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# Advanced study on the extraction of Nickel from its ores

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### Abstract

Nickel is one of the key strategic metals because it has many applications in petrochemical, metallurgical and electroplating industries, making it necessary to find newly developed technologies to produce refined nickel from different ores at competitive costs and at the same time recover other metals such as cobalt and copper. Nickel's extractive metallurgy is the most complex since there are two major types of ores, laterites, and sulfides, which make this paper a valuable guide by providing an overview of the process used to isolate nickel from its ores and an important source of strategies used to enhance its extraction.

### Keywords:

Nickel extraction, laterite ores, sulfide ores, Ni secondary sources, leaching.

## **Introduction**

Nickel is a normally happening metallic component with a gleaming white sparkly appearance. It is the fifth most basic component on earth that happens broadly in its outside layer and center with a wide appropriation in nature as it tends to be found in air, water, and soil under different mineral structures. (**Acharya et al. 1999(a), 2010(b)**) Nickel is mined from two sorts of minerals: laterites and sulfides. Albeit about 70% of the mineral stores are found in laterite metals, just about 40% of the nickel generation is from laterites. Laterites are for the most part used to create ferronickel, which is utilized straightforwardly in steelmaking. Some laterite metals are utilized to make softening evaluation nickel and nickel matte while sulfides are refined to deliver high-grade nickel. It is a characteristic asset that can't be expended like numerous different metals; it is completely recyclable where it very well may be reused over and over without loss of value, adding to the round economy model (CE).

The world is getting progressively reliant on nickel, as it has numerous mechanical and business employments. Most nickel is utilized for the creation of hardened steel and other nickel composites with high consumption and temperature opposition. Nickel metal and its compounds are utilized generally in the metallurgical, substance and nourishment handling ventures, particularly as impetuses and shades. (**McClveen and Negusanti, 1994**), these requests have outpaced the worldwide pace of monetary development which prompts a deficiency of Nickel and numerous basic minerals wares. So to defeat it just as to verify long haul reasonable supplies for its eager financial improvement technique; numerous nations governments over the world entitled various research projects to productively create, use nickel assets just as grow proficiently, green nickel generation innovation and began to build their attention on the preparing of the colossal stores of nickel rich laterite minerals due to declining worldwide stores of nickel sulfides.

This exploration article is a diagram of the procedures utilized in the partition of Ni from its metals and the second asset. It gives likewise an understanding into how conceivably we may improve Ni extraction later on.

## 2. Nickel production process

The nickel mined originates from two kinds of mineral stores:

Magmatic sulfide stores where the essential metal mineral is pentlandite [(Ni, Fe)<sub>9</sub>S<sub>9</sub>]

Laterites where the central metal minerals are nickeliferous limonite [(Fe, Ni) O(OH)] and garnierite (a hydrous nickel silicate). Regardless of lateritic metals establishing 60% of the land-based Ni assets, ~ 60% of essential generation originates from sulfide mineral (**Superiadi, 2007**). Laterite nickel minerals regularly happening in tropical or subtropical districts comprise of weathered ultramafic rocks containing high levels of press and magnesium.

These deposits usually exhibit different layers due to weathering conditions such as a silica-rich layer, a limonite layer dominated by goethite [FeO(OH)] and hematite (Fe<sub>2</sub>O<sub>3</sub>) and a saprolite [(Ni, Mg) SiO<sub>3</sub>.nH<sub>2</sub>O] layer rich in magnesium and basal elements. Between the saprolite and limonite layer, there is a magnesium-rich transition layer (10-20% Mg) with iron, called serpentine [Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>]. The limonitic layer is not very suited for upgrading while upgrading the magnesium-rich saprolitic layer is also limited to concentrate the nickel.

The mined ores (1–4% Ni) are processed to upgrade the metal content with 10–20% Ni in the concentrates. Thus, the preconcentration of nickel ores is an important unit operation to upgrade the nickel before commencing any extraction steps.

Ni is mined from sulfide ores, Nickel ferrolaterite and serpentine. Although the sulfide ores are the preferred source of this metal more than 40% of the world's supply of Nickel comes from laterites and serpentines. (**McCutcheon 2003, Blainey 1994, Dakvi 2004**) (**Figures 1 and 2**).

The production of Ni from sulfide ores is obtained mostly by a pyro-metallurgical process (**Crundwell et al. 2011**). Laterite ores can be divided into 3 main layers: limonite, transition, and saprolite. Limonite and transition are processed by hydrometallurgical processes and saprolite by the pyro-metallurgical process due to the low iron content (**Crundwell et al.2011, Oxley and Barcza 2013**).

There are 2 main hydrometallurgical processes: high-pressure leaching (HPAL) and atmospheric acid leaching.

## **2.1. Nickel laterite processing**

A majority of pyrometallurgical processes (ferronickel and matte smelting) use standard flowsheet involving drying, smelting, calcining/reduction, and electric furnace.

The 2 principal hydrometallurgical methods presently practiced are the Caron method and the HPAL process. Generalized block flow diagrams for the processes are shown in figure 3.

### **2.1.1. Pyrometallurgical process**

A review for pyrometallurgical processes for laterite ores has been done by **Bergman (2003)**. Other reviews include those by **Simons (1998)**, **Taylor (2000)**, **Diaz et al. (1998)** and **Ozberk et al. (1986)**. Pyrometallurgical processes are suited for ore containing predominantly saprolite. These ores contain proportionately lower cobalt and iron compared to the limonitic ores.

The Ni/Co ratio in the smelter feed is generally ~ 40. These ores are smelted to produce either ferronickel or matte.

In conventional pyrometallurgical processing, the ore is dried, calcined (and sometimes reduced) in a rotary kiln and smelted in an electric furnace in the presence of carbon. If matte is the desired product, then sulfur is added to the kiln. The crude metal/matte is further processed/refined to produce the final product.

Pyrometallurgical processes are energy-intensive since all of the free moisture and combined water has to be removed in the process and all of the material has to be first calcined and then melted to form a slag at about 1600°C. This requires both hydrocarbon fuels (coal, oil or naphtha) and electric power.

### **2.1.2. Hydrometallurgical Processes**

A review of hydrometallurgical processes for laterites has been done by **Reid and Barnett (2002)**. A general description is provided by **Simons (1998)**. Other reviews include those by **Taylor (2000)**, **Berezowsky et al. (1991)**, **Berezowsky (1997)**, **Motteram et al. (1996)**, **Urbain et. al (1986)** and **O'Kane (1979)**.

#### **a) Caron Process**

The Caron process could be used for limonitic ores or a mixture of limonite and

saprolite. The ore is dried and nickel is selectively reduced (together with cobalt and some iron) to metallic nickel at ~ 700°C. The metallics are extracted by leaching in an ammoniacal solution. Recovery of nickel and cobalt decreases with the increasing amount of saprolite since nickel and cobalt are locked in a silicate matrix and are difficult to reduce at this temperature.

The Caron process suffers from several disadvantages: The front-end of the Caron process is pyrometallurgical involving drying, calcining and reduction. These steps are energy-intensive. The back-end is hydrometallurgical requiring various reagents. The nickel and cobalt recoveries are lower than for the smelting processes or the HPAL process.

#### **b) HPAL process**

The chemistry of the HPAL process has been reviewed by **Whittington and Muir (2000)**. Mixed ore is briefly slurred and heated at 250-225 C in a titanium-clad autoclave by steam and sulphuric acid injection, and nickel and cobalt are extracted into an acidic solution together with iron and aluminum. At such high temperatures, iron and aluminum hydrolyze and precipitate as hematite and a range of mixed alunite / jarosite phases, depending on the leaching conditions. This hydrolysis generates acid and reduces the overall acid consumption of the HPAL process, leaving approximately 50-60 g / l of free acid in the leaching solution.

