Marja Riekkola-Vanhanen

Finnish expert report on best available techniques in nickel production
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FINNISH ENVIRONMENT INSTITUTE
Foreword


One of the activities included in the Directive concerns the production of non-ferrous metals, according to the definition of category 2.5 (a) in Annex I: “Installations for the production of non-ferrous crude metals from ore, concentrates or secondary raw materials by metallurgical, chemical or electrolytic processes”. These installations are part of the industrial sectors to be studied in 1998.

Within the above mentioned framework, the Finnish Environment Institute and Outokumpu Technology Oy have decided to contribute to the exchange of information in the European Union by making a study on Best Available Techniques for the primary production of non-ferrous metals. Outokumpu Research Oy has been requested to perform this study. The responsible leader for the work has been Raimo Rantanen and the report has been written by Marja Riekola-Vanhanen. Maija-Leena Metsärinta has prepared a literature survey on the subject.

Primary non-ferrous metal production in Finland concerns only copper, nickel, zinc and ferrochromium. Gold and other precious metals are produced as by-products in the copper production. This report describes the primary production of nickel. The primary copper, zinc and ferrochromium productions are described in separate reports.

The main objective of this BAT report is to identify available techniques for the reduction of emissions and energy use of the primary nickel production in Finland. Only the pyrometallurgical flash smelting process is in use in Finland to recover nickel from sulphide concentrates and it is the main process described in this report. The information presented is largely based on environmental permit applications, the corporate environmental programme and permit regulations concerning Outokumpu. Additional information concerning general issues of nickel production and comparison of methods has been obtained from the literature available.

The project has been guided by a steering group that provided comments on the draft reports and offered a platform for discussion on the scope, themes and results of the study. The steering group members represented the following organisations: Finnish Environment Institute, Southwest Finland Regional Environment Centre, Outokumpu Oyj, Outokumpu Technology Oy, Outokumpu Harjavalta Metals Oy, Outokumpu Zinc Oy and Outokumpu Chrome Oy.
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1. General

Nickel is a silver white metal with typical metallic properties. The great importance of nickel lies in its ability, when alloyed with other elements, to increase a metal’s strength, toughness and corrosion resistance over a large temperature range. Chemically, nickel resembles iron and cobalt, as well as copper. One property of nickel is its ability to react directly with carbon monoxide to form a binary carbonyl complex which is volatile at ambient temperatures. At moderate temperature nickel is corrosion-resistant against air, sea water and unoxidizing acids. Another property of nickel is its corrosion resistance to alkalis. In contrast, nickel is attacked by aqueous ammonia solutions /1/.

Nickel is essential to the iron and steel industry notably in the formulation of stainless steel. Nickel-containing alloys have played a key role in the development of materials for the aerospace, automotive, marine, electronics and construction industries. These facts make it a valuable and strategic metal.

1.2 Occurrence

Nickel ranks twenty-fourth in the order of abundance of elements in the earth’s crust with an estimated concentration of 0.008 %. Nickel can be found in the soil in two different types of mineralisations: sulphidic and lateritic. The laterites can further be divided into two types: limonites which are oxidic with lower magnesia (< 5 % MgO) and nickel contents (< 1.5 % Ni), but high moisture contents typically close to the surface of the ore body and saprolites which are mostly silicates with higher magnesia (up to 35 %) and nickel (2–3 % Ni) contents typically deeper in the ore body. Table 1 shows some examples of different types of nickel ores showing in particular to what extent the composition may vary. The cobalt contents are typically fairly high in limonites ranging, however, within wide limits. Similarly in the sulphidic ores the nickel as well as copper and cobalt contents vary a lot. In addition there are varying impurity contents e.g. arsenic and magnesia, which may cause problems in downstream processing.

Further on, nickel products can be divided into three groups:
1. Refined nickel (class I), nickel content 99 % or more. The group includes electrolytic nickel, pellets, briquettes, granules, rondelles and powders/flakes.
2. Charge nickel (class II), nickel content less than 99 %. The group includes ferronickel, nickel oxide sinter and utility nickel.
3. Chemicals, such as nickel oxides, sulphates, chlorides, carbonates, acetates, hydroxides etc.

The variety of raw materials and products as well as the availability of different unit technologies result in a number of different process alternatives depending on the raw material and the product. It is typical for the nickel industry that the processes are in many cases tailored for specific types of raw material. This is dif-
ferent from copper and zinc, the raw materials of which are typically fairly homog-

Table 1. Analyses of some nickel ores /2/.

<table>
<thead>
<tr>
<th>Ore Type</th>
<th>Ni %</th>
<th>Cu %</th>
<th>Co %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Murrin Murrin Laterite</td>
<td>1.25</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Cawse Laterite</td>
<td>1</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Cerro Matoso Laterite</td>
<td>2.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Selebi-Phikwe Sulphide</td>
<td>0.65</td>
<td>0.75</td>
<td>0.06</td>
</tr>
<tr>
<td>Falconbridge, Sudbury Sulphide</td>
<td>1.7</td>
<td>1.8</td>
<td>0.05</td>
</tr>
<tr>
<td>Falconbridge, Raglan Sulphide</td>
<td>3.2</td>
<td>0.9</td>
<td>0.05</td>
</tr>
<tr>
<td>INCO, Copper Cliff Sulphide</td>
<td>1.55</td>
<td>2</td>
<td>0.04</td>
</tr>
<tr>
<td>Outokumpu, Silver Swan Sulphide</td>
<td>9.8</td>
<td></td>
<td>0.11</td>
</tr>
<tr>
<td>Mount Keith Sulphide</td>
<td>0.6</td>
<td>0</td>
<td></td>
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</tbody>
</table>

Traditionally refined nickel has been produced from sulphidic ores and ferronick-

Traditional refined nickel has been produced from sulphidic ores and ferronick-
el from saprolitic laterites. Limonitic laterites have not been utilized almost at all, because of the low nickel content and thus large amounts of ore to be treated. This is due to the fact that the nickel content of laterites cannot be upgraded to any sig-

The development of new technologies and the differences between individ-

1.3 Production

As already described, there are several technologies which can be used in the treat-

Laterite ores, in contrast, are amenable to only limited concentration by screening and drying, and therefore almost the entire volume of ore must go to metallurgical plants. Thus, laterite processing tends to be more expensive, but mining costs are usually much lower than for sulphide ores. These differences, plus the availability of valuable by-products, can have an important influence on the viability of a specific deposit.

There are two types of nickel processing techniques. In pyrometallurgical proc-

Nickel is mined in significant quantities in 21 countries, and produced in about 23 countries. The European nickel producers are shown in Table 2. The nickel pro-

The consumption in the same year was 321,400 tonnes, which is 34 % of the world’s consumption.
Table 2. European nickel producers in 1996.

<table>
<thead>
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<th>Producer</th>
<th>Source of raw material</th>
<th>Capacity</th>
<th>By-products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eramet, France</td>
<td>New Caledonia</td>
<td>16,000 t/a</td>
<td>Cobalt chloride, FeCl₃</td>
</tr>
<tr>
<td>Falconbridge, Norway</td>
<td>Canada, Botswana</td>
<td>85,000 t/a</td>
<td>Cu, Co, H₂SO₄</td>
</tr>
<tr>
<td>Inco, United Kingdom</td>
<td>Canada</td>
<td>41,000 t/a</td>
<td>Nickel sulphate</td>
</tr>
<tr>
<td>Larco, Greece</td>
<td>Greece</td>
<td>20,000 t/a</td>
<td>in ferronickel</td>
</tr>
<tr>
<td>Outokumpu, Finland</td>
<td>Finland, Norway, Australia</td>
<td>32,000 t/a</td>
<td>Cu, Co, H₂SO₄</td>
</tr>
</tbody>
</table>

1.4 Nickel Consumption

The world consumption of nickel remained below 1,000 tonnes per year until 1876, currently it is about 1 million tonnes per year. The world’s primary nickel production in 1996 was approximately 950,000 tonnes and the capacity about 1,200,000 tonnes. The first use of nickel in 1996 is shown in Figure 1.

![Figure 1. Use of nickel.](image)

1.5 Economic Aspects

The Western World nickel consumption increased by an average of 6.5 % per annum from 1945 to 1974. Consumption dropped sharply in 1975 and the demand for nickel remained flat for the next ten years. The new recovery of nickel demand started in 1993 growing about 15 % in 1995 and is continuing today. The demand is expected to remain strong. Stainless steel and other Ni-bearing alloys are widely recycled. Secondary nickel accounted for about 50 % of the stainless steel raw materials supply in the Western World.

