.php?rssid=20267](http://www.purchasing.com/article/439185-Sulfuric_acid_demand_and_prices_set_to_escalate_as_economy_revives.php?rssid=20267)
6. Harris, B., White, C., Dry, M. and Evans, P. Treatment of Nickel Laterites by Chloride and Hybrid Chloride-Sulphate Processes. Paper presented at Nickel & Cobalt 2009, 48<sup>th</sup> CIM Annual Conference of Metallurgists, 39<sup>th</sup> Annual Hydrometallurgy Meeting, Sudbury, Ontario, Canada, 23-26 August 2009.
7. SMS Siemag Process Technologies GmbH. Hydrothermal Hydrochloric Acid Regeneration. [www.sms-siemag.com](http://www.sms-siemag.com)
8. Harris, B., White, C., Demopoulos, G. and Becze, L. Recovery of Metal Oxides and Associated Acid from Process Solutions Using Water as Reagent. ALTA Copper 2008, Perth, Australia, 19-20 June 2008.