The leach slurry is " flashed " from the autoclave, the solids are separated from the liquor by counter-current decantation (CCD), the liquor neutralized to remove iron (III), aluminum and chromium (III) and the soluble nickel and cobalt are subsequently processed. (**McDonald and Whittington 2007**)

The pressure leaching is carried out either in Pachuca tanks (Moa Bay) or titanium lined autoclaves (all modern plants). Leach temperatures vary in the range of 245 to 270°C. Solid-liquid separation is carried out by Counter-Current Decantation (CCD). There are various ways of purifying the nickel-containing solution and separating nickel and cobalt. In modern plants, such separation is carried out by solvent extraction (SX). Final products produced are electro-nickel, nickel oxide or nickel briquettes. Some plants produce intermediate materials (mixed sulfides or mixed

hydroxides) that are refined elsewhere.

### **Other hydrometallurgical processes**

Several newer processes are currently being piloted and evaluated. These include:

c) **AL: Atmospheric Leaching**- Similar to the leaching step described above for saprolite. Atmospheric leaching (AL) at a lower temperature (~ 90 C) and in open vessels avoids the need for expensive HPAL autoclaves. The difference between HPAL and AL is the lack of atmospheric pressure. The caron process is both pyrometallurgical and hydrometallurgical and can be applied to limonite and transition layers. This process involves first drying and calcinating / reduction (pyrometallurgy) and then a leaching process using an ammonia solution. The ion exchange technique may be used in the next step when a purification process is required. (**Whittington and Muir (2000), Motteram et al. (1996), Mudd (2010), Oxley and Barcza(2013), Mohammad Reza F et al. (2014), Norgate et al. (2011), Dalvi et al. (2004)**).

HPAL processes require predominantly limonitic ores; in the case of the dry laterites, they contain nontronite and/or smectite. Generally speaking the ores:

- contain some saprolite
- have lower Mg- usually limited to <4 % (At higher Mg acid consumption is higher)
- require lower Al content (clays are high acid consumers; therefore the Al content should not be too high)

The case for AL vs. HPAL has been under discussion for many years and gives rise to a substantial list of relative strengths and weaknesses as summarized in Table 3.

Considering that the choice between AL and HPAL is an economic one relating to the cost of acid supply, mineralogy of the ore body and recovery trade may not represent a shift in the development of the quantum process and other factors, particularly those related to infrastructure, may require significant improvement. It is clear from Table 3 that several considerations must be examined when determining whether AL is a viable processing option.

d) **EPAL Process**: This includes an additional leaching step for saprolite using residual acid from the HPAL step (+ added acid). Saprolite is leached at atmospheric

pressure and is a high acid consumer (believed to be up to 1 t acid/t ore). This process can consume more saprolite than the conventional HPAL process. This is currently being piloted by BHP-B for Ravens Thorpe.

e) **Acid Heap Leaching** (for saprolitic ores)

Heap leaching is a low-cost technology used in industrial mining to recover precious metals such as gold and uranium, along with several other highly sought-after metals such as copper, from their primary resources (ores and minerals). There has been a growing demand for heap leaching for many decades due to its environmental benefits. Heap leaching provides a benign, effective and economical solution for the environment to mining operators and produces only minor emissions from furnaces. The cost of the heap leaching process is low, making it an attractive option from a financial point of view.

Although early in maturation, heap leaching appears to offer the most cost-effective method for the extraction of nickel from low-grade nickel laterites.

Several companies, including the Yunnan Tin Group, CVRD Inco, and Mirabela Nickel, have examined heap leaching for the treatment of laterite minerals.

In Australia, Metallica Minerals is looking to develop its Lucky Break, Normico projects, and Heron Resources ' Jump up Dam project into production status. Nickel juniors including GME Resources and Cortona Resources are also considering heap leaching to process their deposits.

f) **Chloride Leaching** (for mixed limonitic and saprolitic ores)

The use of hydrochloric acid was proposed to have several advantages as compared with sulphuric acid (**Gibson and Rice, 1997**), namely:

- ✓ The leach liquor is amenable to purification by direct solvent extraction (DSX) with Versatic 10 and to a lesser extent Cynex 301 particularly concerning Ni/Co/Mn/Mg separation and stripping of the extract.
- ✓ Concentrated chloride liquors produced from solvent extraction (SX) containing nickel, iron or magnesium can be spray roasted to produce pure nickel oxide or hematite or magnesia, respectively, together with hydrochloric acid.

Normally, the case against the hydrochloric acid leaching of nickel laterites focused

on the need to use highly corrosion-resistant materials and to control the emission of hydrogen chloride gas. However, there is substantial literature examining the use of hydrochloric acid and many new processes proposed in recent years based on novel chemistry that has only been achieved in strong chloride liquors. (**Table 4**)

## **2.2. Nickel sulfides processing**

Nickel sulfide ores are generally rich in copper, and both copper and nickel are present in the form of sulfides, which are densely embedded with each other, and it is difficult to directly separate copper and nickel by beneficiation methods. Most companies currently use Copper Nickel mixed flotation - copper nickel smelting -high ice nickel crushing process. The main pyrometallurgical processes include flash smelting and molten pool smelting. Flash smelting is a high-temperature (1 450 ~ 1 550 ° C) reaction tower that sprays deeply dehydrated powder concentrate from the top of the reaction tower at high speed.

Within the range of 2 to 3 s, the decomposition, oxidation, and melting of the sulfide are substantially completed. The molten pool smelting is through an intermediate process of osmosis, the sulfide concentrate, partially oxidized roasting calcine, return material and appropriate flux and other materials, at a certain temperature (1 200 ~Melting at 1 300 ° C), through a series of chemical reactions, smelting and dissolution processes to form metal sulfides (nickel ruthenium) and oxides (slag). Low nickel bismuth produced by flash smelting and molten pool smelting cannot meet the processing requirements of the refining process, it is necessary to produce high nickel niobium by further blowing. Then, the high nickel niobium is subjected to grinding-copper-nickel flotation separation to obtain copper and nickel concentrate; so that the copper-nickel is initially separated. The obtained nickel concentrate is then smelted and blown by fire. A nickel sulfide electrode is prepared, and finally, electrowinning is performed to obtain an electrowinning nickel. For high-grade copper-nickel sulfide ore, this treatment method is mature and has high production efficiency. Figure 3 shows the process flow for the production of high nickel bismuth from a typical nickel sulfide ore (China Jinchuan Company)

### **2.2.1. Hydrometallurgical Process**

The hydrometallurgical process of nickel sulfide ore was developed in the 1970s. During the hydrometallurgical development of nickel sulfide, Canada Eagle Bridge Nickel, France Nickel, Finland Outokumpu, and South Africa Impala And so on made a huge contribution. The hydrometallurgy of nickel sulfide is generally based on high nickel niobium, and the extraction process can be divided. (Sahu 2008, Yang et al.2012)

There are two kinds:

1. Soluble anodic electrolytic refining, crude nickel anodic electrolysis and nickel sulfide anodic electrolysis.
2. Selective leaching - clean liquid - electrowinning.

The second process develops rapidly, and depending on the electrolyte system, the selective leaching-cleaning-electrowinning process can be divided into a chlorination-cleaning-electrowinning process and a sulphuric acid cleaning-electrowinning system. (Sahu 2008, Yang et al.2012)

In the process of producing refined nickel by chlorination-cleaning-electrowinning, due to the high chemical activity of chlorine and chloride, the generated chloride has a large solubility and strong complexing ability for impurities, so at normal temperature and pressure, high nickel, cobalt, and copper in the crucible can enter the solution.

