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NICKEL LATERITE PROCESSING TECHNOLOGIES – WHERE TO NEXT?

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ABSTRACT

A review has been completed of current and proposed processing technologies for nickel laterite ores. Although future supplies of nickel depend on laterite ores, their processing is inherently energy intensive and expensive as, unlike sulphide ores, they cannot be significantly upgraded, meaning the entire ore needs to be treated in the process. In addition, hydrometallurgical processes in particular have significant waste disposal problems. However, new technologies are being developed that are attempting to address the current processing issues, including some innovative processes that are in their early stages of development.

Smelting is a well known and proven technology for saprolite ores that is continually being improved. It is a high energy consumer and needs to be performed on a large scale to be cost-competitive. It remains the most popular option for large scale developments based on saprolite ores and accounts for a significant amount of nickel production from laterite sources.

High Pressure Acid Leach (HPAL) remains the process of choice for treating limonite ores, especially for large scale developments. It has the advantages of high nickel and cobalt recoveries and is applicable to a wide range of ores. However, the process does suffer from significant waste disposal issues.

Atmospheric and Heap Leaching. Smaller scale developments are being actively pursued based on Atmospheric Leaching (AL) or Heap Leaching (HL) technologies. These processes do not rely on autoclave technology and are therefore perceived to be less capital intensive and easier to operate. However, they still require significant investment in terms of infrastructure. Heap leaching is the option most investigated, whereas AL is gaining momentum for mixtures of limonitic and saprolitic ores. Waste disposal issues are again significant.

Downstream Product Recovery. The two main downstream processing technologies for nickel recovery from solution are mixed hydroxide precipitation and mixed sulphide precipitation. Refining to pure nickel and cobalt products is an option in the large scale HPAL projects.

NEW TECHNOLOGIES

Hydrochloric Acid Leaching has been investigated on a laboratory scale for some time based on the fact that the acid can be reformed from the waste liquor by pyrohydrolysis or, more recently, distillation. In order to be competitive, these processes require that acid usage is minimised. However, aggressive leach conditions with high acid consumptions are still required to give good nickel recoveries. In some processes, waste disposal can be minimised.

Bioleaching of oxide ores is a concept that is in its infancy, but does offer some advantages over conventional processes. The process uses organic matter to produce organic acids in situ that leach the ore, possibly by-passing the need for expensive mineral acids, and reducing waste disposal problems associated with current processes.

1. INTRODUCTION

Worldwide, the majority of nickel is still produced from sulphide sources, although this is rapidly changing, with production from lateritic sources expected to rise to over 50% by 2012. This trend results from a combination of the relative availability of nickel laterites (more than 70% of land-based nickel resources occur as laterites) and the increasing use of hydrometallurgy for the extraction and recovery of metals (Dalvi et al., 2004).

The choice of technology for the treatment of nickel laterite ores is generally driven by project-specific parameters, which is one reason why there are many different processing options used in currently
operating and proposed process plants. However, these processing options can be categorised under a few main "types" – smelting, high pressure acid leaching, atmospheric leaching and heap leaching.

The main parameters that impinge on the choice of technology are:

- Ore mineralogy and chemistry
- Capital and Operating Costs (especially for consumables)
- Environmental requirements

The capital and operating costs of a processing plant, and the effluent treatment and disposal options, are as important as the ore mineralogy and chemistry in determining the most appropriate processing route for a particular ore.

2. ORE MINERALOGY AND CHEMISTRY

A typical nickel laterite profile can be divided into four zones (Figure 1). The weathering effect progressively increases from bottom to top with the magnesium content of the ore decreasing and the iron content increasing with increased weathering (Elias, 1981; Burger, 1996).

Saprolite. The lowest layer reflects early stages of weathering of the bedrock and produces saprolite, in which the unweathered rock fabric is preserved although most of the original minerals have been altered. They are composed of mainly serpentine or hydrous magnesium silicates, Mg$_3$Si$_2$O$_5$(OH)$_4$ with nickel replacing Mg to form garnierite (Mg,Ni)$_2$Si$_2$O$_5$(OH)$_4$. There are no discrete nickel minerals.

Transition Zone. Above the saprolite, in poorly drained areas, is a more weathered zone containing significant saprolite/garnierite as well as some clays like nontronite (Na$_{0.3}$Fe$_3$(Si,Al)$_4$O$_{10}$(OH)$_8$nH$_2$O). It is referred to as a transition zone and the bulk of the nickel is associated with the nontronite. Colours are typically pale to deep green.

Limonite Zones. As weathering proceeds, the magnesium is increasingly leached and the silicon is partially removed. This results in the destruction of the primary silicates and ultimately the loss of the primary fabric. As a result, aluminosilicates, clays and nontronite as well as limonite (FeOOH) predominate in the lower part of the profile, referred to as the Yellow Limonite zone. Iron increases as more magnesium is leached resulting in a high iron Red Limonite zone. Nickel may substitute for iron(II) in the goethite lattice.
**Ferricrete.** A hard ferruginous crust known as ferricrete can form at the top of the sequence and this can protect portions of the underlying profile from erosion. It has generally been considered as an overburden layer, with nickel and cobalt grades well below commercial levels.

In real orebodies, the situation is more complex. The various zones may be absent or mixed and significant amounts of moisture and clay minerals as well as minor amounts of copper and zinc may be present (Taylor, 2000).

Mineralogical studies on a range of laterite ores have indicated that the nickel and cobalt are often concentrated to some degree in certain minerals. The separation of these nickel and cobalt minerals from the remaining oxide gangue minerals is difficult due to their fine size (generally in the micron range) and similar densities. Depending on the mineralogy of the ore, some beneficiation may be possible, for example, removing some of the minor heavier gangue minerals such as chromite, and more resistant residual quartz and chert particles.

### 3. PROVEN PROCESSING OPTIONS

The processing of nickel laterites falls into two broad categories pyrometallurgical and hydrometallurgical. The pyrometallurgical route (smelting) is the oldest and most widely used process and is used to produce either ferronickel or nickel matte.
In hydrometallurgical processing, the two principal processes currently practiced are the Caron process and the high pressure acid leach (HPAL) process, although less capital intensive acid leaching processes such as atmospheric pressure leaching (AL) and heap leaching (HL) are being practiced or are under intensive investigation for many possible new projects.

Due to the requirements of the various processing methods and the wide range of chemical and mineralogical composition of the laterite profile, the processes are best suited to only a part of the profile, as follows (see Figure 1):

- Red Limonite – best suited to HPAL.
- Yellow Limonite – best suited to HPAL and Caron.
- Transition – best suited to AL, HL and smelting
- Serpentine/Garnierite – best suited to smelting

The most common processing routes used today, including the EPAL process used by BHP Billiton at their former Ravensthorpe operation in Western Australia, are summarised below in Figure 2.

**Figure 2 Summaries of the Smelting, Caron and HPAL Process Technologies**

**Smelting**

1. Drying
2. Calcine/Reduction
3. Smelting
4. Refining or Converting
   - FeNi or Matte

**Caron Process**

1. Drying
2. Calcine & Reduction
3. Ammonical Leaching
4. Purification & Recovery
   - Ni and Co

**HPAL**

1. High Pressure Leaching
2. CCD & Neutralization
3. Precipitation & Redissolution (Optional)
4. Purification & Recovery
   - Ni and Co

**EPAL**

1. Neutralization with Saprolite
2. Jarosite Precipitation
3. CCD

### 3.1 SMELTING

This technology is a well known, robust and widely practiced process for the production of ferronickel or nickel matte. It is the preferred process for the treatment of saprolite ores with high nickel (>2%) and magnesium (10-15%) and low iron (13-20%).