For many years nickel was sold on the basis of posted producer price. In 1979 the London Metal Exchange (LME) started trading in Class I nickel, and it has since become the major factor determining nickel price levels. The London Metal Exchange publishes the official nickel price daily and this is used as a basis in nickel trade world-wide. Nickel price has been volatile last twelve years ranging from US$1.60 per pound (January 1987) to US$ 10.84 per lb. (March 1998). Nickel price is not only affected by market fundamentals, but also by fund trading in LME. The nickel cash price 29.12.1998 was US$ 3,900 per tonne and according to the fundamentals no price recovery will be seen in the immediate future.
2.1 General

Over 90% of the world’s nickel sulphide concentrates are treated by pyrometallurgical processes to form nickel containing mattes /2/. Nickel matte is then treated by various refining processes to produce nickel metal, nickel powder or nickel oxide. A hydrometallurgical process was developed by Sherritt applying ammoniacal pressure leaching, but it is used only for leaching of matte and precipitates today. Figure 2 represents the methods used.

Nickel laterites have historically been treated almost exclusively by smelting processes, and with the exception of Cuba, where nickel ore treatment is all essentially hydrometallurgical, the industry is still predominantly pyrometallurgical. The development of nickel oxide ore smelting has drawn heavily on iron and steel metallurgy for ferronickel production and on copper metallurgy for nickel matte production. Today the development of hydrometallurgical methods for treating laterite ores is proceeding quickly. Figure 3 represents the methods used for laterite ores.

The pyrometallurgical nickel process is the only one used in Finland to recover nickel from sulphidic nickel concentrates. The flash smelting process at Outokumpu Harjavalta Metals is described in this study. A brief description is also given of other nickel producing processes applied elsewhere.
2.2 Pyrometallurgical Methods

The pyrometallurgical treatment of nickel concentrates includes three types of unit operation:
- roasting
- smelting
- converting

In the roasting step sulphur is driven off as sulphur dioxide and part of the iron is oxidised. In smelting, the roaster product is melted with a siliceous flux which combines with the oxidised iron to produce two immiscible phases, a liquid silicate slag which can be discarded, and a solution of molten sulphides which contains the metal values. In the converting operation on the sulphide melt, more sulphur is driven off as sulphur dioxide, and the remaining iron is oxidised and fluxed for removal as silicate slag, leaving a high grade nickel copper sulphide matte.

In several modern operations the roasting step has been eliminated, and the nickel sulphide concentrate is treated directly in the smelter.

2.2.1 Roasting

In the roasting stage the nickel sulphide concentrates are heated in oxygen-enriched air at a temperature of 600–700°C at which oxygen oxidises sulphide to sulphur dioxide and reacts with the metals to form solid oxides, termed calcine.

In order to achieve effective roasting the furnace must provide good contact between the sulphide particles and the oxygen-bearing gas. The furnace system must also be able to provide close control of the degree of sulphur elimination. Both multihearth roasters and fluidized-bed roasters are in current industrial use for nickel concentrate roasting.
2.2.2 Smelting

The smelting step is carried out in a variety of furnaces, including reverberatory, electric and flash furnaces, which provide a wide variety of smelting conditions. Chemical losses of nickel and copper to the slag increase with the oxidation potential of the system. Thus metal losses to slag are much higher in the flash smelting furnace, in which the roasting step is combined with the primary smelting step, and smelting conditions are strongly oxidising, than in the electric furnace, where smelting is carried out under reducing conditions. Consequently, slag from the flash smelting furnace must be treated in a separate step to recover the contained metal values, while the slag from the electric furnace or reverberatory furnace smelting processes can be discarded without further treatment.

Sulphur dioxide containing gas is also generated. SO$_2$ is harmful to the environment and must be removed before the off gas is released into the atmosphere. This is almost always done by capturing the SO$_2$ as sulphuric acid.

2.2.2.1 Flash Furnace Smelting

Flash furnace smelting entails blowing dried concentrate with oxygen-enriched air or oxygen into a hot hearth-type furnace. Once in the furnace, the oxygen of the blast combusts the concentrate to give molten matte, molten slag and SO$_2$-bearing off-gas.

The oxidation reactions provide much or all of the energy for heating and melting. Fossil fuel burners are often employed to control furnace temperatures, but mostly the process is autogeneous. The molten matte and slag are tapped separately from the furnace as they accumulate.

Flash smelting is mostly done in Outokumpu type flash smelting furnaces either applying the conventional smelting process with converting to produce high grade matte, or by the new DON process, in which two different mattes are produced without converting. Today approximately 30% of world nickel production is based on Outokumpu flash smelting. Inco type flash smelting is used by Inco in its own operations in Canada.

2.2.2.2 Reverberatory Furnace Smelting

The reverberatory furnace is a hearth furnace in which a solid charge of concentrates and flux is melted at about 1,200°C by hot combustion gases sweeping over the hearth. The combustion gases are provided by burning fossil fuel in endwall or roof burners. The products of the process are molten matte and molten slag.

Reverberatory furnace smelting is primarily a melting process in contrast to flash smelting which is an oxidation/melting process. Reverberatory smelting makes little use of the energy from sulphur and iron oxidation for heating and melting. It also produces large quantities of fossil fuel combustion gas containing about 1% of SO$_2$. It is difficult to remove SO$_2$ at this low concentration which means that the off-gases are an air pollution problem.

2.2.2.3 Electric furnace

Roasting and electric smelting is used to produce Bessemer matte. In the roasting stage a considerable part of the sulphur content is oxidised and the remaining sulphur dioxide is used for sulphuric acid manufacture.

The calcine formed is smelted in electric furnaces and converted to produce matte for further refining.
2.2.3 Converting

Nickel converting consists of air oxidation of the molten matte from smelting. Liquid matte is transferred from the smelting furnace in large ladles and poured into the converter through a large central mouth. The oxidising blast is then turned on and the converter is rotated, forcing the blast into the matte through a line of tuyeres along the length of the vessel. The heat generated in the converter by iron and sulphur oxidation is sufficient to make the process autogeneous.

Peirce-Smith converters are normally used for the treatment of nickel furnace mattes. This is due to their simplicity and high chemical efficiency. There is, however, significant leakage of SO₂ into the atmosphere during charging and pouring.

Sulphur dioxide-containing gas is also generated. SO₂ is harmful to the environment and must be removed before the off-gas is released into the atmosphere. This is almost always done by capturing the SO₂ as sulphuric acid.

2.2.4 Slag cleaning

The nickel smelting slag is cleaned in an electric furnace. The slag is tapped through slag tap holes along launderers into the electric furnace. Coke and reverts are added through the furnace roof. Slag from the electric furnace is tapped into granulation and transported to the slag storage area. Matte from the electric furnace is periodically tapped through tapping holes and launderers into ladles and transferred by cranes to converters for further treatment.

There are three or six electrodes in the electric furnace to supply energy into the furnace. Electric power is needed for the reduction reactions, heat losses and smelting of reverts. The reductive agent is coke. Electric furnace off gases are first burned in an incinerator, then cooled and lead through a bag filter or scrubber to the stack.

2.2.5 Conventional Flash Smelting process

Figure 4 shows the flow sheet of the conventional Outokumpu nickel smelting process.

There are four smelters in the world which use this process. Two of these use a flash smelting furnace designed by Western Mining Corporation, where the smelting and slag cleaning furnaces have been built to one integrated unit.

There are differences in operations between the smelters. The most visible difference is the matte grade. Differences in the raw material composition may also cause variation.
2.3 Refining processes

Nickel-containing mattes are mostly used for the production of nickel metal either as cathodes or powder. Figure 5 shows principally different refining processes and does not exhaustively cover all available process alternatives. Practically, each refinery is different, because the processes have been developed for predefined raw materials.

In most cases nickel matte is leached, either in sulphuric acid solution, chloride solution or ammoniacal solution. The solution is purified using either traditional precipitation methods, such as hydrogen sulphide or hydroxide precipitation, or modern solvent extraction methods, recovering simultaneously copper and cobalt values of the matte. Finally nickel is recovered by electrowinning or hydrogen reduction.