By adjusting the relative addition rates of chlorine and feedstock, the redox potential of the leaching can be controlled and a continuous leaching process can be achieved.

The hydrometallurgical process of nickel sulfide ore in China mainly adopts a selective sulfuric acid leaching-cleaning-electrowinning process. In 1993, China's Xinjiang Fukang smelter used copper-nickel high-nickel bismuth sulfuric acid to selectively leach the metallurgical process, becoming the first domestic manufacturer of nickel metallurgy wet process. (Sahu 2008, Yang et al. 2012)

### **2.2.2. Pyrometallurgical process**

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### **2.3. Ni secondary resources**

There are not many significant nickel mineral resources. It is therefore essential to consider the secondary sources of Ni from various industrial wastes. It exists in different sources, such as spent batteries. (Yang et al. (2016), Joulié et al. (2014) ), catalysts (Akcil et al. (2015)), wastewater (Benvenuti (2014), Shen et al. (2015)) and electronic wastes(Hadi et al. (2013), Robotin et al. (2011)). Two routes can be employed for Ni recovery from wastes: (i) leaching of wastes and subsequently recovering Ni solution (hydrometallurgical process); (ii) thermally treating wastes (pyrometallurgical process) Coman et al. (2013)

#### **2.3.1. Nickel recovery from spent solution**

Existing methods used to remove nickel from industrial effluent, including chemical precipitation, chemical reduction, flocculation, filtration, evaporation, solvent extraction, biosorption, activated carbon adsorption, ion exchange, reverse osmosis, electro dialysis, membrane separation processes, etc.

Spent plating baths are another source of high amounts of dissolved Ni (**Tanaka et al. 2008**). Methods used to treat such waste include electro dialysis (**Li et al. 1999**), electro-winning (**Vegliò et al. 2003**) and continuous extraction of solvents (Tanaka et al. 2008). **Widyarani et al. (2017)** evaluated the performance of a double chamber electrodeposition cell (DCEC) using water hyacinth as a cell separator for the removal of nickel ion. **Benvenuti et al. (2014)** extracted 97.9 percent Ni in a lab-scale electro dialysis system to treat a solution simulating the nickel plating of the rinse water. The process saved 120 kg/month of Ni on a large scale with the complete reuse of the rinse water. **Dube et al. (2016)** used  $< 50 \mu\text{m}$  magnetite powder (Cermag 10.1) to extract 98% Ni from the rinse water (29.8 ppm) of the plating plant in Zimbabwe.

### **2.3.2. Nickel recovery from spent batteries**

**Glencore, 2017**, estimated that more than 10 M electric vehicles will be sold annually in 2025, generating net additional primary nickel requirements of more than 400Kt Ni. This is one of the reasons why the recycling of spent batteries appears to be an attractive option to meet the demand for a nickel while avoiding environmental risks.

In nickel-based rechargeable batteries, the active material used is Ni(III) oxy-hydroxide ( $\text{NiOOH}$ ), which is converted to  $\text{Ni(OH)}_2$  during discharge and reformed during recharge (**Beck and Rüetschi 2000**). Cadmium, a highly toxic metal, can be replaced by a hydrogen-absorbing alloy in NiMH batteries that is less benign and increases the performance of such batteries (**Beck and Rüetschi 2000; Fetcenko et al. 2007**). Nickel is present in LIBs as  $\text{Li}_{0.85}\text{Ni}_{0.05}$  ( $\text{NiO}_2$ ) in + 2 states in the nickel oxide layered structure (**Meshram et al. 2015b**)

#### **a. Recovery of Ni from spent Li batteries**

Li-ion batteries are commonly used as phone power sources, but their continued use will degrade their capabilities. (**Armaroli and Balzani. 2011**).

In 2020, the quantity and weight of Li ions may exceed 25 billion units and 500

thousand tons (**Zeng et al. 2014**). By using Li-ion batteries, their capabilities will continue to deteriorate and the battery needs to be replaced. As a result, the increased consumption of Li batteries can produce waste to the environment, a recovery process to obtain Ni is therefore necessary.

Spent Li batteries containing lithium and other metals are mainly treated with hydrometallurgical processes and are also treated in combination with pyrometallurgical treatment. This may involve integrated pre-treatment steps such as pyrolysis or mechanical processing. To investigate the extraction of cobalt, nickel, manganese, etc. from LIBs, different acids such as HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and a few organic acids such as DL-malic acid, citric acid, etc. have been leached (**Meshram et al. 2014**). Most of the work using LiCoO<sub>2</sub>-based batteries reported very low levels of nickel; however, quite recently, many researchers have used LIBs of mixed chemistry, which contain substantially nickel, as an important element for sustainable processing.

#### **Recovery of Ni from Ni-Cd batteries**

Batteries such as Ni-Cd have been part of the most widely used systems; therefore numerous studies have been carried out in recent years on the treatment and recycling of batteries and hydrometallurgical processes.

**Bartolozzi et al. (1995)** described the hydrometallurgical process for the recovery of nickel and cadmium from spent Ni-Cd batteries. After primary treatment (grinding, drying, mechanical separation), the leaching of the powder obtained from primary treatment was performed with H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> at pH= 0.3 for 60 min at 60 ° C. As a result, 98% of nickel was recovered in this process. Nogueira and Margarido (2004) investigated the leaching behavior of electrode materials from spent nickel-cadmium batteries in sulfuric acid media. Sulfuric acid leaching was the first chemical step in their process. The hydroxide phases of Ni, Cd, and Co were readily soluble at a low acid concentration (e.g. pH~1) for 30 min at room temperature. Electrode metallic nickel was reported to have completely leached at high temperatures (95 ° C) and mild acid concentrations (2.5 mol H<sub>2</sub>SO<sub>4</sub>) after 4 h. **Kim et al. (2009)** investigated the recovery of nickel, copper, tin and lead from waste multi-layer ceramic capacitors (MLCC) through a hydrometallurgical process. The nickel extraction was reported to

be 97% with 1 mol HNO<sub>3</sub> at 90 ° C for 90 min and 5 gL<sup>-1</sup> pulp densities.

Currently, spent Ni-Cd batteries are industrially treated pyrometallurgical, e.g. in Inmetco (USA), Accurec (Germany), SabNife (Sweden) or Snam-Svam (France). Hydro methods are also used in Batenus (Germany) or TNO (Holland) processes. These are primarily based on solvent extraction followed by electroplating, ion exchange or membrane technology (**Rudnik and Nikiel 2007**).

Cadmium distillation is performed either to recover CdO in an open furnace or metallic Cd and high Ni-containing alloy in a closed furnace under controlled atmosphere (**Espinosa et al. 2004a, 2004b**). **Espinosa and Tenório (2006)** optimized the process of distillation of cadmium using coal as a reductive agent. The recovery of Cd metal was too slow below 900°C with Zn as the main impurity.

Yang has also used a potentiostat electrodeposition technique to recover heavy metals from spent Ni-Cd batteries (**Yang 2003**). The best results have been achieved with the complete recovery of Cd and Ni in 4 M HCl at 60 ° C. However, the high leaching efficiency of 9 M HCl at 120 ° C was achieved by **Stefănut et al. 2008**. The electrodeposition of both metals was carried out from the solution of leaching (pH 4.9) in the range of potential applications -200 to -1300 mV. The deposit was 10.12% Cd and 7.67 % Ni at a scanning rate of 50 mV / s, while the deposit was 23.05 % Cd and 14.44 % Ni at 10 mV / s. **Peng et al. 2012** studied the extraction of cadmium from acidic solutions into paraffin wax using different extractors at temperatures between 55 and 65 ° C. Cd and Ni are the main components of the leach liquor in Ni-Cd batteries (Reddy et al. 2005). Using the Cyanex 923 solvent, more than 99.9% of cadmium was extracted from the leach liquor (**Reddy et al. 2005; Reddy and Priya 2006**). However, **Babakhani et al. (2013)** used a 5:1 ratio of Cyanex 302 to D2EHPA to completely extract cadmium at pH 2 with < 5 percent of Ni extraction. Earlier **Nogueira and Delmas (1999)**, proposed a flow sheet for the recovery of metals in pure form from sulfate solutions.