Ferronickel smelting is the most widely practiced technology (Stober et al., 2008). In this process (the Rotary Kiln – Electric Furnace or RKEF process) the ore is blended with coal or coke and then dried and calcined in a rotary kiln at 900–1,000°C. Some pre-reduction of the iron and nickel may occur during this stage (Figure 3).
The calcine is then smelted with extra coal or coke in an electric furnace at 1,550°C reducing all of the nickel and about 60-70% of the iron to form ferronickel. The remaining iron, magnesium and silica report to the slag.

\[
\begin{align*}
\text{NiO} + \text{CO} & \rightarrow \text{Ni} + \text{CO}_2 \\
\text{Fe}_2\text{O}_3 + 3\text{CO} & \rightarrow 2\text{Fe} + 3\text{CO}_2
\end{align*}
\]

The ferronickel is then refined by removing impurities such as sulphur, carbon, silicon, chromium and phosphorus. Sulphur is first removed in a ladle by addition of soda ash, and the desulphurised ferronickel is treated in a converter with sand and lime to remove the other impurities and produce a final ferronickel product containing about 25% nickel that can be used directly in the production of stainless steels.

A high grade nickel matte can also be produced (Figure 4) by adding sulphur in the form of elemental sulphur or pyrite to the calcined reduced ore in the klin. The electric furnace then produces a crude matte which is converted by air blowing to a final product containing 77-78% nickel and 21-22% sulphur and less than 1% iron. Ores best suited to produce a matte are those with relatively high Fe/Ni ratio (>6) and SiO₂/MgO ratio of 1.8-2.2 (e.g. Soroako, Indonesia).
The main advantages of ferronickel production by smelting are:

- The process is simple and well proven
- It can handle high magnesium ores (that generally contain high nickel concentrations)
- Recoveries of nickel are high (90%)
- Residues are granular and are readily disposed
- Reagents are generally inexpensive and readily available.

The main disadvantages of ferronickel production by smelting are:

- Capital costs are high
- The energy usage is high and project economics are very sensitive to the cost of power
- It can handle only high magnesium ores – blending required to maintain SiO₂/MgO ratios
- Cobalt is not recovered as a separate product.

However, smelting still accounts for a significant proportion of the nickel produced from laterites, and further projects are being developed. Examples of current smelting operations are Cerro Matoso (Hanna, BHP Billiton, Columbia), Doniambo (Eramet, New Caledonia), Pomalaa (Aneka Tambang) and Soroako (PT Inco) in Indonesia and Onça Puma in Brazil (2009, Vale Inco). Koniambo in New Caledonia (Xstrata Nickel) is well advanced. In addition, there are a number of Japanese smelters treating imported ore from the Philippines, Indonesia and New Caledonia.
3.2 CARON PROCESS

A typical process flowsheet is shown in Figure 5.

Figure 5 Typical Caron Process Flowsheet

This process was first developed by Professor Caron in Holland in the 1920s and can be used for limonite ores with some tolerance for saprolites. It is based on the selective reduction of the nickel and cobalt to metals, followed by dissolution in ammonia/ammonium carbonate solution. A small amount of iron is reduced forming an alloy with the nickel and cobalt, with the remainder being reduced to magnetite.

The roasting reaction (~850°C) can be written as:

\[
\text{NiO} + 2 \text{Fe}_2\text{O}_3 + 3\text{H}_2 \rightarrow \text{FeNi} + \text{Fe}_3\text{O}_4 + 3\text{H}_2\text{O}
\]

The ore is then cooled to 150–200°C and quenched in an ammonia/ammonium carbonate solution. The nickel and cobalt are solubilised as ammonia complexes and the iron is oxidised and precipitated as iron hydroxide leaving an iron-free leach solution.

\[
\text{FeNi} + 1.25\text{O}_2 + 2.5\text{H}_2\text{O} + 4\text{NH}_3 + (\text{NH}_4)_2\text{CO}_3 \rightarrow \text{Ni(NH}_3)_6\text{CO}_3 + \text{Fe(OH)}_3\text{(s)}
\]

After solid-liquid separation, the cobalt is recovered as cobalt sulphide while nickel is recovered as basic nickel carbonate by steam stripping.
2 Ni(NH₃)₆CO₃ + Steam (H₂O) → Ni₂(OH)₂CO₃(s) + 12 NH₃ + CO₂

The basic nickel carbonate can be calcined to produce a nickel oxide final product.

The main advantages of the Caron process are:

- The technology is well proven and can be applied to low grade ores.
- Separate nickel and cobalt products are obtained, although cobalt recovery can be low.
- The ammonia leaching step in the process is highly selective for nickel and cobalt, and the ammonia is recycled, meaning reagent costs are low.
- Standard materials of construction can be used and corrosion problems are minimal.
- Relatively mild operating conditions are used.

The main disadvantages are:

- The initial drying and calcining of the high moisture-content ore is very energy intensive.
- Nickel and cobalt extractions are generally low (<90% Ni and <80% Co) when compared to the HPAL and other processes, and are very sensitive to ore composition.
- Limited to limonite (low Mg) ores.

Examples of the Caron process are at Punta Gorda (started 1986) and Nicaro in Cuba (1944), Yabulu in Australia (1974) and Tocatins in Brazil.

Plants were also constructed at Nonoc in the Philippines (1986) and Las Camariocas in Cuba (started but never completed). The process is considered unlikely to be used in the future due to the high energy usage (Wedderburn, 2009).

3.3 HIGH PRESSURE ACID LEACH (HPAL)

This process is best used for limonite ores, although the aluminium and magnesium contents should not be too high as these increase acid consumption. The ore is leached in an autoclave with sulphuric acid at 240-270°C dissolving most of the ore into solution. The high temperature ensures fast reaction times of 60-90 minutes, and also results in the precipitation of much of the dissolved iron as hematite or jarosite and aluminium as alunite. A typical process flowsheet for HPAL with mixed sulphide precipitation of the nickel and cobalt is shown in Figure 6.
Because of the aggressive leaching conditions, greater than 95% of the nickel and cobalt and more than 90% of the magnesium and manganese is dissolved into solution during the HPAL process. Most of the iron, aluminium, silica, and chromium report to the solids, although minor amounts remain in solution and add to the complexities of downstream processing.

**Ore Dissolution:**

Limonite: \[ 2 \text{FeOOH} + 3 \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2\text{(SO}_4)_3 + 3 \text{H}_2\text{O} \]

Gibbsite: \[ 2 \text{Al(OH)}_3 + 3 \text{H}_2\text{SO}_4 \rightarrow \text{Al}_2\text{(SO}_4)_3 + 6 \text{H}_2\text{O} \]

Garnierite: \[ (\text{Mg,Ni})_2\text{Si}_2\text{O}_5(\text{OH})_4 + 3 \text{H}_2\text{SO}_4 \rightarrow 3 (\text{Mg,Ni})\text{SO}_4 + 2 \text{SiO}_2 + 5 \text{H}_2\text{O} \]

**Iron and Aluminium precipitation:**

Hematite (Fe$_2$O$_3$) Formation: \[ \text{Fe}_2\text{(SO}_4)_3 + 3 \text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 3 \text{H}_2\text{SO}_4 \]

Jarosite Formation: \[ 1.5 \text{Fe}_2\text{(SO}_4)_3 + 7 \text{H}_2\text{O} \rightarrow (\text{H}_3\text{O})\text{Al}_3\text{(SO}_4)_2(\text{OH})_6 + 2.5 \text{H}_2\text{SO}_4 \]

Alunite Formation: \[ 1.5 \text{Al}_2\text{(SO}_4)_3 + 7 \text{H}_2\text{O} \rightarrow (\text{H}_3\text{O})\text{Al}_3\text{(SO}_4)_2(\text{OH})_6 + 2.5 \text{H}_2\text{SO}_4 \]

An advantage of saline water (as used at Cawse, Bulong and Ravensthorpe) is that the sodium ion (Na$^+$) replaces hydrogen ions (H$_3$O$^+$) in the jarosite and alunite, forming natrojarosite and natroalunite, and releasing more acid back into solution (Kyle, 1999; Marshall et al., 2004).