Figure 5. Nickel matte refining processes.
Nickel oxide and carbonyl nickel are also produced from nickel mattes. When nickel oxide is produced, the matte is roasted, the calcine formed is refined by chlorination and nickel oxide is reduced with hydrogen. Carbonyl nickel is produced from nickel matte by first converting it to nickel metal with a top blown rotary converter (TBRC) and the resulting metal is subjected to the carbonyl process to produce nickel powder.

2.4 Traditional laterites processing

Saprolitic laterites with higher nickel contents have mostly been used for the production of ferronickel to be used as raw material in stainless steel production. The process itself is relatively simple including the feed preparation step, upgrading, drying and perhaps briquetting. The material is then reduced in large kilns or shaft furnaces, where the final ferronickel reduction takes place. The crude ferronickel is refined to decrease the sulphur content and sometimes the silicon and phosphorus contents, too.

The nickel content in most laterite ores is low. The production has to take place at the mine site, because high tonnages have to be treated and the ore cannot be upgraded in the same way as the sulphide ores. For the same reasons the energy consumption is very high. However, in contrast to sulphide mines, the mining costs of laterites are fairly low.

The saprolitic laterites can also be used to produce nickel matte. This differs from ferronickel smelting in that the reduction kiln product is sulphidised by injecting sulphur at the discharge end of the kiln. The resulting matte after electric smelting is shipped to be used in nickel production.

Limonitic laterites with lower nickel contents have been utilised in nickel production only to a very limited extent so far. A lot of work has been invested in the development of new hydrometallurgical processes during the last few years. As a result a number of new processes are available and production facilities are under construction.

2.5 Direct Outokumpu nickel flash smelting process (DON) and nickel refining at Harjavalta

The direct Outokumpu nickel flash smelting process involves several stages as shown in Figures 6 and 7. These stages have been briefly described in this paragraph. The plant is situated in Harjavalta and integrated with the copper flash smelting process. Outokumpu Harjavalta Metals Oy is a part of the Outokumpu Base Metals business area. It produced in 1997 200,000 tons of copper and nickel in Harjavalta and Pori in Western Finland. Outokumpu Harjavalta Metals Oy produces nearly 30 products. A considerable part of the production is exported.

The nickel Flash Smelting Furnace and nickel electrolysis began their operations in 1959–1960. The latest expansion of the plant was completed in 1996, when the newly developed DON-process was commissioned. The number of personnel is about 1000. The number of personnel working in the nickel process is only 470.

Work is certified to ISO 9002 requirements. Safety functions are organised to be an essential part of normal business unit operations.
2.5.1 Raw material reception and storage

The raw material for nickel smelting is nickel sulphide concentrate. These concentrates are mainly bought abroad by using long-term delivery agreements. Most concentrates are bought from Australia. Some nickel-containing precipitates and scrap are also used. Nickel matte is also bought from abroad and fed directly to the nickel refinery. All raw material purchasing is made by the company’s own service organisation.

Most of the raw materials are imported to Mäntyluoto harbour, Pori. The concentrate is unloaded directly to the harbour transit terminal from the ship with grabs. The railway wagons are loaded in the terminal with front-end loaders. The wagons are covered with hydraulic lids. The wagons are weighed electronically both in loaded and empty conditions. The loaded wagons are delivered by train to the Harjavalta works, which is located some 45 km from the harbour. The concentrates are stored in Harjavalta in a large ware house designed for 25,000 tonnes of concentrate.

2.5.2 Blending and drying of the concentrates

Preparation of primary feed mixture is carried out automatically by unloading a certain amount of the feeding material from the feeding bins to a belt conveyor. The mixture is dried in a rotating drum, which is heated with waste oil. Gas from the copper anode furnace or nitrogen is added to prevent the material from catch-
ing fire. The dried material is screened. The fine material is conveyed to the feeding bins of the Flash Smelting Furnace. The coarse material is fed to the electric furnace.

The gases are precleaned in electrostatic precipitators and conducted through a bag filter to the stack. Dust is returned to the feeding bins of the flash smelting furnace. The iron oxide precipitate from the leaching of the electric furnace matte is conveyed to the same bins.

### 2.5.3 Direct nickel flash smelting (DON process)

Dried nickel concentrate feed mixture and oxygen-enriched air is fed into the reaction shaft of the furnace through a concentrate burner. The mixing of gas and feed is effective and the concentrate particles react rapidly in suspension with oxygen in the hot reaction shaft. The melting heat is formed by the oxidation of sulphur and iron. Because the process is not autogeneous, oil burners are used to produce more heat, when needed. The reactions and partial melting occur in the gas-solid suspension. The reaction products from the reaction shaft drop down to the molten slag in the settler part of the furnace. Reactions still continue in the thin reaction layer on the molten slag. The heavier matte layer descends into the bottom of the furnace and the lighter slag layer remains on the surface. The target content of copper + nickel in matte is about 75%. The iron content of the matte is between 2–6%.

The nickel matte tapped out of the furnace is granulated directly from the furnace by water quenching of the sprinkled melt. The facility for the flash smelting furnace matte granulation is located next to the furnace. The matte is tapped through a launder into a spray head, which spreads small molten matte particles into a granulation tank. The solidified matte granules settle in a conical section of the tank, from where they are pumped with water on to a dewatering screen. The granules are lifted in a bucket elevator into an intermediate bin, from where they are taken on a belt conveyor to grinding and to the hydrometallurgical nickel plant. The slag is laundered to the electric slag cleaning furnace where nickel is recovered as metallised matte-containing iron.

The cooling water is pumped into the granulation tank through several inlet nozzles situated on the tank wall. The water flow is turbulent enough to avoid overheating and evaporation. Overflow water is discharged into the clarifier. The water which conveys the granules flows through a screen in the screw classifier and further as overflow to the clarifier. Clarified water is pumped to the cooling towers from where it is circulated back to the granulation.

The flash furnace cooling water circuit is closed. Water is circulated between the furnaces, two cooling towers and storage ponds.
2.5.4 Gas cleaning

The gas produced in the reactions in the reaction shaft exits through an uptake shaft and is cooled in a forced circulation waste heat boiler consisting of a radiation section followed by a convection section. The boiler is a forced circulation boiler, which produces saturated steam. Part of the dust settles in the waste heat boiler and the rest in the electrostatic precipitator. All the dust is collected together and conveyed by pneumatic conveyor into the flue dust bin of the flash smelting furnace in order to be recycled.

After the electrostatic precipitator there are process gas fans which maintain a slight under-pressure in the furnace, waste heat boiler and precipitator and blow the process gases to the sulphur recovery. The high sulphur dioxide content of the gas makes it possible to recover sulphur as liquid SO₂ and sulphuric acid.

There is a separate duct to carry the hot gases by passing the waste heat boiler and electrostatic precipitator to the stack. This can be used during feed stoppages and other disturbances, when the gases cannot be sent to the acid plant.

2.5.5 Processing of nickel-containing slag in the electric furnace

The nickel slag from the flash smelting furnace is cleaned in the electric furnace as a batch process using coke as a reducing agent. The reactions mainly occur during tapping when the slag flows through the coke layer.
Crushed reverts and different types of scraps are also processed in the electric furnace. The melting point and the viscosity of the matte can be reduced by raising the sulphur concentration. This is carried out by injecting nickel concentrate into the electric furnace melt. The matte formed is granulated in the same way as nickel flash smelting matte. The slag from the electric furnace is granulated and taken to be landfilled. Part of it is sold to be used in sand blasting.

Carbon monoxide formed in the electric furnace is burned in a water-cooled combustion chamber with excess air and led to the ventilation gas system. The matte granules are ground and fed to the hydrometallurgical nickel plant.

2.5.6 Leaching of the flash smelting furnace matte

The finely ground Flash Smelting Furnace matte is leached in the FSF-matte leaching circuit with the aid of oxygen and sulphuric acid (see Figure 7). Sulphuric acid is recycled from nickel electrowinning.

Leaching is done in three steps which are countercurrently connected: atmospheric copper removal, nickel atmospheric leach and nickel pressure leach. In the first leaching stage nickel is leached as sulphate with the aid of copper cementation. Iron is oxidised to iron oxide, which precipitates. The solution is filtered and conveyed to solvent extraction. In the second atmospheric leach, nickel and copper are leached from the residue, while the iron is kept precipitated. The solution is returned to the cementation step.