### 2.3.3. Ni extraction from spent catalysts

The extraction of Ni can be carried out efficiently from spent catalysts. The recycling

of spent catalysts has become an unavoidable task, not only to reduce their costs but also to reduce waste catalysts to prevent environmental pollution. Although pyro-based processes have been used earlier, recent developments in the processing of such materials have mostly involved hydrometallurgical processes.

The initial composition of nickel catalysts depends on the reaction involved. For example catalyst for hydroalkylation reaction contains other metals such as tungsten, besides nickel. The spent HDS catalysts generally consist of 10–30% Mo, 1–12% V, 0.5–6% Ni, 1–6% Co, 8–12% S, 10–12% C and rest as alumina (**Zeng and Cheng 2009**). Since disposal is the last option with great liability, several processing methodologies are reported including those industrially used (**Marafi and Stanislaus 2008a, 2008b**). (**Table 5**)

#### **2.3.4. Recovery of Ni from polymetallic sea nodules**

Ocean nodules are the potential source of Ni and other metals, although the economic potential for the recovery of Ni, Cu, and Co from nodules has long been recognized, it was only in the last two decades or so that experiments on extracting methods were conducted.

Ocean nodules and low-grade nickel sulfide ore are important, but less viable, mineral resources of Ni, Cu, and Co. In low-grade nickel sulfide ore, nickel minerals appear as fine particles closely associated with copper, cobalt, iron and other minerals, resulting in a low recovery of valuable metals from traditional ore enrichment (**Wegorzewskiet al. 2018**). Ni, Cu, Co, and other metals fill the interstitial sites of manganese oxide mineral lattice in ionic form, leading to the necessary destruction of the high-valence manganese mineral lattice for the extraction of metals from polymetallic nodules (**Padhan et al. 2014**) **Table 6**

### **3. Disadvantages and alternative technologies**

Overall, each approach has significant issues, some of which are in common with the other processes as well as their process. Specific issues such as high capital costs (PAL, EPAL), high energy consumption (Caron), high acid consumption with certain types of ore (PAL), high corrosion and maintenance costs (PAL, EPAL) and process complexity (PAL, EPAL). Other processes have been tested and, in some cases,

implemented for projects. These include high-pressure acid leaching combined with atmospheric pressure agitated leaching (PAL + AL) in the case of EPAL in Ravens Thorpe, and stand-alone atmospheric pressure agitated tank leaching (AL) in Weda Bay, Indonesia, along with heap leaching (AL) in Çalda, Turkey. Other processes using chloride leaching have been tested but have not been applied to the commercial recovery of laterites.

### **Microbial leaching**

Microbial leaching began in the 1950s as a hydrometallurgical process for the dissolution of metals in ore by the catalysis of certain microorganisms. Microbial leaching metal is suitable for the treatment of low-grade and other difficult mineral resources in the metallurgical industry because of its low investment, low cost, simple process, and environmental friendliness. **(Wang et al. 1993, Liu et al. 1995, Zhai et al. 1997, Wang et al. 2011)**

A variety of metals were involved in the application. Of these, copper, uranium, and gold have been industrialized from their ores. The bioleaching process of metals such as nickel, cobalt, lead, and cadmium is still undergoing experimental research. Microbial leaching is generally considered to be the direct extraction of metals and the replacement of conventional smelters. **(Wang et al. 1993, Liu et al. 1995, Zhai et al. 1997, Wang et al. 2011)**

Microbial mineral processing is an interdisciplinary process involving the application of microorganisms for the extraction of metal values under ambient conditions. Application of microbes for mineral processing has been extensively studied in the recovery of copper, gold, cobalt and uranium metals (Rawlings et al. 2002(a), 2003(b), Olson et al. 2003). Microbial processing offers many advantages over conventional metallurgical mineral processing methods for the recovery of metals from low-grade ores and minerals due to its simple operation, low energy and reduced capital investment and eco-friendly nature **(Acevedo 2000, Castro et al. 2000)**. Although microbial mineral processing has attracted a great deal of attention in recent decades, a thorough understanding of the underlying mechanisms is needed to improve the efficiency of these processes. In the bioprocessing of minerals, microbes act as

catalysts for the leaching of metals from complex minerals or act as pre-treatment agents to alter the mineral structure, making them susceptible to lixiviant or leaching agents.

Microorganisms that play a pivotal role in the bioprocessing of minerals are broadly classified as heterotrophic and autotrophic according to their nutritional behavior. Heterotrophic microbes are non-photosynthetic; they derive energy from organic carbon sources for their metabolism. These microorganisms secrete metabolites such as hydroxycarboxylic acids, exo-polysaccharides, and these microbial metabolites are metal complexing and chelating agents that help dissolve metals by lowering the pH of the medium (**Tzeferis 1992**). Autotrophic microorganisms, on the other hand, are photosynthetic; they use atmospheric CO<sub>2</sub> as a carbon source. However, the chemolithotrophic group of microbes belongs to autotrophic microorganisms that rely on reduced inorganic iron and sulfur compounds for their nutrition.

### **Strategies to improve mining and moving towards commercialization**

Mining activities have the potential to have a significant impact on people and ecosystems. Exploration, mining, processing, and related activities include measures to prevent, minimize and mitigate environmental impacts. They also expect land once used for mining to be restored to a more natural state. Responding to these expectations builds public trust and promotes a sustainable, competitive industry.

Strong environmental and economic performance requires ongoing and expanded efforts and resources to minimize the industry's dependence on water, reduce the potential for harmful discharges, improve tailings management, improve water-processing technologies and reduce habitat and biodiversity loss. The mining industry is looking for ways to improve energy efficiency and reduce greenhouse gas (GHG) emissions to reduce its environmental footprint. (**The Mining Association of Canada, 2016**) Activities such as processing ore, discharging effluent and managing tailings are based on the use of water. If not properly managed, mining activities can cause water pollution due to acid mine drainage, metal contamination, and erosion and sedimentation. Climate change brings with it further challenges related to the availability of freshwater, droughts, floods, snowmelt patterns, changes in water

temperatures and other issues. (Natural Resources Canada, 2016, [Impact.canada.ca](http://Impact.canada.ca), 2018) Comminution is a process of crushing and grinding rock to release valuable minerals. This process accounts for more than 50% of the energy consumption of the mine site and up to 3% of all the electricity generated in the world. Air ventilation is essential for the safety of workers in underground mining. This is also an energy-intensive process. Improving energy efficiency in these and other areas is an important environmental and economic opportunity for the industry. (The Deloitte, 2017)

Energy management programs with renewables as a major component can reduce energy costs by 25% in existing mines and 50 % in new mines.

Renewable energy sources can reduce or eliminate the dependence on diesel. Examples exist, such as Glencore's two three-megawatt turbines and storage facilities at its Raglan nickel mine in Northern Quebec. However, issues related to year-round access to sunlight and the intermittent nature of wind today limit the use of such technologies. Mining value from waste can also reduce environmental costs, particularly in older operations. For example, sulfide minerals that cause acid mine drainage can be extracted from tailings to reduce the potential harm to the environment and the associated costs of liability for companies.