Natrojarosite Formation: \[ \text{NaCl} + 1.5 \text{Fe}_2\text{(SO}_4)_3 + 6 \text{H}_2\text{O} \rightarrow \text{NaFe}_9\text{(SO}_4)_6(\text{OH})_{16} + 2.5 \text{H}_2\text{SO}_4 + \text{HCl} \]

Natroalunite Formation: \[ \text{NaCl} + 1.5 \text{Al}_2\text{(SO}_4)_3 + 6 \text{H}_2\text{O} \rightarrow \text{NaAl}_8\text{(SO}_4)_6(\text{OH})_{16} + 2.5 \text{H}_2\text{SO}_4 + \text{HCl} \]
The precipitation of iron as hematite and/or jarosite is one of the main advantages of the HPAL process as it reduces acid consumption and precipitates the iron in a form in which it is readily settled and separated from the nickel-rich solution. As shown later, iron control in other acid leaching processes such as atmospheric and heap leaching is not so readily performed, and does not result in the regeneration of acid to the same extent as occurs in the HPAL process.

The autoclave discharge slurry contains about 5-7 g/L nickel and 45-60 g/L free sulphuric acid in solution. This free acid is neutralised with limestone and the remaining iron precipitated as iron hydroxide prior to solid-liquid separation.

After further solution purification, the nickel and cobalt are then extracted from the clarified leach liquor by a variety of methods to produce either intermediate products such as mixed sulphides or mixed hydroxides, or more refined products such as metals or oxides. Some nickel and cobalt losses occur during these steps to reduce overall nickel recoveries to about 90-92%.

The main advantages of the HPAL process are:

- The process can be applied to relatively low grade laterites (<1.5% Ni)
- The process relies upon a very high dissolution of solids in the slurry and consequently has great flexibility with respect to ore types
- Much acid is regenerated in situ by iron hydrolysis
- Overall nickel and cobalt leach extractions are better than other processes (generally >95%) and can be recovered as separate products if required
- The burning of sulphur to produce the sulphuric acid produces an overall positive energy balance. Commonly, this energy is harnessed for the production of steam and the generation of electricity for other site services
- The energy intensive processes of ore drying and calcining are eliminated
- Some ores can be upgraded by screening prior to processing
- The process can be used in saline water environments.

The main disadvantages are:

- The process cannot be economically applied to saprolitic ores containing high concentrations of acid consuming gangue minerals
- The high pressure acid leach is highly corrosive and requires exotic and expensive materials of construction, and extensive and costly maintenance
- High impurity levels in leach liquor ensure further expensive processing is required for the production of separate refined nickel and cobalt products from a mixed intermediate
- Sulphuric acid consumption, although lower than competing acid leach processes, is still high (generally from 350 to 500 kg per tonne of ore) and depends on the ore chemistry and mineralogy (especially magnesium and aluminium levels) and hence the project economics are very sensitive to the cost of sulphur used to produce sulphuric acid
- Excess free sulphuric acid remains at the end of the leaching process that must be neutralised with limestone
- The process produces a large amount of magnesium sulphate effluent liquor that must be disposed, recycled or converted into by-products. In dry climates where net evaporation exceeds precipitation, this effluent is stored in evaporation ponds. However, in tropical environments, the
liquor must be disposed into the ocean (e.g. Coral Bay, Goro and proposed for Ambatovy) or precipitated and stored on land.

Existing HPAL operations are Moa Bay (1959, upgraded 2000, Sherritt, Cuba), Murrin Murrin (1999, Minara, Australia), Coral Bay (2004, Sumitomo, Philippines) and Goro (2009, Vale Inco, New Caledonia). Two others – Cawse (Norilsk, 1998) and Ravensthorpe, (2008, BHP Billiton) were closed during the recent world economic downturn.

A further two projects are committed and/or under construction: Ramu in Papua New Guinea (Metallurgical Construction Corp.) and Ambatovy in Madagascar (Sherrill). Vermelho in Brazil (Vale Inco) is still under investigation.

In addition, Heron have completed a PFS for the Kalgoorlie Nickel Project (KNP), proposing a HPAL process to produce up to 36,000 t/a nickel with a mine life of 34 years. A HPAL flow sheet was selected as the best leaching technology for the project because of high Ni and Co extractions of approximately 96% and 93% respectively, and low acid consumption of approximately 280 kg/t. The PFS only considered 4 of the 14 deposits defined by Heron that make up the KNP and additional project enhancement will be obtained through the inclusion of the remaining 10 deposits and other optimisation opportunities (Heron, 2010a).

The HPAL process has been very popular over the last 10-15 years due to improvements in autoclave technology and acid resistant materials, higher energy costs and low sulphur costs and the availability of relatively cheap sulphuric acid for some projects. It remains to be seen whether the recent spike in the price of sulphur and the poor success rate of recent projects will see a trend away from this process.

**Enhanced Pressure Acid Leaching (EPAL)**

Atmospheric leaching (AL) was pioneered by BHP Billiton (2001, Liu et al., 2004). They installed it alongside HPAL at their Ravensthorpe operation in Western Australia to produce the hybrid Enhanced Pressure Acid Leach (or EPAL process). For the AL part of the process, nickel and cobalt extractions are generally not as high as in the HPAL.

A typical EPAL flowsheet with nickel and cobalt recovery as mixed hydroxide is shown below in Figure 7.
The atmospheric leach uses saprolite ore to neutralise the highly acid slurry remaining at the completion of the HPAL process, thereby increasing the nickel tenor of the solution. In the second stage, or induced jarosite precipitation, further saprolite leaching occurs and increases the pH to assist in the precipitation of some iron from solution as goethite (Liu et al., 2004) or, in the presence of seawater, natrojarosite.

Saprolite Neutralisation: $(\text{Mg,Ni})_3\text{Si}_2\text{O}_5(\text{OH})_4(s) + 3 \text{H}_2\text{SO}_4 \rightarrow 3 (\text{Mg,Ni})\text{SO}_4 + 2 \text{SiO}_2(s) + 5 \text{H}_2\text{O}$

Goethite Formation: $\text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} \rightarrow 2\text{FeO(OH)}(s) + 3\text{H}_2\text{SO}_4$

Natrojarosite Formation: $\text{NaCl} + 1.5\text{Fe}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} \rightarrow \text{NaFe}_2(\text{SO}_4)_2(\text{OH})_6(s) + 2.5\text{H}_2\text{SO}_4 + \text{HCl}$

The combined process, called enhanced pressure acid leaching (or EPAL), has been patented by BHP Billiton (November 1996, July, 2001).

**Downstream Metal Recovery Options**

Following acid leaching by HPAL, there are two main process options in general practice for the recovery of an intermediate mixed nickel-cobalt product. These are mixed sulphide precipitation (MSP) and mixed hydroxide precipitation (MHP). These processes are described below along with applicability to different types of laterite ores.
Mixed Sulphide Precipitation

This is the longest established process, being used at Moa Bay since 1959. It has also been employed at Murrin Murrin (Minara) and Rio Tuba (CNBC, Sumitomo), and will be established at Ambatovy (Sherrill).