The residue from atmospheric leaching undergoes to selective and total pressure leaching steps. In the selective leaching autoclave, nickel is dissolved and copper is precipitated as copper sulphide. Iron is also dissolved. In the total leaching autoclave the rest of nickel and a part of copper sulphides are leached. The solution from FSF-matte pressure leaching goes to EF-matte atmospheric leaching for iron removal. The leaching residue from the pressure leaching is copper sulphide, which is introduced to the copper smelter for copper and precious metals recovery.

2.5.7 Leaching of the electric furnace matte

The finely ground granulated electric furnace matte is leached in the EF-matte leaching circuit. In this process nickel, copper and cobalt are leached and iron is precipitated in a controlled way.

The EF-matte leaching contains two leaching steps. In atmospheric leaching, nearly all the iron dissolves first and then precipitates as oxide. The solution from the atmospheric leaching is then subjected to iron removal. The rest of the dissolved iron is precipitated in an autoclave under highly oxidising conditions. The solution undergoes to the FSF-matte first atmospheric leaching. The iron oxide precipitate is fed to the nickel flash smelting furnace. The residue from the atmospheric leaching is leached under pressure as completely as possible. The iron oxide residue left is fed to the nickel flash smelting furnace. The solution is pumped back to the atmospheric leaching.

2.5.8 Cobalt solvent extraction

The nickel raw solution obtained from the leaching is cleaned with solvent extraction. First the solution is washed with kerosene in order to separate possible organic impurities.
Cobalt is extracted to the organic phase in four counter-current extraction cells. Since nickel is also extracted with cobalt and other impurities, the organic phase is washed with a solution of aqueous sulphuric acid in order to remove nickel. Part of the resulting nickel solution is fed to nickel hydrogen reduction and rest of it to nickel electrowinning depending on the production. Cobalt is stripped from the organic solution to the water phase by adjusting the pH value of the solution. The cobalt sulphate solution is purified and sold to customers to be used in powder production. It is also possible to produce pure cobalt powder by hydrogen reduction.

2.5.9 Hydrogen reduction of nickel

In nickel hydrogen reduction, ammonia and ammonium sulphate are added to the clean nickel solution. Hydrogen gas at high temperature and pressure is fed to the solution, with effective stirring, in the presence of nuclei. Nickel is reduced to nickel powder and sulphuric acid is formed. Sulphuric acid is neutralised with the ammonia present in solution. The reaction continues until the nickel has almost completely been reduced.

The nickel reduces on the surfaces of the nucleation powder and the particle size grows. After about 20 densifications a part of the nickel powder is discharged and new feed solution is added. The powder remaining in the autoclave serves as nuclei for the new feed solution. After the last reduction batch the whole content of the autoclave is blown off.

The solution undergoes metals precipitation and then ammonium sulphate crystallisation. Part of the ammonium sulphate is fed back to the reduction process, part is sold. After each reduction series the nickel deposits formed on the autoclave walls, stirrers and pipes are removed by leaching.

The nickel powder is washed and dried. A part of the powder is packed into drums and sold to customers. The rest of the powder is pressed with a binding agent to nickel briquettes and sintered.

2.5.10 Nickel electrowinning

After cobalt removal a part of the nickel solution is fed to nickel electrowinning, where pure nickel metal is recovered using insoluble lead anodes. The nickel starter sheets are precipitated in the starter seed cells. The starter sheets are further precipitated in the commercial cells. The nickel cathodes are inserted inside diaphragm bags and the lead anodes in the solution between the bags. The catholyte solution surface is slightly higher than the anolyte solution surface around the bags. The solution flows from the catholyte side through the diaphragm to the anolyte side. Anolyte is removed as an overflow from the electrowinning cells. The metallic nickel is reduced to the cathodes by the electric current. Sulphuric acid and oxygen gas are formed at the anodes.

After a growing period of seven days, the nickel sheets are harvested from the cells, washed, stacked and weighed. They are cut into squares and packed into drums.

The anolyte, which is gained as an overflow from the cells, is routed back to the atmospheric leaching of the flash smelting furnace nickel matte.
2.5.11 Auxiliary operations

In the factory area there are also oxygen and hydrogen plants and a power plant. The three oxygen plants produce oxygen for smelting and leaching. At the same time they produce argon, which is sold. The two hydrogen plants produce hydrogen for the nickel process. Hydrogen is also used in the purification of argon.

The power plant operates the waste heat boilers of the Flash Smelting Furnace and converters and distributes the steam generated for internal use. Electricity is generated from the extra steam. Process heat is sold for district heating and is also used for heating the plant.

The analytical laboratory is well equipped and is also able to conduct environmental analyses. The laboratory is covered by the plant’s ISO 9002 certificate.
3

Present Consumption and Emission Levels

3.1 Present consumption levels

3.1.1 Energy Consumption

The energy consumption of nickel production at the Harjavalta plant is as follows:

- Power consumption:
  - Ni smelter: 2,600–2,800 kWh/t Ni
  - Ni refinery: 5,000–5,500 kWh/t Ni

- Fuel oil consumption:
  - Ni smelter: 440–480 l/t Ni

- Total energy consumption:
  - Ni smelter: 28–32 GJ/t Ni
  - Ni refinery: 18–20 GJ/t Ni

3.1.2 Energy recovery

The hot gases produced in the Flash Smelting Furnaces of copper and nickel and copper converters are cooled in waste heat boilers by generating steam from which the energy is recovered. The steam formed is used for example in the drying of concentrates, in the pre-warming of the process air of the Flash Smelting Furnace and in the nickel process. Electricity is made from the extra steam in the power plant. In 1996 389,640 t of steam was regenerated from the waste heat boilers. The amount of 52,230 MWh was sold as district heat and 32,230 MWh was used for heating the plant and worker’s homes.

3.2 Environmental emissions

3.2.1 General

The main environmental issues of the refined nickel producing industry are air and water pollution and the generation of hazardous wastes. Nickel plants usually have their own water treatment plants. This chapter describes the emissions and abatement techniques for air and water pollution and the waste production and treatment for nickel industry in Finland.

Outokumpu produces both copper and nickel at its Harjavalta plant. Both production processes use The Outokumpu Flash Smelting Technique and use sulphidic concentrates in this integrated process. The main end products are anode copper, electrolytic nickel and nickel powder. The emissions to air and water measured are a result of the integrated process. The only way to get data about the nickel process alone is to divide the emissions by the ratio of copper and nickel tonnes produced.
The production values in 1997 were:

- Cu anodes: 159,300 t
- Ni: 35,300 t
- H₂SO₄: 580,200 t
- SO₂ (liquid): 35,900 t
- Cu cathodes: 116,300 t
- Au: 3,900 kg
- Ag: 32,200 kg
- Se: 43,200 kg
- NiSO₄: 900 t
- CuSO₄: 3,200 t
- Pt-, Pd-concentrate: 450 kg
- CCA wood preservative: 1,740 t
- Cu telluride: 4,200 kg

3.2.2 Emissions to air

The emissions to air are metal-containing dust and SO₂. Sulphur dioxide gas arises in the case of nickel from the flash smelting furnace and it is conducted to the sulphuric acid plant. Dust is formed whenever the concentrate is handled, during concentrate unloading, steam drying, in the Flash Smelting Furnace and in the electric furnace. All these dust containing gases are led through bag filters to the stack. All collected dust is sent back to the Flash Smelting Furnace.

The sources of dust and sulphur dioxide in the production of nickel are shown in Table 3.

Table 3. Relevance of components with respect to air pollution.

<table>
<thead>
<tr>
<th>Emission source</th>
<th>Dust and metals</th>
<th>Sulphur dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material handling</td>
<td>relevant</td>
<td>not relevant</td>
</tr>
<tr>
<td>Storage</td>
<td>relevant</td>
<td>not relevant</td>
</tr>
<tr>
<td>Drying</td>
<td>relevant</td>
<td>relevant*</td>
</tr>
<tr>
<td>Smelting</td>
<td>relevant</td>
<td>relevant*</td>
</tr>
<tr>
<td>Leaching</td>
<td>not relevant</td>
<td>not relevant</td>
</tr>
<tr>
<td>Solution purification</td>
<td>relevant</td>
<td>not relevant</td>
</tr>
<tr>
<td>Solvent extraction</td>
<td>relevant</td>
<td>not relevant</td>
</tr>
<tr>
<td>Hydrogen reduction</td>
<td>relevant</td>
<td>not relevant</td>
</tr>
<tr>
<td>Electrowinning</td>
<td>relevant</td>
<td>not relevant</td>
</tr>
<tr>
<td>Sulphuric acid plant</td>
<td>not relevant</td>
<td>relevant</td>
</tr>
</tbody>
</table>

* The emissions from the smelting stage are treated in the gas cleaning steps and sulphuric acid plant; the remaining emissions of sulphur dioxide of the sulphuric acid plant are still relevant.