### **Conclusion and recommendation**

The global mining sector is under pressure. In the short term, falling commodity prices are squeezing cash flows. Looking ahead, many existing mines are ripening, resulting in the extraction of lower ore grades and longer distances from the face of the mine; ore-body-replacement rates are declining, and new-mine-development times are increasing. On top of that, global mining operations are as much as 28% less productive today than they were 10 years ago— and that's after adjusting for declining ore grades (Ajay Lala et al. 2015). The industry has shifted its focus to improving productivity by "sweating" existing assets, but this strategy will only go so far. Despite the booms and busts of the industry, the nature of mining has remained the same for decades. Achieving a breakthrough in productivity performance requires rethinking how mining works. The potential for such a breakthrough is now coming

within the reach of the industry through digital and technological innovations that could transform key aspects of mining. In this article, we describe some digital technologies that have been in operation for a long time and are now available and affordable enough to operate on a scale across the mining industry. Their applications include building a more comprehensive understanding of the resource base, optimizing the flow of materials and equipment, improving anticipation of failures, increasing mechanization through automation, and monitoring of performance in real-time. Each of these opportunities alone has real potential; together, they represent a fundamental shift in both potential safety outcomes and how value can be captured in the mining sector.

Research on the mineral phase transition during mineral remodeling is of great importance. On this basis, the technical difficulties in combining pyrometallurgical and hydrometallurgical processes will be resolved and the development of new, clean and efficient metallurgical methods and technologies will lead to the future development of nickel production alongside the recycling of metals that have already created a win-win scenario for both the environment and industry.

## Appendix

**Table 1 Nickel bearing minerals Boldt (1967), Pal and Deb (2009), USGS (2015)**

Types of minerals	Mineral	Chemical formula	The most common mode of occurrence	Location	%Ni
Sulfides	Pentlandites	(Ni, Fe) <sub>9</sub> S <sub>8</sub>	Sulfide phase basic and ultra-basic intrusive igneous rocks.	Russia, south Africa, Canada, Australia, Norway	~34
	Millerite	NiS	In limestone and dolomite cavities.	Australia, Canada, USA	64-65
	Heazlewordite	Ni <sub>3</sub> S <sub>2</sub>	In serpentine, probably of hydrothermal origin	USA, Australia	~73
	Polydymite	Ni <sub>3</sub> S <sub>4</sub>	In hydrothermal veins. Forms a series with limmaeite	Germany	58
	Siegenite	(Co, Ni) <sub>3</sub> S <sub>4</sub>	In hydrothermal veins with other Cu-Ni-Fe sulfides.	Germany, Czech Republic, USA, Zaire	28-29
Arsenides	Violarite	Ni <sub>2</sub> FeS <sub>4</sub>	In hydrothermal origin with other sulfides	Canada	39
	Niccolite/Nickeline	NiAs	In ore veins with silver, copper, Nickel, arsenides, and sulfides; ocean nodules	Canada, Australia	44
	Rammelsbergite	NiAs <sub>2</sub>	In Ni and Co veins formed and moderate Temperature	Canada, Germany	~28
	Gerdorffite	NiAsS	In hydrothermal vein deposits formed at a moderate temperature.	Austria, Morocco	~35
Antimonides	Breithauptite	NiSb	Hydrothermal calcite veins associated with Co-Ni-Ag ores	Canada, Norway, Australia, Italy, India	32-33
Silicates and oxides	Garneirite/Falcondodite	(Ni,Mg) <sub>4</sub> Si <sub>6</sub> O <sub>15</sub> (OH) <sub>2</sub> .6(H <sub>2</sub> O)	In laterites related to ultramafic rocks; Ni analog of sepiolites	Indonesia, Columbia, Dominican Republic, USA	<24
	Nickeliferous limonite	(Fe,Ni)O(OH).nH <sub>2</sub> O	In laterites related to ultramafic rocks	Indonesia, Greece, India	0.32-1.17 (NiO)

**Table 2 World primary nickel usage and production (INSG, 2018)**

World Primary Nickel	2016	2017	2018f
Usage	2.033Mt	2.192Mt	2.344Mt
Production	1.991Mt	2.07Mt	2.224Mt

**Table 3 Advantage and disadvantage of atmospheric leaching (stirred tank or heap) as compared to pressure acid leaching**

<b>Expected advantages</b>	<b>Refs</b>	<b>Expected disadvantages</b>	<b>Refs</b>
Lower CAPEX	b, d, e, g, h	Higher acid consumption ( to obtain	a, b, c, d, e, g, h
Conventional equipment	c, e, f, h	acceptable nickel recoveries)	
technology	b, h	Residue more voluminous ( from	h
Cheaper (less exotic) materials of		tank leaching )	
construction	c, d, e, h	More magnesium in the waste	g, h
Lower maintenance costs	c, h	liquor compared to HPAL	
Higher plant availability	h	May consume more limestone	h
Faster ramp-up	h	No significant improvement in	h
Easier startups and shutdowns	h	OPEX ( depending upon how	
Not prone to catastrophic		second-generation HPAL plants	
shutdowns	h	perform)	a, e, f, h
Less specialized workforce for		Cannot be applied to all ore bodies	
construction operations and		( mineralogy dependent); less	
maintenance	h	effective for treating limonites	h
Many suppliers of major common		Not yet commercially proven	c, d, h
equipment	h	Slower extraction kinetics and	
Better acid utilization	b,h	hence longer residence times	b, d, e
Lower energy consumption,		Produces highly contaminated	
leaching autogenous	h	liquor with significantly lower	
Simpler energy system	h	nickel to iron ratio; downstream	
Simpler process control	h	processing more challenging (e.g.	c, d, f
Easier recycle of process water	e, h	solid-liquid separation)	
Heap leaching far less complex		Lower nickel and cobalt extractions	c, f, g
than HPAL or AL (eg. No CCD,		( esp. from neutralizing ores)	

no tailing disposal)	h	Presence of more jarosite in tailing	c, d, f, g
May lower cut off grades	h	potentially an environmental	e
May be better suited to remote, undeveloped locations	e, f, h	problem	e
Process both limonite and saprolite	a, b	Longer residence times	e
Lesser scale and corrosion problems	a	CAPEX still relatively high	f, g
Economic if cheap sulphuric acid available	c, e	Requires correct blending of limonite and saprolite	
Use of seawater to provide sodium for iron rejection	i	Heap permeability critical	
Smaller operations allow for substantially lower investment with heap leaching		Sulfate losses due to jarosite formation	

a. Centerfold ( 1979), b. Chander ( 1982), c. Reid and Barnett (2002), d. Griffin et al. ( 2002), e. Wedderburn (2005), f. Neudorf and Huggins ( 2006), g. Smit and Steyl ( 2006); h. Neudrof ( 2007), i. Santos de Pontes Pereira and De Araujo Gobbo ( 2007).