In mixed sulphide precipitation, the autoclave discharge slurry is only partially neutralised to pH 2.5-3.0 prior to solid-liquid separation. There is minimal co-precipitation of nickel and cobalt. The copper and zinc can be removed (ion exchange, sulphide precipitation) prior to precipitation of the nickel and cobalt.

After reduction of any remaining iron(III) to iron(II), the precipitation of the nickel and cobalt is then achieved in an autoclave at 90-120°C under an overpressure of H₂S gas of up to 1,000 kPa. Retention times range from 30 to 60 minutes.

\[ \text{NiSO}_4 + \text{H}_2\text{S} \rightarrow \text{NiS}_{(s)} + \text{H}_2\text{SO}_4 \]

Because the reaction produces sulphuric acid, which inhibits the reaction by decreasing the solubility of the H₂S gas in the reactant solution, the process is best suited to lower nickel tenors. The process is selective for nickel and cobalt over manganese, iron, aluminium, chromium and magnesium. Unless removed prior to precipitation, copper and zinc will co-precipitate with the nickel and cobalt.

Generally, there is a significant recycle of the mixed nickel-cobalt precipitate into the reactor to provide active surfaces for further precipitation. This maximises the extent of precipitation, increases the product size, and minimises scaling in the autoclave. A generic flowsheet for MSP precipitation is shown below in Figure 8.

**Figure 8** Generic Block Flowsheet for MSP Precipitation

- **Clear Solution** ex CCD
- **Copper Removal** → NaHS
- **Copper Sulphide**
- **Solid/Liquid**
- **Mixed Sulphide Precipitation**
  - 90 - 120°C
  - 200-1,000 kPa H₂S
  - 0.5-2.0 hrs
  - 100-400% Solids Recycle
  - Solution to effluent treatment
- **Solid/Liquid**
- **Ni/Co Sulphide Product**
The mixed sulphide product, which contains about 55-60% nickel and 35% sulphur, is generally refined by pressure oxidation to re-dissolve the metals followed by nickel and cobalt separation and purification by solvent extraction, and pure metal recovery by hydrogen reduction or electrowinning.

The MSP process has been considered "difficult compared to MHP" in recent years. This is because it requires the use of autoclaves (considered expensive) and hydrogen sulphide gas (considered dangerous). The reality is that the capital cost of an MSP circuit is competitive with MHP and the occupational health and design fault issues have been limited. However, the process does require highly trained operators to avoid any safety issues (Willis, 2008).

The main advantages of mixed sulphide precipitation are:
- Precipitation > 99% in a single stage
- There are no significant metal impurities
- Minimal recycles except for precipitate
- Product has low moisture content (10-15%)
- Small shipping mass (1 tonne nickel per 2 wet tonnes product)
- Capex competitive with MHP
- Suitable for all ore types.

The main disadvantages of mixed sulphide precipitation are:
- OH&S issues with the use of H2S gas
- Cost of H2S reagent
- Autoclave scaling issues (can be controlled).

In summary, the process has many advantages, especially for ore types where MHP is problematic, and should not be omitted from an evaluation because of its recent "bad press".

Mixed Hydroxide Precipitation

This process was first implemented at Cawse in 1998 and was also employed at Ravensthorpe (BHP Billiton). It is proposed as a temporary facility at Goro (Vale Inco) and is in the development phase for Vermelho (Vale Inco) and Ramu in Papua New Guinea (MCC, China).

In mixed hydroxide precipitation, the autoclave discharge slurry is only partially neutralised to pH 3.0-3.5 prior to solid-liquid separation (CCD) during which there is minimal co-precipitation of nickel and cobalt. After CCD, further neutralisation to pH 4.5 to 5.0 is required for near complete iron, aluminium and chromium removal. During this stage, up to 10% of the nickel and cobalt can be co-precipitated, and the iron hydroxide product must be recycled to the autoclave discharge for nickel and cobalt re-dissolution and recovery. This results in a significant re-circulating load.

Following removal/recycling of the secondary neutralisation solids (iron hydroxide containing co-precipitated nickel and cobalt), the precipitation of the MHP is achieved by addition of magnesia (MgO) slurry in a two-stage precipitation process. Retention times can range from 3 to 6 hours. Generally 90-95% nickel and cobalt and 15-30% manganese precipitation is achieved in the first stage. A generic flowsheet for MHP precipitation is shown in Figure 9.
The process is not selective for nickel and cobalt over manganese, iron, aluminium, and chromium, but is so for magnesium. The iron, aluminium, and chromium must be removed prior to precipitation of the nickel and cobalt as they can cause problems during re-dissolution. Manganese is partially co-precipitated with the nickel and cobalt and constitutes a major impurity. The removal of manganese prior to precipitation by oxidation and precipitation as manganese dioxide has been investigated at laboratory scale but has not to my knowledge been practiced commercially in nickel laterite processing operations (Zhang et al., 2002; 2009).
The mixed hydroxide product, which contains about 35-40% nickel, is recovered by settling and filtration. It does not de-water well and the final product for shipping contains 40-50% moisture. The product can be refined by atmospheric acid leaching (Companhia Niquel Tocatins), ammonium carbonate dissolution (Cawse, Yabulu) or ammonium sulphate (Surigao). Metal separation and purification is carried out by solvent extraction, and pure metal recovery by hydrogen reduction, electrowinning or direct crystallisation of nickel sulphate.

The MHP process has been considered “easy compared to MSP” in recent years. This is because it does not require the use of autoclaves or “dangerous” reagents such as hydrogen sulphide gas. The reality is that the capital cost of a MHP circuit is similar to MSP and the separation processes are difficult and result in significant recycle streams. In addition, aluminium and manganese can be major problems.

Aluminium, if not removed, reports to the MHP as a gelatinous aluminium hydroxide that coats the MHP particles and prevents their re-dissolution in ammonia solutions. Manganese, apart from being the major contaminant in the MHP product (Zhang et al., 2009), also requires removal to low levels following MHP precipitation as it cannot be recycled in the process or released to the environment. Lime at high pH is required for this process and can result in excessive lime consumption by magnesium co-precipitation with the manganese. The hydroxides and gypsum precipitates are generally co-disposed with the process tailings, but the former can re-mobilise if the pH is allowed to fall below 9. As with all lime addition processes, there are associated scaling issues.

The main advantages of mixed hydroxide precipitation are:

- Simple technology, atmospheric pressure process (no autoclaves required)
- Capex competitive with MSP
- Suitable for most ore types, especially saprolitic ores (High Ni, Low Mn, Al)

The main disadvantages of mixed hydroxide precipitation are:

- There are significant metal impurities, especially manganese
- Fe, Al, Cr must be removed prior to nickel and cobalt precipitation
- There are significant recycle streams
- High shipping mass (1 tonne nickel per 4-5 wet tonnes product)
- Not suited to high manganese or high aluminium ores (Willis, 2008).
- Scaling issues in iron and manganese removal stages.

There are alternatives to the use of magnesia in mixed hydroxide precipitation which all have there disadvantages and are not generally considered. These reagents include caustic soda (NaOH, which improves the selectivity over manganese, but is generally considered to be too expensive), soda ash (Na₂CO₃ or sodium carbonate, which has lower selectivity over manganese) and lime (CaO, which lowers nickel in product by including gypsum in the precipitate and is not favoured for ammonia refineries as it introduces sulphate to the circuit). Lime can be considered if the refinery uses an acid leach.
4. HEAP LEACHING

4.1 HISTORY

Research into heap leaching began at the National Technical University of Athens in the early 1990s. They studied some Greek laterites that were mainly hematite with nickel contained in chlorite. These laterites were very amenable to heap leaching extracting up to 80% nickel and 60% cobalt at a minimal acid consumption of about 120 kg/t.