Beside these process emissions, components will also be emitted diffusely. This can lead to locally enhanced concentration levels. The abatement of this fugitive emission is an ongoing process and demands good housekeeping. Possible measures include better sealing of equipment, forced ventilation combined with bag filters etc.

3.2.2.1 Sulphur dioxide

Sulphur dioxide can be emitted from the primary feed preparation and drying stages but the concentration is usually very low so that simple scrubbing of gases is an adequate operation. The most significant sources of sulphur dioxide occur in
the smelting stage. The sealed Flash Smelting Furnace allows the sulphur dioxide to be collected. The oxygen enrichment used produces a high sulphur dioxide concentration with minimal variations in concentration. This therefore allows efficient conversion to sulphuric acid in the double contact sulphuric acid plant.

After heat recovery and cleaning in electrostatic precipitators the gases are diluted, if necessary, to a processing concentration of 8.5–13 % SO₂. A source of sulphur dioxide emission is also the sulphuric acid plant, where the gas is converted with an efficiency of at least 99.7 % to sulphuric acid in the double absorption process. There is, however, still a small amount of SO₂ in the offgas.

During electrolysis there are emissions of aerosols, sulphuric acid and metal salts to the tank house. These emissions leave the tank house via the ventilation and are classified as fugitive emissions.

3.2.2.2 Dust and dust bound metals

These can be emitted from most stages of the process. Direct and fugitive dust emissions from the smelting are potentially high. The significance of the emissions is also high as this process stage is used to remove volatile metals such as Zn, Pb, As, Cd and Hg from the nickel and these metals are present in the dust. The Flash Smelting Furnace is effectively sealed to minimise fugitive emissions. Good maintenance of the furnace and ducts is practised and the gases are treated in dust removal systems and the sulphur recovery process.

In the leaching process of FSF-matte, the gases from the atmospheric reactors and thickeners are fed to the stack. In the leaching of EF-matte, all gases are collected into a scrubber and washed before the stack.

In the cobalt solvent extraction stage all gases are collected into scrubbers. The ammonia-containing gases from hydrogen reduction are washed in three scrubbers with water to which sulphuric acid has been added.

3.2.3 Legislation and regulation in Finland

Finland has no single environmental law at the moment. The environmental legislation is composed of a number of individual acts /3/. A new Environmental Protection Act is currently under preparation and will combine the environmental acts according to the requirements of Council Directive 96/61/EC of September 1996 concerning integrated pollution prevention and control (IPPC).

Presently, the integrated approach is included in two separate permit procedures: the environmental permit procedure according to the Environmental Permit Procedure Act (735/1991) and Decree (772/1992) and the water discharge permit procedure according to the Water Act (264/1961) and Decree (282/1962).

The Environmental Permit Procedures Act combines the permit procedures of the Air Pollution Control Act and Decree, the Waste Act and Decree, the Health Protection Act and Decree and the Adjoining Properties Act. The competent authority in environmental permit matters is, depending on the line of activities, either the Regional Environment Centre or the local environmental board.

When discharging waste waters, the Regional Environment Centre must be notified in advance regarding any plans for the discharge of waste water in the cases listed in the Prior Notification Decree. The Centre assesses the notification and judges whether the activity will cause water pollution. If the pollution is unavoidable, the polluter must apply for a permit from the Water Court or from the local environmental board. Substantial polluters send their applications directly to the Water Court. Polluting of groundwater is totally forbidden; this means that no permit can be granted for discharging pollutants into the ground water.
In the metallurgical industry, an environmental permit granted by the Regional Environment Centre and a water discharge permit granted by the Water Court are required.

Although the environmental legislation is based on a sectoral approach, the permit system in each sector follows certain uniform lines including the following elements (both in environmental and water permit matters):

• An application describing the activity and its environmental effects is to be submitted to the competent authority. The data and information that the operator of an industrial plant (the applicant) has to submit in the form of an application to the authority is described in the above mentioned Acts and Decrees.

• The documents are public and the persons and organisations affected by the project have a right to comment on them.

• The competent authority makes a decision including emission limits and other permit conditions.

• Those concerned have a right to appeal against the decision.

• A revision of the decisions and permit conditions is made by a certain deadline stipulated in the permit (3–10 years where wastewater discharges are concerned) or when there are significant changes in operation or emissions or when unexpected effects are detected.

Right at the preliminary stage of planning a new establishment, the necessary permits and environmental aspects are to be surveyed. The enterprise is expected to recognise that the environmental criteria may affect siting as well as other economic and technical decisions. Even in the case of changing the production, raw materials or technical devices at an existing plant, the authorities must be informed as soon as these decisions are made, and negotiations shall be initiated to survey the possible need for renewing the permits.

The legislation is based on the Polluter Pays Principle in the sense that the polluter pays all pollution abatement costs, which also include the monitoring costs. In addition, polluters of watercourses are obliged to pay indemnities to the owners of water and shore areas as well as to professional fishermen for any damage caused. A typical feature of the permit procedure is the case-by-case consideration of applications and tailor-making of the permit conditions. The permit conditions are expressed as emission limits and compulsory measures and not as technical standards.

3.2.4 Emissions to air at Outokumpu Harjavalta Metals

The ambient air concentrations allowed for the whole integrated Harjavalta plant, which produces both copper and nickel, (permit dated 27.2.1995) by the authorities are as follows:

3.2.4.1 SO₂

1. SO₂ concentration (mean value during an hour) in ambient air has to remain under 250 µg/m³ after 31.12.1999 and the mean value during 24 hours must remain under 80 µg/m³. From the hourly means not more than 1% can exceed 250 µg/m³ during 30 days and from the daily means one can exceed 80 µg/m³ during 30 days.

2. If the SO₂ concentration is exceptionally high or exceeds 250 µg/m³, the reason for the high value must immediately be found out.
3. If the SO$_2$ concentration exceeds 1,000 $\mu$/m$^3$ during three consecutive hours, the emissions have to be further restricted.

4. The sulphur emissions from the sulphuric acid plant must not after 1.1.1997 be more than 2.7 kg/ton of 100% sulphuric acid produced calculated as a mean of six months.

5. The oil fuels used must not contain more than 1 weight-% of sulphur. This does not concern use in places, from which the gases are fed to the sulphuric acid plant.

6. The total emission of sulphur compounds calculated as SO$_2$ must not exceed 4,500 t/a after 1.1.1997.

3.2.4.2 Dust

7. The separation systems of dust in the drying of copper and nickel concentrates must be such, that the dust content of the gas does not exceed 10 mg/m$^3$. The bag filters used for the gas coming from the smelters, converters and anode furnace must be designed in such a way that the dust content after the filters does not exceed 1 mg/m$^3$.

8. The dust emission from the power plant must not exceed 40 mg/MJ.

9. The total dust emission from the plant must not exceed 90 t/a after 1.1.1997.

10. The heavy metals and arsenic emissions must not exceed the following limits after 1.1.1997:

<table>
<thead>
<tr>
<th>Element</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>12 t/a</td>
</tr>
<tr>
<td>Ni</td>
<td>5 t/a</td>
</tr>
<tr>
<td>Zn</td>
<td>10 t/a</td>
</tr>
<tr>
<td>Pb</td>
<td>5 t/a</td>
</tr>
<tr>
<td>As</td>
<td>2 t/a</td>
</tr>
<tr>
<td>Cd</td>
<td>0.5 t/a</td>
</tr>
<tr>
<td>Hg</td>
<td>20 kg/a</td>
</tr>
</tbody>
</table>

3.2.5 Off-gas monitoring

In Harjavalta the emissions to air are measured from all stacks where the emissions are significant. The dust emissions are measured once a month for 1–2 weeks from the stacks after the filtering devices. The SO$_2$ emissions and the gas flows are measured continuously from the stacks. The results are registered in the local network.