**Table 4 Advantages and disadvantages of atmospheric chloride leaching as compared to atmospheric sulfate leaching**

<b>Atmospheric chloride leaching advantages (vs. sulfate AL)</b>	<b>Atmospheric chloride leaching disadvantages (vs. sulfate AL)</b>
<ul style="list-style-type: none"> <li>● Faster extraction kinetics [j]</li> <li>● Recovery of acid and magnesia by pyrohydrolysis eliminating final effluent [j]</li> <li>● Precipitation of hematite allows high recovery of hydrochloric acid [j]</li> <li>● Reduced capital requirements [k]</li> <li>● Suitable for treating limonite and saprolite</li> </ul>	<ul style="list-style-type: none"> <li>● Maintaining magnesium concentration of acidic brine and water balance a challenge [j]</li> <li>● Not suitable for treating high magnesium saprolites [j]</li> <li>● Not suitable for treating high magnesium saprolites [j]</li> <li>● Chloride medium requires special corrosion</li> </ul>

<p>fractions [k]</p> <ul style="list-style-type: none"> <li>● Reduced reagent requirements [k]</li> <li>● Good settling and filtration characteristics of iron-containing precipitates [k]</li> <li>● Environmentally stable iron hydrolysis products like hematite can be formed [k]</li> <li>● Recovery of magnesium as kieserite reduces discharge to the environment [k]</li> </ul>	<p>precautions [k]</p> <ul style="list-style-type: none"> <li>● Water balance difficult to maintain [k]</li> </ul>
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[J] Harris et al., ( 2003, 2006 b), [k] Smit and Steyl (2006)

**Table 5 Nickel extraction from spent catalysts**

Highlights	Ref
Testing the spent catalysts for recycling of critical metals	<b>Simens et al. (1986)</b>
An HCl leaching process to leach nickel (~ 73%) at 80°C and recovery NiO from a spent catalyst sample (17.7% Ni) was reported.	<b>Chaudhary et al. (1993)</b>
~ 99% Ni leaching from a spent catalyst of steam reforming plant with 50% sulfuric acid at 100°C in > 5 h time was reported.	<b>Al-Mansi and Abdel Monem (2002)</b>
High Ni extraction(~ 98%) with sulfuric acid from a spent fertilizer catalyst was achieved.	<b>Sahu et al. (2005)</b>
Combining acids (HNO3/H2SO4/HCl to treat the spent	<b>Lai et al. (2008)</b>

<p>hydride sulfurization catalyst showing similar leach efficiency (99% Ni and V, and ~ 90% Mo).</p>	
<p>Treating spent Raney nickel catalyst by sulfuric acid leaching and soda ash precipitation.</p>	<p><b>Lee et al. (2010)</b></p>
<p>A simple leaching process to recover over 99% Ni by sulfuric acid was proposed.</p>	<p><b>Nazemi and Rashchi (2012)</b></p>
<p>The diffusion-controlled model to represent the kinetics was proposed.</p>	<p><b>Parhi et al. (2013b)</b></p>
<p>Investigating the dissolution kinetics of nickel from the spent catalyst in nitric acid medium.</p>	<p><b>Sheik et al. (2013)</b></p>
<p>The study of kinetics and statistical analysis of nickel leaching in nitric acid solutions</p>	<p><b>Ramos-Cano et al. (2016)</b></p>
<p>subjecting spent catalysts (3.31% Ni) with separate acidophiles.</p>	<p><b>Kim et al. (2009) and Srichandan et al. (2014)</b></p>
<p>Describing a two-stage process to treat the spent catalysts using the bio-and chemical leaching.</p>	<p><b>Pradhan et al. (2013)</b></p>
<p>The revelation of chemolithotrophic sulfur-oxidizing bacteria can recover Ni (~ 88%) and other valuable metals from the vanadium-rich spent refinery catalysts.</p>	<p><b>Mishra et al. (2007, 2008) and Pradhan et al. (2009)</b></p>
<p>The extraction of 83% Co, 16% Ni along with 95% Mo with <i>A.thiooxidans</i>, better results (37% Ni)</p>	<p><b>Gholami et al. (2015)</b></p>

Using a mixed culture of <i>A. ferrooxidans</i> , <i>A. thiooxidans</i> and <i>L. ferrooxidans</i> achieving the extraction yields of Ni and V (83% and 90%, respectively)	<b>Beolchini et al. (2010)</b>
Using <i>A. thiooxidans</i> to extract 92% Ni in 48 h using iron and sulfur supplements	<b>Bosio et al. (2008)</b>
A group of researchers treated spent catalysts with 61 ppm Ni by various microorganisms.	<b>Bharadwaj and Ting 2013; Vyas and Ting 2016</b>
The time of 30d for Ni dissolution of 95% with <i>A. ferrooxidans</i>	<b>Vyas and Ting 2016</b>
A two-steps extraction process ~96% Ni in 6d at 70°C using a thermophile, <i>Acidianus brierleyi</i> .	<b>Bharadwaj and Ting 2013</b>
Leaching efficiency of (97% Ni) was obtained using another thermophile, <i>Sulfolobus metallicus</i> at 75°C in 6 d.	<b>Kim et al. (2012)</b>
Achieving the recoveries of 58.2 and 78.5% Ni with unadapted and adapted <i>Aspergillus niger</i> , respectively, in 30 d used from spent catalysts (6.09% Ni).	<b>Santhiya and Ting (2005, 2006)</b>
Extraction of 32% Ni from the spent FCC catalysts in 21 d with <i>A. niger</i>	<b>Bayraktar (2005)</b>
Extraction of ~ 45.8% Ni from the decoked catalyst in 30d with <i>A. niger</i> .	<b>Amiri et al. (2012)</b>

**Table 6 Recovery of nickel from polymetallic sea nodules**

<b>Highlights</b>	<b>Ref</b>
manganese nodules have been identified as a potential source of not only nickel but cobalt, copper, and manganese	<b>Monhemius 1980; Randhawa et al. 2016a)</b>
Summarizing the R & D approach and the large scale trials conducted to process the sea nodules.	<b>Monhemius (1980)</b>
Summarizing the hydro and biohydro-metallurgical options for the treatment of sea nodules in the last two decades	<b>Mukherjee et al. (2004a)</b>
Updating on extraction processes to treat polymetallic nodules developed/up-scaled in different parts of the world including India.	<b>Randhawa et al. (2016a)</b>
describing a process developed at Sumitomo Metal Mining Company (Japan) for the recovery of five metals (Cu, Ni, Co, Fe & Mn) from the Pacific Ocean nodules	<b>Kohga et al. (1995)</b>
Reductive leaching of sea nodules in aqueous media has often been reported. The reductants used are: SO <sub>2</sub> in aqueous, ammonia solutions, glucose in ammonia, pyrite in HCl, chalcopyrite in HCl, metal sulfide-rich matte in HCl, H <sub>2</sub> O <sub>2</sub> in sulfuric acid, aliphatic alcohols in HCl and phenols in H <sub>2</sub> SO <sub>4</sub>	<b>Khalafalla and Pahlman 1981, Acharya et al. 1999; Das and Anand 2017, Das et al. 1986, Kanungo 1999a, 1999b, Chen et al. 1992, Kawahara and Mitsuo</b>