Other major mining companies followed the lead of Greece and began investigating heap leaching of laterite ores in the mid- to late-1990s. The main driver was the high capital cost of the current technologies of ferro nickel smelting and the HPAL process.

4.2. PROCESS OVERVIEW

Heap leaching was originally thought to be only applicable to certain laterite ores, such as the Greek laterites, or highly saprolitic ores. However, the process is now being investigated for limonite ores as well, using the process of agglomeration with sulphuric acid to improve the permeability of the ores.

Following agglomeration, or ore preparation as required, the ore is stacked into heaps and irrigated with sulphuric acid. The leachate is collected, re-acidified, and recycled to build up the solution tenor prior to the solution going through a metal recovery process.

Typical leach recoveries of nickel of 65 – 85% have been reported over 120-150 days with acid consumptions ranging widely from 200 to 600 kg/tonne of ore, but generally being at the top end of the range (Wen et al., 2006; Oxley et al., 2006; Steemson and Smith, 2009; Readett and Fox, 2009).

To date, most projects are looking to produce a final product that is a mixed nickel/cobalt hydroxide, carbonate or sulphide that can be sold to a refiner. A typical flowsheet for heap leaching is shown below in Figure 10.
The key challenges in heap leaching are:
- the maintenance of the bed permeability under acidic leaching conditions
- control and treatment of impurity metals (iron, aluminium, magnesium and manganese)
- control of acid consumption
- inventory and cycle time management
- water management, especially in high rainfall environments.

The main advantages of heap leaching are:
- relatively low capital cost compared to other process technologies
- low energy requirements. The burning of sulphur to produce the sulphuric acid produces an overall positive energy balance
- production of a clear leachate solution for downstream product recovery
- no need for CCD circuit or tailings dam.
The main disadvantages are:

- At this stage, not generally recommended for limonite ores alone
- Higher acid consumption and lower metal extractions than HPAL and AL
- Longer residence time for metal recovery and larger metal inventory in process
- Ores cannot be upgraded prior to processing
- Risks of bed permeability decreasing as acid leaching progresses
- Large amounts of iron and magnesium sulphate effluent liquor for treatment and disposal
- Requires covers on heaps and run-off management in high rainfall environments.

4.3. ADVANCED PROJECTS

Çaldağ, Turkey

This project has focussed on the so-called Balkan laterites that have a low clay content and is expected to be the world's first commercial nickel laterite heap leach operation. The project is situated in Turkey near the deep water port of Izmir. The orebody has a total indicated and inferred resource of nearly 40 million tonnes at 1.14% nickel and 0.05% cobalt (2005). In full scale production, it will produce 20,000 tonnes per annum nickel and 1,200 tonnes per annum cobalt in a mixed hydroxide product. The operation will produce two nickel-cobalt hydroxide products – the first containing 34% nickel, about 1.1% cobalt with less than 2% manganese. The second product will contain 24% nickel, 0.8% cobalt with less than 8% manganese. Construction of the project is ready to commence and is awaiting finalisation of the financing arrangements (European Nickel, 2009).

Murrin Murrin

Murrin Murrin has been investigating heap leaching over the past six years and has spent significant funds on research and process development including pilot plant trials, culminating in 2007 in a heap leach demonstration plant to produce nickel and cobalt from scats and low grade ores. The 400,000 t/a heap leach demonstration plant has been integrated with the HPAL operations so that the heaps are irrigated with acidic autoclave discharge solution and the pregnant leach solution is being returned to the main plant for nickel and cobalt recovery (Readett and Fox, 2009). The operation is currently producing about 2,000 tonnes of nickel and 150 tonnes cobalt (as metal) per annum. Feasibility studies are continuing on possible expansions of the operation (Minara, 2010).

Other Possible Australian Projects

GME Resources

The NiWest Nickel Project is located at Murrin Murrin in the North Eastern Goldfields of Western Australia. They are currently conducting a feasibility study for a heap leach project targeting 75 Mt of ore at 1% Ni. The feasibility study is investigating a 3.5-4.5 Mt/a over a minimum 20 year life producing 30-35,000 tonnes per annum nickel. The process flowsheet includes a sulphur burning acid plant to provide acid, power and steam to the project, on-off heap leach pads, PLS treatment by calcrite neutralisation followed by metal precipitation to produce a high grade mixed sulphide product. A novel aspect of the flowsheet is acid regeneration by high temperature, high pressure hydrolytic precipitation of iron to enable sulphuric acid to be returned to the heap leach (GME Resources, 2010).
Nickelore

Nickelore completed a Scoping Study in 2008 on their Canegrass Deposit near Kalgoorlie. Nickelore have acquired mineral rights to mine and extract 140,000 tonnes of nickel metal in laterite nickel products from the Canegrass Nickel Cobalt Project. The commercial plant designed to produce around 20,000 tonnes per annum of nickel over the life of mine in the form of a mixed hydroxide intermediate product, suitable for sale. The study found that Canegrass ore is ideal for heap leach processing (Tan, 2008).

Metallica Minerals

The Lucky Break project is a joint venture between Metallica and Metal Finance Corporation (MFC). MFC is completing a definitive feasibility study for the production of ~800 t/a nickel from a heap leach operation (Metallica Minerals, 2010).

A number of other Australian and overseas companies, having investigated heap leaching, are now pursuing Atmospheric Leaching as a more cost effective process for treating their lateritic ores. These projects include Heron Resources (Yerilla project), Metallica Minerals (Greenvale and Lucknow projects) and Oriel Resources (Shevchenko project).

5. ATMOSPHERIC LEACHING

5.1 PROCESS OVERVIEW

Acid leaching of nickel laterite ores at atmospheric pressure has been pioneered by BHP Billiton, who has patents issued over the process (BHP Billiton, July 2001). The crucial part of the patent is the formation of an iron jarosite or goethite that will remove a significant amount of the iron from solution and in the process regenerate sulphuric acid for further leaching of saprolite ore.

Atmospheric leaching of laterite ores involves contacting the laterite ore (usually limonite) with a concentrated solution of a mineral acid (usually sulphuric acid) to partially or completely dissolve the iron and nickel into solution. This process is undertaken at just below the boiling point of the slurry at atmospheric pressure (usually about 100°C) for up to 12 hours. During this process, sulphur dioxide, or another suitable reducing agent, can be added to the leach slurry to assist in cobalt dissolution.

The long leach time is to not only leach the nickel into solution but also to encourage the precipitation of iron from solution. At Ravensthorpe, sea water was used to assist in this process.

Following this reaction, the excess sulphuric acid is neutralised by the addition of saprolite ore to the leach slurry dissolving further nickel into solution. The leach solution is then separated from the solids and the nickel and cobalt recovered from the leach liquor by conventional means.

The main advantages of the Atmospheric Leach process are:

- The process can be applied to relatively low grade laterites (<1.5% Ni) and utilises both limonite and saprolite ores
- Nickel and cobalt extractions are high compared to heap leaching (generally >90% for nickel and >80% for cobalt)
- Excess free sulphuric acid is neutralised with saprolite ore
- The burning of sulphur to produce the sulphuric acid produces an overall positive energy balance.
The main disadvantages compared to HPAL are:

- The leaching times are much longer and metal recoveries are lower
- Sulphuric acid consumption is higher (generally from 500 to 700 kg per tonne of ore)
- Solid-liquid separation is not as efficient
- A large amount of magnesium sulphate effluent liquor is produced for disposal.