3.2.6 Releases into air

Actual sulphur dioxide emissions at the Harjavalta plant in 1997 are presented in Table 4. The total volume of gas at Harjavalta plant is 1,700,000 Nm$^3$/h, of which 1,000,000 Nm$^3$/h goes through the filters. The amount of gas from the sulphuric acid plant is 200,000 Nm$^3$/h.
Table 4. Sulphur dioxide emissions at Harjavalta in 1997.

<table>
<thead>
<tr>
<th>Height of stack</th>
<th>Area</th>
<th>t/a 1997</th>
<th>specific emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smelter ventilation gases 140 m</td>
<td>Converters</td>
<td>1 066</td>
<td>16 kg SO₂/t metal(Cu+Ni)</td>
</tr>
<tr>
<td></td>
<td>Smelting furnaces</td>
<td>1 176</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sum</td>
<td>2 242</td>
<td></td>
</tr>
<tr>
<td>Offgases from sulphuric acid plant 140 m</td>
<td>R6</td>
<td>229</td>
<td>1.6 kg SO₂/t H₂SO₄</td>
</tr>
<tr>
<td>Acid plant</td>
<td>R7</td>
<td>294</td>
<td>0.7 kg SO₂/t H₂SO₄</td>
</tr>
<tr>
<td></td>
<td>Sum</td>
<td>523</td>
<td></td>
</tr>
<tr>
<td>Dryer’ s stack 70 m</td>
<td>Ni-dryer</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ventilation gases</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Cu drying</td>
<td>40 m</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Fugitive gases</td>
<td></td>
<td>147</td>
<td></td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td>2 980</td>
<td></td>
</tr>
</tbody>
</table>

The SO₂ concentrations in the ambient air are measured in three places in the vicinity of the plant. The values measured have been low, and concentrations have been much lower than the limit values.

The design values for the bag filters have been 1 mg dust/Nm³. With the new bag filters installed the actual emissions were lower than the limit values in 1995. During the next two years there were difficulties with the filters and the limit values were not reached. This year, 1998, the matter has been brought under control.

Table 5. Dust and metal emission to the air.

<table>
<thead>
<tr>
<th>Limit t/a</th>
<th>t/a in 1998</th>
<th>Specific emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dust</td>
<td>90</td>
<td>72</td>
</tr>
<tr>
<td>Cu</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Ni</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Zn</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>As</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Pb</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Cd</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Hg</td>
<td>0.02</td>
<td>&lt;0.02</td>
</tr>
</tbody>
</table>

3.2.7 Emissions to water

Effluent to the waterbodies contains process waters from the acid plant and a bleed of the water used in the slag concentrator, cooling waters, e.g. the water used to cool the anodes, circulating via cooling towers and surface drainage. All these waters are collected and treated in the waste water treatment plant. The cleaned waters are pumped to the river which flows by the side of the plant. The precipitates are sent back to the Flash Smelting Furnace. A part of the sewage water from the plant is treated in the waste water treatment plant owned by the community. Cooling water and process waters are recycled within the process as far as possible.

3.2.7.1 Suspended solids and metal compounds

These are emitted from most stages of the process. Surface water can result from either rainfall or from the wetting of stored material to prevent dust formation. The other potential sources of suspended solids and metal compounds are the cooling and granulating steps. In general, these systems are either sealed and the water...
is recirculated or they are not in contact. System leakage may also occur. Wash waters, spent electrolyte and process effluents are also produced in the tank house and in the scrubbers. These effluents contain significant quantities of metal compounds in solution and are treated along with liquors bled from the sealed cooling and granulating systems before discharge to the waterbody. Weak acid from the sulphuric acid plant is sent to Pyhäsläimi mine and Kokkola zinc plant to be used in the processes there.

Sludges from processes are usually returned to the Flash Smelting Furnace in order to recover their metallic portion. In the mercury removal step in the sulphuric acid plant the circulating acid in the drying towers is treated with thiosulphate to precipitate mercury. This precipitate is sent to the company’s mercury plant in Kokkola.

The permit conditions for Harjavalta (permit granted by Water Court 31.12.1992) are as follows. The process waters must be cleaned so that the effluents released from the plant do not contain more than:

\[
\begin{align*}
\text{Cu} & \quad 3.6 \text{ t/a (=10 kg/day)} \\
\text{Ni} & \quad 3.6 \text{ t/a} \\
\text{Zn} & \quad 3.6 \text{ t/a} \\
\text{As} & \quad 1.8 \text{ t/a} \\
\text{Pb} & \quad 0.108 \text{ t/a} \\
\text{Cd} & \quad 0.010 \text{ t/a} \\
\text{Hg} & \quad 0.001 \text{ t/a}
\end{align*}
\]

3.2.7.2 Waste water monitoring stations

The drain system outlets are equipped with flow measuring and sampling stations. Temperatures and pH are also measured on a continuous basis. Flow measurements are carried out using electromagnetic flowmeters. Flow, pH and temperature readings are registered into the plant control system. Sampling is done proportionally to the flow. Composite samples are taken for analysis every day.

3.2.7.3 Analysis and reporting of waste waters

The analytical laboratory analyses the necessary metal compounds from the daily composite samples. Results are reported internally via the local network. The laboratory is covered by the plant’s ISO 9002 certificate.

3.2.7.4 Effluents in 1997

The emissions to water at Harjavalta in 1997 are shown in Table 6. The total water flow was 31,000,000 m³/a, including cooling waters.

The high nickel values were due to heavy rains, which washed dust from the courtyards to the waste water treatment plant. The rain water pond was not large enough to hold all rain waters and so more water came to the waste water treatment plant than could be treated. In the year 1998 a new big rain water container was built in order to prevent overloading of the waste water treatment plant.
Table 6. Actual emissions at the Harjavalta plant in 1997.

<table>
<thead>
<tr>
<th>Limit t/a</th>
<th>t/a 1997</th>
<th>Specific emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>3.6</td>
<td>0.023 kg/t Cu</td>
</tr>
<tr>
<td>Ni</td>
<td>3.6</td>
<td>0.124 kg/t Ni</td>
</tr>
<tr>
<td>Zn</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>1.8</td>
<td>0.4</td>
</tr>
<tr>
<td>Pb</td>
<td>1.08</td>
<td>0.124 kg/t Pb</td>
</tr>
<tr>
<td>Cd</td>
<td>0.11</td>
<td>0.06</td>
</tr>
<tr>
<td>Hg</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

3.2.8 Solid waste management

Many of the materials generated during the production of nickel can be defined as hazardous wastes. Most of these materials, however, contain recoverable quantities of nickel and other non-ferrous metals and are therefore used as raw materials in their own right. All nickel-containing materials are recycled back to the nickel process.

Outokumpu is an integrated metal producer, as illustrated in Figure 8. All possible materials are recycled to a plant where they can be used either as raw materials or as chemicals. Harjavalta Metals produce copper and nickel, Poricopper copper products, Kokkola Zinc zinc and Polarit stainless steel. Pyhäsalmi Mine produces copper, zinc and pyrite concentrates.

In nickel smelting, a large tonnage of waste is solid, principally discarded slag. Depending upon the nickel content of the concentrate, the amount of slag can vary between 4 to 12 times the quantity of nickel produced. The slag is cleaned, if necessary, to reduce nickel and cobalt losses, in an electric furnace. The composition of typical nickel slags is shown in Table 7. The purified slag is fayalite, which consists mainly of iron oxide and silica sand. The granulated slag from the electric furnace is conveyed to the storage heap on the site.
Table 7. Composition of typical nickel slag (%).

<table>
<thead>
<tr>
<th>Component</th>
<th>Reverberatory</th>
<th>Electric furnace</th>
<th>Outokumpu flash*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>0.2</td>
<td>0.17</td>
<td>0.1–0.3</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.1</td>
<td>0.06</td>
<td>0.1–0.25</td>
</tr>
<tr>
<td>Copper</td>
<td>0.08</td>
<td>0.01</td>
<td>0.05–0.25</td>
</tr>
<tr>
<td>Iron</td>
<td>38</td>
<td>35–43</td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>36</td>
<td>35</td>
<td>30–39</td>
</tr>
<tr>
<td>Lime</td>
<td>2</td>
<td></td>
<td>0.5–7</td>
</tr>
</tbody>
</table>

*After cleaning in electric furnace

Other solids produced in the nickel smelter, such as ladle skulls, scrap, boiler and precipitator dust, are recycled into the smelting furnace and not discarded as wastes. The only solid wastes are the slag and sludges produced in the neutralization of plant effluents.