<p>Establishing two-stage leaching [NH<sub>3</sub>-(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>] scheme to treat Indian Ocean nodules following the reduction roast-ammonia leach process</p> <p>Achieving a high recovery of Co (71.3%) along with 92.5% Cu and 91.5% Ni.</p> <p>The study of an Acidithiobacillus ferrooxidans-coupled leaching of Ni, Cu, Co, and Mn from oceanic polymetallic nodules and low-grade nickel sulfide ore, and focuses on the electrochemical behavior of the ores in simulated bio-leaching solutions.</p>	<p><b>1992, Jana et al. 1995, Zhang et al. 2001</b></p> <p><b>Jana et al. (1999a, 1999b)</b></p> <p><b>Mishra et al. (2011)</b></p> <p><b>Kang et al. (2019)</b></p>
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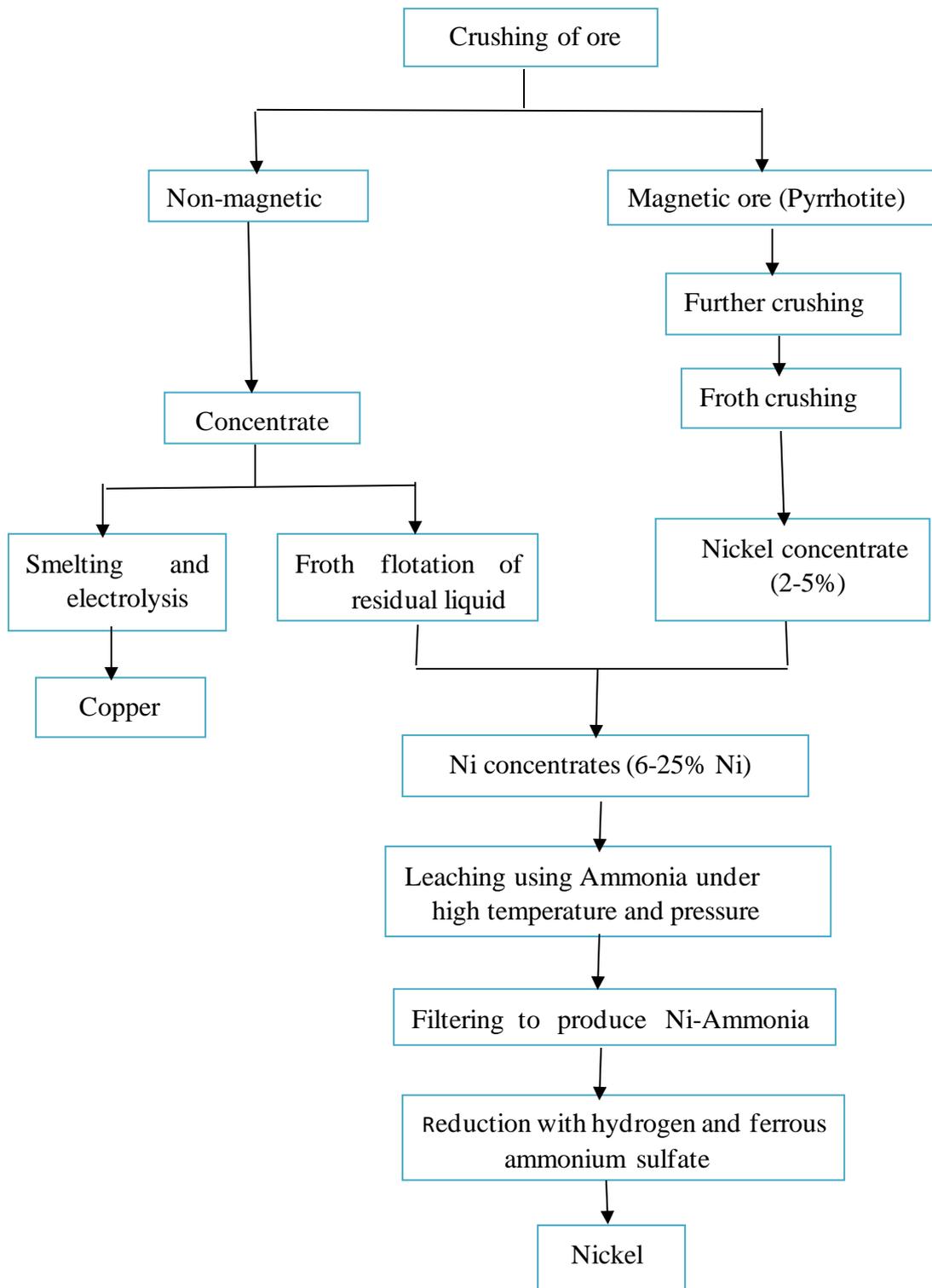