5.2 PROPOSED PROJECTS

BHP Billiton have not as yet commercialised atmospheric leaching technology in its own right although it was used in at Ravensthorpe in conjunction with HPAL in a process they have called enhanced pressure acid leaching (EPAL).

Eramet

Eramet has stated that they will use atmospheric leaching technology they have developed over the last ten years for their Weda Bay deposit in Indonesia as well as their Prony and Creek Pernod deposits in New Caledonia (Steel Guru, 2009). Construction is expected to start in 2010 with production in 2013 (Eramet, 2008).

Oriel Resources

Oriel Resources plc (October, 2007), the London-based chrome and nickel mining and processing company, has completed an extensive comparative analysis of all appropriate technologies for the development of the Shevchenko Nickel Project, Kazakhstan, including ferronickel production, atmospheric tank leaching and heap leaching. HPAL was not investigated due to the high capital cost. The Company chose to proceed with continuous atmospheric tank leach technology, as it provided significantly better economic and technical performance compared to the other technologies.

Heron Resources

Heron has also been looking at options for its 100% owned Yerilla nickel-cobalt project. In February 2008, heap leach development was put on hold in favour of pursuing atmospheric leaching. This followed pre-feasibility estimates of capital expenditure of AUD$682 million and operating costs of A$6.39 per pound of nickel produced for a 10,000 tonnes per annum nickel operation at a head grade to heap leach of 1.0% nickel and a 15 year mine life.

Atmospheric leaching eliminates the risk of maintaining the integrity of the ore heaps during leaching, and has the additional benefits of using upgraded ore as feed, faster leaching times compared to heap leaching, and better control of leach chemistry resulting in improved recoveries and more efficient reagent use (Heron, 2010b).

Metallica Minerals

Following acquisition of the Greenvale and Lucknow nickel-cobalt projects, Metallica Minerals have suspended a feasibility study for the Nornico heap leach project and have investigated an atmospheric acid leach process (AL) with SX/EW to produce 10,000 tonnes per annum of nickel metal and more than 1,000 tonnes cobalt as sulphide. The project will process 1.0 million tonnes per annum of ore and have its own acid and power plants (Metallica Minerals, 2010).
Skye Resources

Skye Resources (now HudBay Minerals) have successfully completed pilot plant testing of its proprietary Sulphation Atmospheric Leach ("SAL") Process using bulk samples of nickel and cobalt bearing laterites taken from their Fenix Project in Guatemala in 2004-05 (Verbaan et al., 2007). This process is detailed below in the section on new technologies.

5.3 WASTE TREATMENT OPTIONS

The HPAL process produces a number of significant waste streams. The tailings contain the hematite and jarosite produced in the autoclave, and also the iron hydroxide produced from the primary neutralisation circuit. In general the residue produced in the HPAL process is a mixture of hematite and jarosite and tends to contain too much sulphur to be a saleable by-product.

The HPAL residue is mixed with iron hydroxides or oxyhydroxides from primary neutralisation. Although a smaller waste stream, these iron hydroxides are voluminous and contain other metal hydroxides (possibly including aluminium, chromium, and base metal hydroxides) as well as gypsum.

The other main effluent stream is the magnesium sulphate clear liquor, produced as an effluent stream. In Australia, where evaporation generally exceeds precipitation, it can be treated in evaporation ponds. Conversely, in tropical environments, the preferred method of disposal is discharge into the ocean, the liquor not being significantly different in quality to the discharge from a desalination plant. However, the quantity of the discharge is generally much higher and a reason for potential concern (Steyl et al., 2008).

In heap leaching (HL), the spent ore may be competent enough to leave in the heaps or move for backfill. The other effluents from an HL circuit would include the iron hydroxides and gypsum from the iron removal stage and the magnesium sulphate waste liquor. The amounts would be more significant than in a HPAL circuit due to the higher acid usage and iron dissolution in the process.

Magnesium By-products

In all processes (HPAL, AL or HL) the magnesium sulphate liquor is reasonably free of deleterious metals and may be treatable to produce magnesium-based products such as caustic-calined magnesia (used for solution purification and neutralisation in the mining and environmental industries) or dead-burned magnesia (used as a refractory). In both cases, the only reagent required is lime (obtained from limestone) or sodium carbonate. However, as the laterite ores contain 5-8 times more magnesium than nickel, it is difficult to see how these magnesium by-products could be cost effectively produced and sold. The amount of magnesia produced from a normal 50,000 t/a nickel HPAL plant would be sufficient to satisfy a large percentage of the current world demand for these magnesia products.

In addition the reagent costs (either lime or sodium carbonate) would be substantial, and the waste streams produced (either gypsum slurry or a sodium sulphate liquor) would still require disposal or treatment prior to releasing the waste water into the environment.

Sulphuric Acid

With the increasing costs of sulphuric acid, the possibility of recycling the magnesium sulphate and regenerating sulphuric acid and magnesia from this waste stream may be worthy of investigation, although rising energy costs would also need to be considered. The critical features of such a process would be:
• The recovery of crystalline magnesium sulphate by concentration and evaporation and it's thermal decomposition are both highly energy intensive, especially as the water of crystallisation increases (Steyl et al., 2008)

• The concentration of the sulphur dioxide stream to meet the requirements of the acid plant

• The market for the magnesia produced from the process.

The significant waste streams produced by sulphuric acid based leaching processes, and the inability to recycle these streams cost-effectively using current technologies, are some of the reasons why more sustainable processes for nickel laterite processing are being actively pursued.

The chloride atmospheric leach processes discussed below attempt to overcome some of these problems of waste disposal. In addition, they attempt to add value to the overall process by producing saleable by-products from the process waste streams, although the actual saleability of these products has been questioned (Steyl et al., 2008).

6. NEW TECHNOLOGIES

6.1 SULPHATION ATMOSPHERIC LEACH (SAL) PROCESS

A block diagram of the SAL process is shown in Figure 11 below. The novelty of this process lies in the ore preparation stage in which the concentrated sulphuric acid is added directly to the limonite ore in a pug mill. The combined effects of high acidity and heat of reaction leads to good sulphation of the nickel and cobalt.

Following sulphation, the sulphated limonite ore is mixed with crushed saprolite and water, and ground to produce a leach slurry which is leached (AL) at 90-100°C and atmospheric pressure. Sulphur dioxide may be added to the leach to improve cobalt dissolution. Following iron removal as goethite, counter-current decantation (CCD) and solution purification, a mixed hydroxide precipitate for sale to nickel/cobalt refiners is produced (Verbaan et al., 2007).
Key data and results from a 10-day integrated pilot plant campaign was summarised as follows (Skye Resources, October 2006):

- Overall feed composition: 1.8% Ni, 0.09% Co, 26% Fe, 10.2% Mg
- Acid/Feed Ratio: 600 kg H_2SO_4/tonne feed (dry basis)
- Leach Extractions: 87% Ni, 88% Co
- Overall Recoveries: 85% Ni, 85% Co
- Product Composition: 41.6% Ni, 2.5% Co, 1.2% Mg, 4.5% Mn, 3.8% S.

6.2 HYDROCHLORIC ACID LEACHING PROCESSES

Hydrochloric acid has been proposed to have several advantages over sulphuric acid for the atmospheric leaching of nickel laterites. These include:

- The production of hematite as a final iron product meaning less acid is required
- The hematite may be a salable product, or is disposed more readily than goethite or jarosite (McDonald and Whittington, 2008)
- The use of lime to precipitate the MHP without production of gypsum
- The ability to recycle the acid by pyrohydrolysis or other means
- The ability to treat both limonitic and saprolitic ores
- The leach liquor is more amenable to downstream processing by solvent extraction and spray roasting to produce a final nickel oxide product (Gibson and Rice, 1977).