All flue dusts collected in the electrostatic precipitators are fed back to the flash smelting furnace. The dust from the bag filters is also fed to the flash smelting furnace. The metals precipitated in the waste water treatment plant are also fed to the flash smelting furnace.

The mercury precipitate from the sulphuric acid plant is transported to the company’s mercury plant in Kokkola. The weak acid from the sulphuric acid plant is used in Outokumpu’s zinc plant in Kokkola and in Pyhäsalmi mine.

The gypsum ferriarsenate precipitate from the sulphuric acid plant is stored dry in impermeable basins. Metal scrap is sold to the scrap business and paper waste to a cardboard plant. Oils and solvents, filter materials, demolition wastes and storage batteries and lamps are sent to the hazardous waste treatment plant. Recycled oil is used as fuel in the furnaces. 48,000 t nickel slag was sold for sand blasting in 1997.

3.2.8.1 Overview of the solid wastes produced

**Materials to be recycled**

- autoclave residue 1,600 t/a to flash smelting furnace
- iron precipitate 10,900 t/a to Ni flash smelting furnace
- flue dust from Ni smelter to Ni flash smelting furnace
- crushed reverts etc. to electric furnace
- pressure leaching residue to Cu flash smelting furnace
- Hg-precipitate (acid plant) 50 t/a to Outokumpu’s zinc plant

**Wastes for final disposal**

Wastes solely from the nickel process in 1997:
- nickel slag 90,000 t/a to the storage area
- gypsum ferriarsenate 2,000 t/a to impermeable basin

During 1997, the following wastes (Cu + Ni) were generated at Harjavalta:
- final slag 350,000 t/a to the final slag pond
- metal scrap 750 t/a sold to scrap business
- oils and solvents 150 t/a to hazardous waste treatment plant
- filter materials 75 t/a to hazardous waste treatment plant
- storage batteries and lamps 1 t/a to hazardous waste treatment plant

3.2.9 Noise abatement

For noise abatement in Harjavalta all possible measures have been taken in order to reduce the noise level from the machinery. The noise level in the plant is mon-
The noise immission levels in the vicinity of the plant do not exceed the noise immission levels which are set on basis of the Decision of the Council of State.

### 3.2.10 Environmental management system

Internally, the environmental management system means that the environmental viewpoint shall be taken into consideration in all fields of operation: production, maintenance, planning, research etc. The development of environmental management aims at concrete improvements in environmental actions.

The entire staff participates in fulfilling this environmental management system. Each and every person must take responsibility for the environment. In accordance with the environmental policy, work is performed in a responsible manner without wasting energy or resources or damaging the environment.

### 3.2.11 Data management and training

Data management of environmental matters is realised with the use of databases. The system is an active real-time reporting channel and also serves as an environmental manual and archive. All users of the local networks have access to the databases.

The databases improve information distribution, and thus give better possibilities for follow-up and development of environmental procedures.

In order to effectively implement the environmental management system, the whole personnel has been trained to be aware of the effects of their work on the environment, and the possibilities of influencing environmental performance through their own initiative. New workers are familiarised with practical environment work in connection with their on-the-job training.
4.1 General

The pyrometallurgical treatment of sulphidic nickel concentrates commonly includes three types of operation: roasting, smelting and converting. In roasting, nickel concentrate sulphur is removed as sulphur dioxide and iron is oxidized. In smelting, the roaster product is melted with a siliceous flux, which reacts with the oxidized iron forming a liquid silicate and produces a solution of molten sulphides. In converting, more sulphur is removed from the sulphide melt, and the remaining iron is oxidized and fluxed for removal as a silicate. The final product is a matte or nickel-rich sulphide ready for further processing.

The pollutants of main concern here are those associated with liquid and solid wastes and, above all, with the gaseous emissions.

Liquid effluents from pyrometallurgical processes are of minor importance because these processes are essentially dry. Liquid waste results from the cooling water system and when a sulphuric acid plant is attached to the smelter, weak acid from the wet-gas cleaning systems. Wet gas cleaning systems, like those required to clean process gases for acid production, remove sulphur trioxide and produce a weak acid. They also collect arsenic, mercury, selenium and fine dust particles containing other impurities.

In nickel smelting, a large tonnage of waste is solid, principally discarded slag. Depending upon the nickel content of the concentrate, the amount of slag can vary between 4 to 12 times the quantity of nickel produced. Other solids produced in a nickel smelter, such as ladle skulls, scrap, boiler and precipitator dust, are recycled to the smelting furnace and not discarded as wastes. The only solid wastes are the slag and sludges produced in the neutralization of plant effluents.

The major environmental challenges in pyrometallurgy sulphide ores result from the release of SO₂ and particulate emissions, which can be categorized as either process or fugitive emissions.

Every smelting process may contain several of the following process units:
- concentrate storage and feed preparation
- drying
- roasting
- smelting
- slag cleaning
- granulating, drying and grinding
- converting
- refining
- gas cooling
- gas cleaning
- acid plant
- tail gas and secondary gas cleaning
- waste acid and water treatment.

Each of the process steps used must be optimized and function in the best possible way in order to be a Best Available Technique. The nickel production process is always a compromise, the process has to produce nickel at a profitable price and
at the same time minimise the use of energy and raw materials and the formation of emissions and wastes.

In this chapter all unit processes are discussed and compared, based on the literature available.

4.2 Feed preparation

The concentrates are transferred by conveyor belt up to the dosage silos in the concentrate warehouses. The warehouses have truck washing stations so that the spreading of concentrate from the wheels and truck beds can be avoided. The washing facilities cannot be used in the Northern countries in winter.

Feed preparation is carried out by means of variable speed feeders which unload individual products of known composition from the day storage bins onto a common belt conveyer which takes them to the dryers.

4.3 Drying

4.3.1 Rotary dryer (rotary kiln)

The dryer is fired with natural gas or oil. Nitrogen is sometimes utilized in place of secondary air to control the temperature and also to maintain an oxygen deficient atmosphere which reduces the possible concentrate ignition and combustion. The dry charge, averaging 0.1 % moisture, is discharged through a double trommel screen onto a drag conveyor for transport to the pneumatic lift system. Dryer offgas is directed to a electrostatic precipitator or bag filter for dust removal. All dust is returned to the dryer discharge drag conveyor. Off-gas from the electrostatic precipitator/bag filter passes through an induced draft fan to the stack.

4.3.2 Steam dryer

The multicoil steam dryer has been adapted for concentrate drying on commercial scale during this decade. It consists of a rotor in a stationary receptacle. Heating coils are located parallel to one another. Each set is constructed from several concentric tube rings. The steam from the waste heat boiler system, which is controlled by two reducing stations, serves as a thermal carrier which flows through the coils and is thus used for drying purposes. The steam used is fed back into the steam network and the condensate recycled back to the feed water system of the waste heat boiler.

The concentrate and additives must be screened before being fed into the coil dryer. For this reason there is a screening device installed in the concentrate conveyor. The material is screened to less than 15 mm particle size. A magnet separator removes iron pieces before sieving. The oversize particles are crushed after screening by a crusher and recycled /4/.

The dryer coil spacing has been designed for smooth product flow and less wear and tear. As the exhaust gas volumes are low, only a small size bag filter needs to be provided to the dryer to clean offgases before discharging through a stack to the atmosphere. Dust leakage is very low because the dryer body is stationary and no difficult sealings are needed. Additionally the bag filter is integrated into the steam dryer so that the dust drops back straight into the dryer and no other dust handling or transportation is needed. This results in very low dust emissions. The multicoil dryer is environmentally safe. Only water is evaporated and the gas
volume and emissions are minimal. In steam drying the saturated steam produced in the waste heat boiler connected to the flash smelting furnace can be utilized. This means that a part of the chemical energy of the concentrate is used for drying and no excess fossil fuel is needed for heating /5/.

Investment costs for a steam drying installation are low. Operating costs are also low. For example the consumption of electrical energy is only 60 % compared to a rotary dryer. The high efficiency, safety and cleanliness characteristics of this technology are widely proven /6/.