Figure 1 Flowsheet summarizing typical processing of magmatic sulfide ores

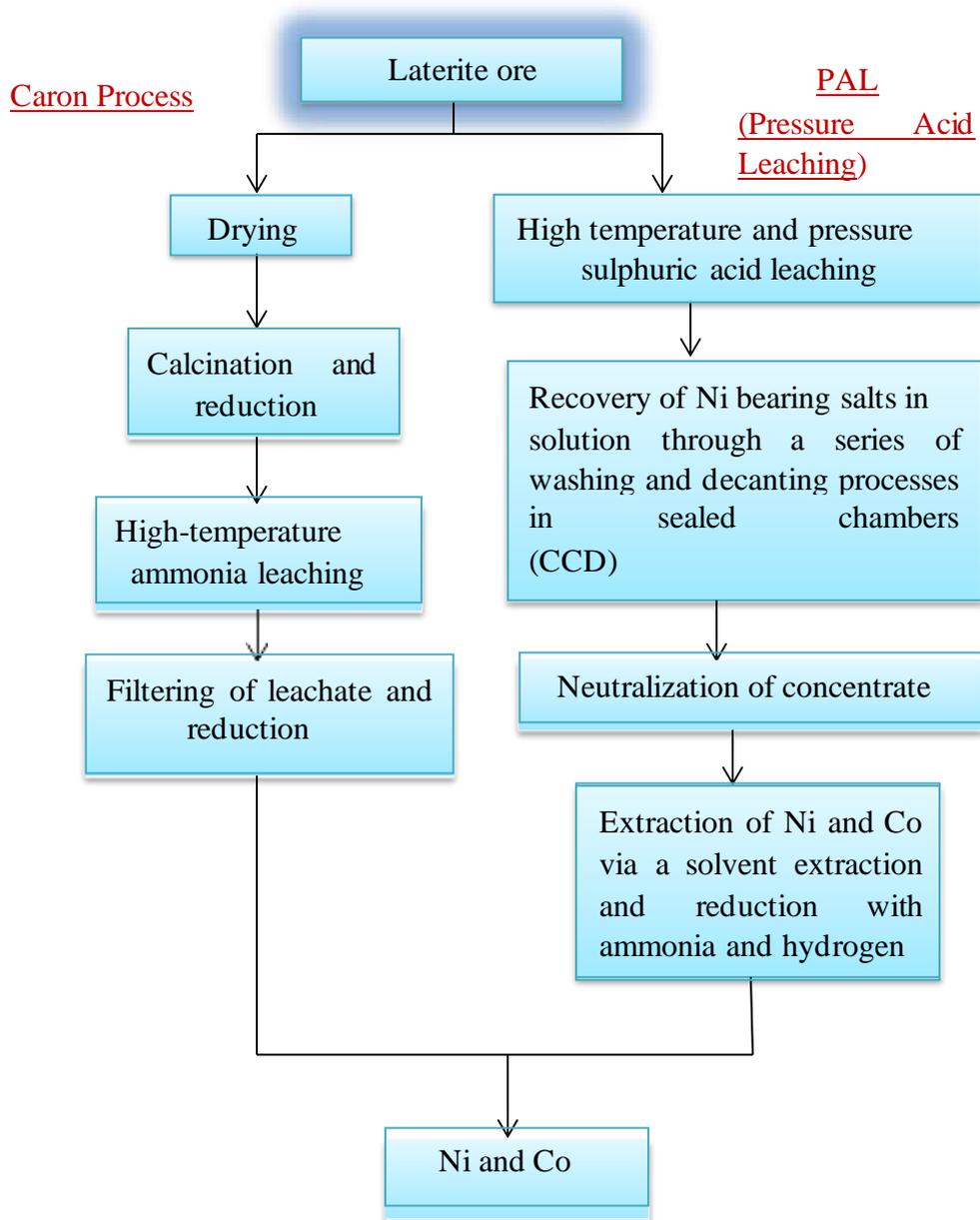


Figure 2 A flow sheet summarizing the processing of lateritic ores

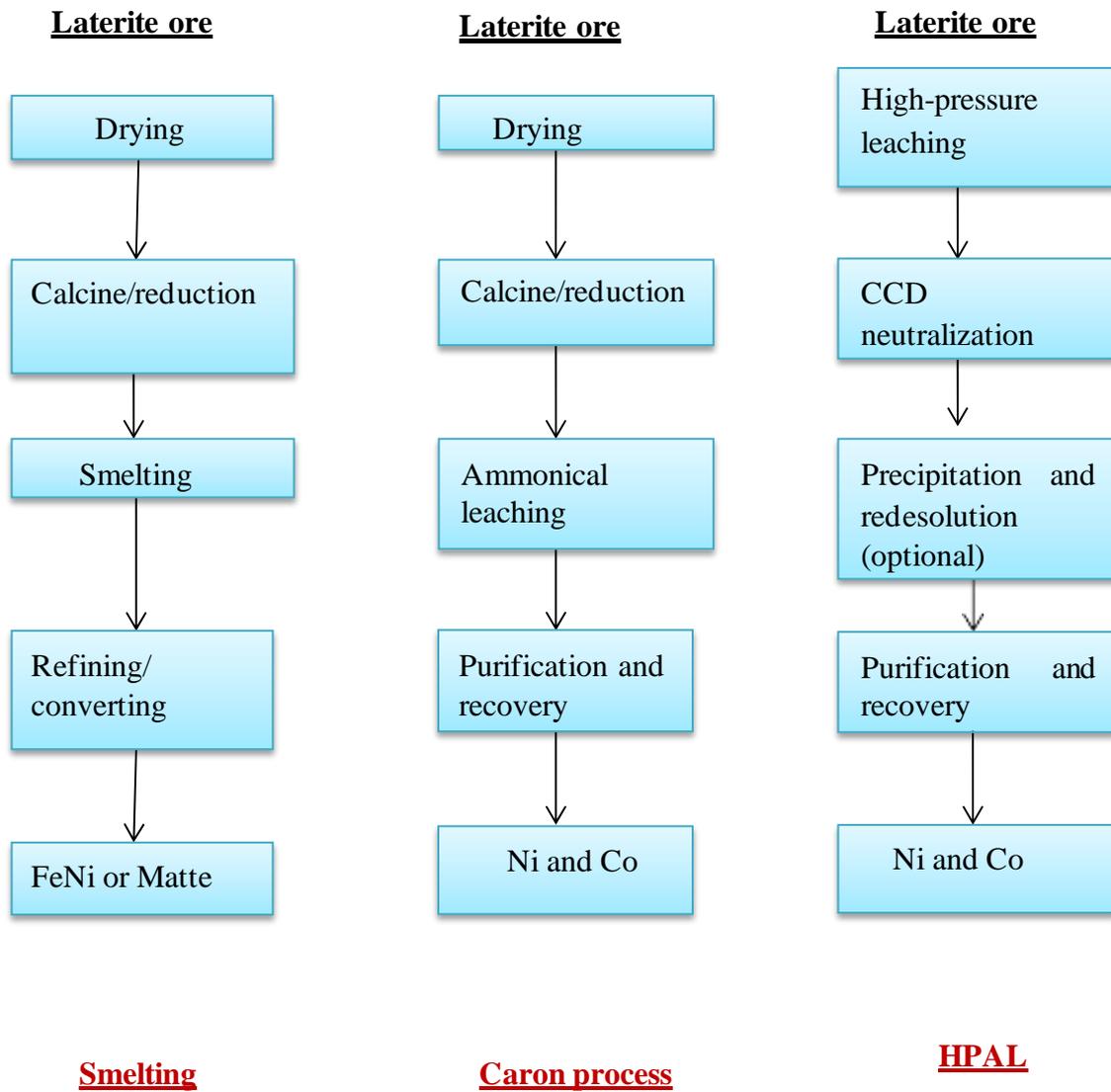


Figure 3: A generalized block flow diagram of laterite processes

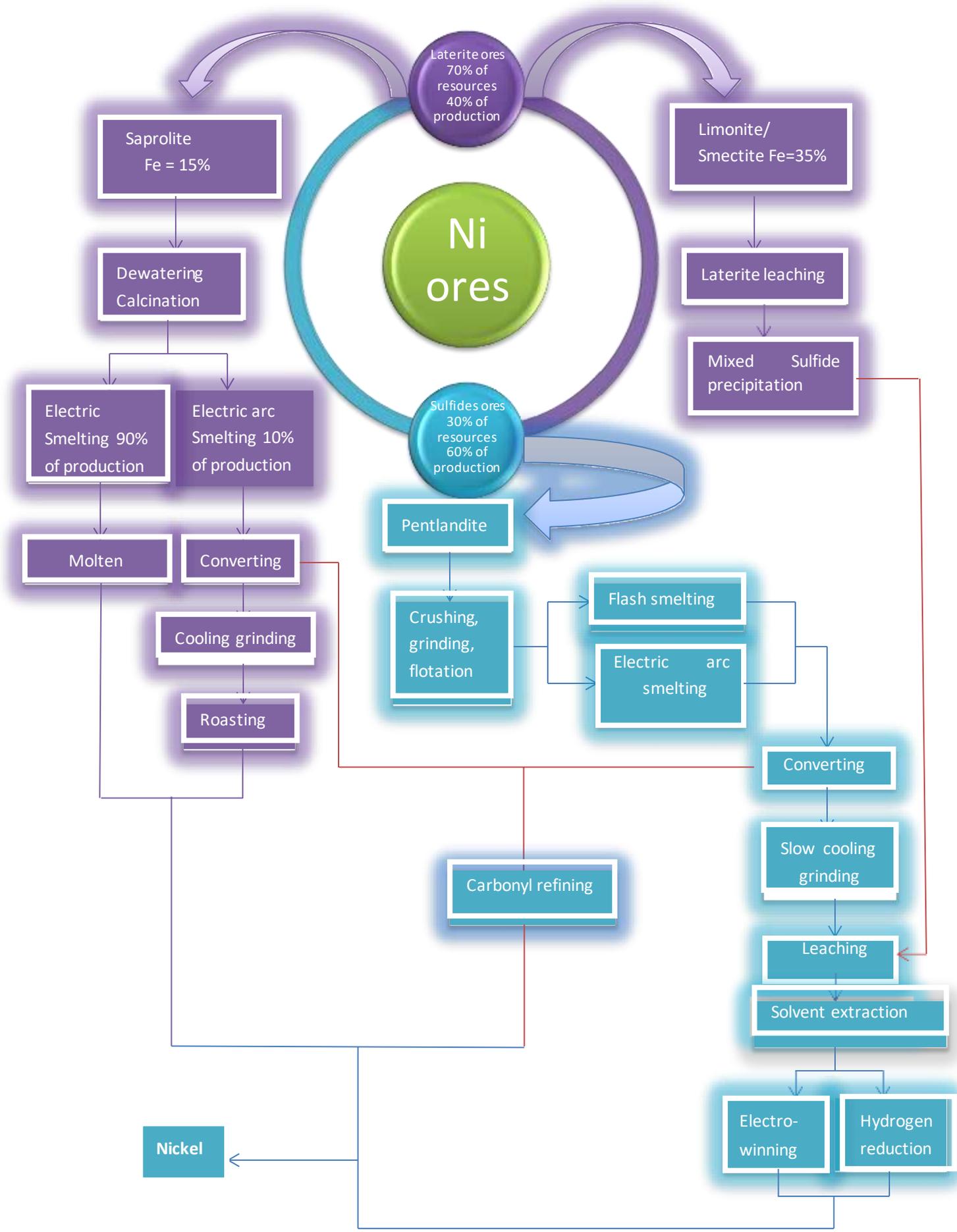


Figure 4 Summary of the processing of different nickel ores

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