Three new processes using hydrochloric acid are discussed here – the Jaguar Nickel Atmospheric Chloride Leach Process, the Intec Laterite Process, and the AARNi process.

Jaguar Nickel Atmospheric Chloride Leach Process

Apart from being performed at atmospheric pressure, the Jaguar Nickel's Atmospheric Chloride Leach Process, when first presented in 2003, suggested it could overcome two of the main problems inherent in the hydrometallurgical processing of nickel laterite ores by acid leaching – iron control and acid consumption.

The patent application claimed that the sequential leaching and precipitation of iron in the leach reactors, using the properties of the concentrated magnesium chloride brine matrix and the inherent alkalinity of the saprolite fraction of the ore, would permit a very low addition rate of hydrochloric acid to be used (<150 kg/tonne dry laterite, Harris et al., 2006a). This was because the high brine concentration increased the activity of the hydrochloric acid leading to higher dissolution of the ore (Harris et al., 2004).

Combined with this leaching approach, hydrochloric acid was to be regenerated via pyrohydrolysis of magnesium chloride liquor after nickel and cobalt recovery. Since pyrohydrolysis is an energy-intensive process, the process as described by Jaguar could only be economic if the amount of solution requiring pyrohydrolysis was kept to a minimum, and the acid consumption was kept low (Harris et al., 2006b). It would appear from their news releases that Jaguar was unable to control either the extent of magnesium leaching, or of maintaining the acid addition at reasonable levels, and therefore any further work on the development of the process was discontinued. Criticisms of the process are generally concerned with the corrosiveness of the hydrogen chloride gas and the significant energy required for the pyrohydrolysis stage (McDonald and Whittington, 2008).

However, the process development of this process has continued albeit with a number of significant process changes that replace pyrohydrolysis with distillation of the hydrochloric acid (see Harris et al., 2006a, 2006b, 2008). The concept of recycling of the key reagents (hydrochloric acid and magnesium chloride) and leaching at atmospheric pressure however, remain, and for this reason the process, although apparently complex, is worthy of further investigation.
Intec Laterite Process

This is similar to the Jaguar process, but overcomes the need for pyrohydrolysis by using sulphuric acid to produce the hydrochloric acid required for recycle, and uses calcium chloride as a cheaper alternative to magnesium chloride brine. However, to get high nickel and cobalt dissolution, elevated temperatures of 150-180°C are required for >95% nickel and cobalt dissolution within 2 hours. A block diagram of the process is shown in Figure 12 (Moyes et al., 2005; Wood and Tong, 2005).

The leaching reaction requires the addition of hydrochloric acid and calcium chloride to the ore slurry. This is formed by the addition of sulphuric acid to the calcium chloride solution formed as a by-product of the process. Bassanite (CaSO₄·0.5H₂O) is also produced and would need to be disposed with the leach residue or sold as a by-product.

\[
\text{H}_2\text{SO}_4 + \text{CaCl}_2 + 0.5 \text{H}_2\text{O} \rightarrow \text{CaSO}_4·0.5\text{H}_2\text{O}_{(s)} + 2\text{HCl} \quad \text{(acid addition to leach)}
\]

The hydrochloric acid produced is capable of leaching the nickel and cobalt by dissolving the limonite ores at atmospheric pressure, while the excess calcium chloride increases the activity of the hydrochloric acid (Königsberger et al., 2008).

\[
\text{NiO}_{(s)} + 2 \text{HCl} \rightarrow \text{NiCl}_2 + \text{H}_2\text{O}
\]

\[
\text{FeOOH}_{(s)} + 3 \text{HCl} \rightarrow \text{FeCl}_3 + 2 \text{H}_2\text{O}
\]

The high temperature and high calcium chloride concentration in the leach medium causes the precipitation of hematite rather than jarosite or goethite, thereby regenerating hydrochloric acid for further leaching.

\[
2 \text{FeCl}_3 + 3 \text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 (s) + 6 \text{HCl}
\]

The hematite formed is readily filterable and a sold to be a saleable by-product. It is claimed that acid consumption is significantly reduced by this process, thereby improving process economics. Although the leach can be a single stage process, acid consumption can be further reduced by using a 2-stage counter-current leach.
Figure 12  Block Diagram of the Intec Laterite Process

Crushing/Grinding/Beneficiation

Chloride Leach

Solid/Liquid Separation → Leach Residue

Sulphuric Acid

HCl Brine

Fe Precipitation

Solid/Liquid Separation → Hematite

Limestone

Solid/Liquid Separation

Ni/Co Precipitation

Solid/Liquid Separation → Nickel/Cobalt Mixed By-Product

Lime

Mg Precipitation/Evaporation?

Solid/Liquid Separation → Magnesium Oxide By-Product

Lime

HCl Generation

Solid/Liquid Separation → Calcium Sulphate (Anhydrite) By-Product

Sulphuric Acid
Counter-current washing is required to wash valuable metals from the leach residue after which the nickel and cobalt can be precipitated from the clear liquor with hydrated lime. This produces a clear calcium chloride solution for recycle (after evaporation to retain the water balance).

$$\text{NiCl}_2 + \text{Ca(OH)}_2 \rightarrow \text{Ni(OH)}_2(s) + \text{CaCl}_2$$

Alternatively, solvent extraction or ion exchange could be used to recover the valuable metals and produce acid for recycle. Elution of nickel from the resin would produce a concentrated nickel sulphate solution suitable for crystallisation or electrowinning.

$$\text{NiCl}_2 + \text{H}-(\text{Resin})-\text{H} \rightarrow \text{Ni}-(\text{Resin})_2 + 2 \text{HCl}$$

Magnesium must also be removed from the liquor prior to recycle by the addition of lime to produce a magnesium oxide by-product.

$$\text{MgCl}_2 + \text{CaO} \rightarrow \text{MgO(s)} + \text{CaCl}_2$$

Although the process promises lower acid consumption and leaching at atmospheric pressure, the little data available to date indicates about 600 kg/t of sulphuric acid is required at 150°C for nickel and cobalt recoveries in excess of 95%, much higher than for HPAL processes (Wood and Tong, 2005).

The advantages of the Intec process compared to HPAL are:

- the lower operating temperatures and the production of saleable by-products, rather than a magnesium sulphate liquor requiring treatment or disposal
- the capital and operating costs would probably be lower than HPAL due to the lower operating temperatures and pressures in the leach.
- By-product revenue may make this process substantially more attractive than other current processes (although this has been questioned by Steyl et al., 2008).

The main disadvantages with this process are:

- the use of high chloride concentrations (sodium chloride and calcium chloride) increases capital costs significantly due to the use of exotic chloride-resistant materials
- the need to evaporate the wash water prior to recycle of the calcium chloride solution will add significantly to energy costs.

The ARNi Process

The Anglo Research Nickel Process (ARNi) is also an atmospheric pressure hydrochloric acid leaching process that attempts to, as far as possible, eliminate waste streams and regenerate and recycle the primary reagents.

A block diagram of the process is shown in Figure 13. (Steyl et al., 2008).
The primary ore (limonite) is treated in an Atmospheric Leach with hydrochloric acid regenerated from the Magnesium Removal (MR) stage (from cheaper sulphuric acid).

\[
\text{H}_2\text{SO}_4(\text{aq}) + \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{MgSO}_4 \cdot \text{H}_2\text{O}(\text{s}) + 2\text{HCl}(\text{aq})
\]

At this stage in the process, the activity of the hydrochloric acid is at its highest as is required for limonite leaching. The nickel and cobalt in the ore are solubilised with the iron.

\[
2\text{Fe(Ni,Co)OOH(ore) + 6HCl(aq) \rightarrow FeCl}_3(\text{aq}) + 4\text{H}_2\text{O}
\]

Depending on the ferric concentration in solution, part of the acid requirement may be introduced as SO₂ gas, which can reduce the size of the acid plant.

\[
\text{SO}_2(\text{aq}) + \text{FeCl}_3(\text{aq}) + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4(\text{aq}) + 2\text{HCl}(\text{aq}) + 2\text{FeCl}_2(\text{aq})
\]
In Primary Neutralisation (PN), iron is preferably hydrolysed to hematite due to its environmental stability, high iron content, high density and low inclusions of other base metals. In the high chloride solutions, hematite formation is favoured at temperatures >95°C in the presence of seed.

\[ 2\text{FeCl}_3 (aq) + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 (s) + 6\text{HCl} (aq) \]

The acid formed during hydrolysis needs to be continuously neutralised to sustain the hydrolysis reaction. This is achieved by adding saprolite ore to the PN and dissolving some nickel into solution, albeit at a lower recovery than under aggressive leaching conditions.

\[ \text{Mg}_2\text{Si}_2\text{O}_5\text{(OH)}_4 (s) + 6\text{HCl} (aq) \rightarrow 3\text{MgCl}_2 (aq) + 2\text{SiO}_2 (s) + 5\text{H}_2\text{O} \]

The nickel and cobalt may be recovered from solution as a mixed hydroxide. Strict pH control is required to minimise chloride contamination of the product (as Mg(OH)Cl) and therefore precipitation is not complete, and some of the valuable metals need to be recycled.

As in all processes involving the recycle of reagents, water removal is required. This is achieved with the liquor after product recovery. Because of the reverse solubility of kieserite (MgSO_4·H_2O) some of the salt is formed in this stage and acts as seed for the MR stage.

The authors (Steyl et al., 2008) have claimed that in a continuous mini plant operation, 95% nickel and cobalt was leached from a ferruginous ore (50% Fe) in AL using 750 kg/t sulphuric acid equivalent (50% as S_2O_3(g)), with a further 375 kg/t sulphuric acid being required for the MR stage. Using no additional acid in PN, 90% of the nickel was leached from the saprolite ore (15% Mg).

The operating conditions were 15% solids and 95°C for the AL and MR. A temperature of 100°C was used in PN.

6.3 BIOLEACHING OF OXIDE ORES

Bioleaching seems to offer a new "clean and green" technology for extracting metals from nickel laterite ores with lower costs and lower energy demand than conventional processes. It has been claimed to offer the potential for a step change in the technology for treating these ores (Valix et al., 2001a) by using a more selective leaching agent targeting the nickel and cobalt, rather than the currently used mineral acids that dissolve almost all the ore.

Bioleaching of oxide ores is based on the activity of the organic acids produced by microbial action to solubilise mineral oxides.

For example: \( \text{C}_6\text{H}_12\text{O}_6 \) (sugar) + \( 4\frac{1}{2} \text{O}_2 \) + microbe \( \rightarrow 3 (\text{COOH})_2 \) (oxalic acid) + \( 3 \text{H}_2\text{O} \)

Then: \( (\text{COOH})_2 \) (oxalic acid) + NiO \( \rightarrow \text{Ni(}COO)_2 \) (aq) + \( \text{H}_2\text{O} \)

Or: \( 3 (\text{COOH})_2 \) (oxalic acid) + 2 FeOOH (goethite) \( \rightarrow 2 \text{Fe(COO)}_3 \) + 4 \( \text{H}_2\text{O} \)

This solubilisation can occur with a range of organic acids such as citric acid, oxalic acid and others. Organic acids are well known for their ability to dissolve iron oxide minerals, including hematite and goethite (Bosecker, 1986) and therefore may selectively dissolve the nickelliferous iron oxides in the ore.

Bosecker (1986) initially tested fifteen different commercial organic acids (including oxalic, acetic, formic, citric, ascorbic, succinic, fumaric and tartaric acids) for their ability to dissolve nickel from limonitic and silicate type laterite ores. Surprisingly, in these chemical leaching experiments, he found that very little
mobilisation of nickel occurred from the limonite ores, but up to 90% nickel was extracted from the silicate ores with 0.5M citric acid.

In the bioleaching experiments, using micro-organisms rather than the organic acid chemicals, the *Penicillium* bacteria were more effective than *Aspergillus niger* in tolerating nickel in solution. As in the chemical leaching experiments, the silicate minerals were dissolved more readily than the limonites, with up to 70% nickel dissolution. Unfortunately, magnesium dissolution was also above 50%. In the bioleaching experiments, bacteria capable of producing organic acids are mixed with a suitable nutrient (generally a purified sugar derivative) and the ore (BHP Minerals, 2002).

In experiments on Greek hematitic and garnieritic nickeliferous ores, Tzeferis and Agatzini-Leonardou (1994) also found that citric acid was the most effective organic acid for leaching, and was more selective for nickel dissolution over both iron and magnesium than sulfuric acid. Oxalic acid was very selective for iron dissolution over nickel, leaching up to 46% iron but only 1.6% nickel in one ore sample. This was probably due to the formation of a nickel oxalate precipitate which has a low solubility.

However, more recent data by Tang et al. (2006) suggest that the leaching of metals from low grade limonite and nontronite ores from New Caledonia depended more on the acidity rather than the type of the organic acid used. She found that citric, malic and lactic acids gave similar metal dissolutions after a fixed leaching period when the extent of metal extraction was plotted against the initial acidity of the organic acid, where acidity was defined as $10^{-pH}$.

For the limonite ore, the selectivity of leaching was Co > Mn > Mg > Ni > Cr > Al > Fe and for nontronite Co > Mn > Mg > Al > Ni > Fe. These data confirm the greater amenability of the serpentine phases to bioleaching compared to the goethite and illite phases.

Very little work has been done on the recovery of the nickel and cobalt from solution. Chelating resins have been used to recover nickel and cobalt, but the selectivity of the resins was low and the adsorption capacities less than for aqueous metals (Deepatana and Valix, 2006). In another approach, Hernandez et al., 2007 demonstrated recovery of nickel as the insoluble oxalate salt. Apart from more leaching studies, further fundamental work is required on metal recovery from solution.

Another one of the main issues to be addressed is to obtain a cheap source of organic carbon for the bacteria, which will be site specific. Although laboratory studies use sugars such as sucrose and glucose, other suitable and cheaper sources of organic carbon need further investigation. These include molasses, sugar beet chips, pear pulp and whey permeate from cheese making (Burgstaller and Schinner, 1993).

**7. CONCLUSIONS**

Although the current technologies for leaching nickel laterite ores using pressure leaching with sulphuric acid have been shown to be capital intensive with high operating costs, most large project developments are continuing along the same route.

Atmospheric leaching, again using sulphuric acid continues to be investigated for smaller projects, being less capital intensive than HPAL, but with higher acid and limestone consumptions.

The Australian based operations appear to have a significant advantage in terms of waste disposal with stable flat areas available for tailings, and space for evaporation ponds for magnesium sulphate disposal. However, tropical laterite projects are finding significant economic and environmental issues with waste disposal, both tailings and magnesium sulphate brines.
New technologies are required for nickel laterite leaching that will overcome the economic and environmental issues associated with sulphuric acid leaching processes. Two areas that offer hope for the future are atmospheric chloride leaching and bioleaching processes.

8. REFERENCES