For the following reasons the steam dryer system has often been chosen instead of a fossil fuel fired rotary dryer:

a) Low heat losses and a small exhaust gas volume, resulting in good thermal efficiency in the drying process and low copper losses.
b) There are no sulphur dioxide emissions and no risk of fire outbreak due to low and even operation temperature of around 120°C.
c) Because of the low volume of gases (in Nm³), only a bag filter needs to be provided for dust collection and recycling.
d) Dust leakage is very low as the dryer body is stationary and good arrangement is possible.
e) The size of the dryer is one third of a conventional fuel fired dryer. Investment and operational costs are expected to be about 80 % and 50 % of the conventional dryer respectively /7/.
f) The choice of multicoil type dryers is often based on environmental considerations. The carrier air to absorb the water steam is sucked from the environment at a 1:1 ratio. The moist off-gas is de-dusted in a jet filter plant. The residual dust content of the off-gas is less than 5 mg/Nm³ /4/.

The reason for selecting a multicoil drying plant in preference to a conventional rotary dryer is the relatively simple off-gas system and its insensitivity to material variations (moisture, composition and quantity) and the small space required /4/. This means that the investment and operation costs are low.

### 4.3.3 Pneumatic drying/Flash dryer

In the flash dryer, the concentrate particles dispersed into the hot gas flow are dehydrated by heat transferred from hot gas through flow movement. Currently, the flash dryer performs the important role of effective utilization of off-gases from the super heater and the anode furnace.

The pneumatic drying system consists of three parts: rotary kiln, cage mill and pneumatic duct. The feed is scattered, and the moisture is reduced to 3 % or less in the cage mill. At the outlet of the mill, there is a classifying funnel. Coarse material is discharged from this funnel. In the pneumatic duct the moisture is further reduced to 0.3 % or less /8,9/.

Electrical energy consumption per tonne of dry concentrate is 10–12 kWh /9/. A comparison of drying systems prepared by Outokumpu Engineering is presented in Table 8.
Table 8. Comparison of drying systems.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Spray dryer</th>
<th>Rotary dryer</th>
<th>Steam dryer</th>
<th>Flash dryer</th>
<th>Fluid bed dryer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment cost</td>
<td>--</td>
<td>++</td>
<td>+++</td>
<td>+</td>
<td>--</td>
</tr>
<tr>
<td>Operating cost</td>
<td>--</td>
<td>+</td>
<td>+++</td>
<td>–</td>
<td>--</td>
</tr>
<tr>
<td>Gas flow</td>
<td>--</td>
<td>++</td>
<td>--</td>
<td>–</td>
<td>--</td>
</tr>
<tr>
<td>Fugitive emission control</td>
<td>–</td>
<td>–</td>
<td>++</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Operational flexibility</td>
<td>+</td>
<td>++</td>
<td>+++</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Material handling</td>
<td>+</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Future expansion</td>
<td>–</td>
<td>+</td>
<td>++</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Environmental compliance</td>
<td>–</td>
<td>–</td>
<td>++</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Process sophistication</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Generality</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
</tr>
</tbody>
</table>

**4.4 Dry concentrate conveying system**

Dried concentrate would be stored in the intermediate bin. Dried concentrate is extracted with a drag conveyer and charged to a dense phase pneumatic conveying system that will convey it to a dry concentrate bin. Air from the pneumatic conveyer is cleaned in the bag filter and cyclone before being vented into the atmosphere through a stack.

**4.5 Concentrate feeding system**

The control requirements of a modern high-intensive flash smelting furnace with high oxygen enrichment are very high. The concentrate feeding system must be able to produce a constant and accurate concentrate feed to the burner. High oxygen enrichment means autogeneous operation.

The latest generation of Outokumpu concentrate burner is specifically designed for high oxygen enrichment, wide turn-down ratio, precise control requirements as well as for high feed rate in the flash smelting furnace /5/.

**4.5.1 Volumetric concentrate feed system**

A volumetric concentrate feed system is usually designed for a flash furnace. This system has sometimes been associated with inherent problems such as fluidisation, resulting in uncontrolled concentrate exposure to the furnace. The most difficult challenge is to keep the feed density constant.

**4.5.2 Loss-in-weight feeding system**

Outokumpu has developed a gravimetric feed system which is an application of the loss-in-weight feeder. The gravimetric feed system consists of a dosing valve and a dosing bin provided with an underneath screw conveyor.

The operation of the loss-in-weight feeder starts with filling of the dosing bin both in local and remote mode. The filling is stopped when the bin is at high level (max) and the feeding is started. When the material reaches a low level the bin is refilled. During refilling the screw conveyer runs at a previously controlled speed until the filling stage is completed.
The material is fed by screw conveyor onto a charge drag conveyor which transfers the material further via a concentrate chute into the concentrate burner of the furnace. This arrangement secures good accuracy and constant feed rate of concentrate to the furnace.

One important progress step in the development of the process has been the adoption of the loss in weight feed system by which the real material amount entering into the furnace can be controlled. This has shortened the time during which the feed mixture and oxygen are not in balance /10,11/.

### 4.6 Smelting

The major pyrometallurgical nickel producers are Inco, Norilsk, Falconbridge, Outokumpu, Bamangwato Concession Ltd. and Western Mining Corp. Practically in all cases sulphidic nickel raw materials are smelted to produce nickel matte which is refined to produce nickel metal, nickel powder or oxide.

The total production of these plants represents about 30 % of the world refined nickel production and about 55 % of the annual nickel production based on sulphide ore. Inco type flash smelting is used by Inco in its own operations in Canada. In Falconbridge’s Sudbury and Inco’s Thompson operations, the concentrate is first roasted and the calcine is smelted in electric furnaces to produce matte, which is converted to Bessemer matte, which, in addition to nickel, contains considerable amounts of copper.

#### 4.6.1 Conventional Outokumpu nickel smelting

The original Outokumpu nickel smelter process is applied in two smelters, Selebi-Phikwe in Botswana and Norilsk in Russia.

BCL operates the nickel/copper mine, concentrator and smelter complex at Selebi Phikwe in North Eastern Botswana. The smelter has a production capacity of 46,000 tonnes of high grade matte per year. The concentrate is pumped to atomizer spray drying plants from which the dried concentrate is pneumatically conveyed to the Outokumpu Flash Smelting Furnace. It is fed into the furnace with silica flux, pulverized fuel and recycled boiler dust. Reaction air is steam heated to 250 °C and enriched to 24.5 % oxygen. Slag, tapped continuously from the furnace, is treated in electric arc slag cleaning furnaces. Low grade matte, tapped intermittently from the furnace, is concentrated to a high grade matte in Peirce-Smith converters.

The waste heat boiler performs two functions. The first one is to cool the dust-laden flue gases before they enter two parallel electrostatic precipitators and the second one is to capture part of the dust load from the gases and return it to the furnace. The draft through the system is provided by induced draft fans downstream of the electrostatic precipitators. The dust falling out in the precipitators is returned to the furnace and the cleaned gas vented through the stack. There is no acid plant /12/.

The smelter in Norilsk consists of spray dryers, flash smelting furnace, Peirce-Smith converters, slag cleaning furnaces, waste heat boiler and electrostatic precipitators. Nickel concentrates are smelted with an oxygen enrichment up to 45-55 %. Nickel matte is treated in a Peirce-Smith converter. Exhaust gases from the flash furnaces are used for technical sulphur production /13/.
4.6.2 Modified Outokumpu flash smelting

The Kalgoorlie (Australia) and Jinchuan (China) smelters use an Outokumpu flash smelting furnace, where the smelting and slag cleaning furnaces have been built together to form one integrated unit.

In 1993, the WMC Resources Ltd. owned Kalgoorlie Nickel smelter underwent a capacity upgrade. This capacity increase was offset by air quality control restrictions limiting the smelter’s availability to 80%. As a direct result of this limitation, WMC Resources Ltd commissioned a double absorption contact acid plant for the desulphurisation of furnace waste gas in August 1996 /14/. WMC Resources Ltd (WMC) currently produces yearly 95,000 tonnes of nickel as high grade matte /14/.

The sulphide concentrate is smelted in an Outokumpu flash smelting furnace using air enriched with 35–40 % oxygen and preheated to 380–410 °C. Up to 1,000 Nm³/h of natural gas is injected down the centre of each of the four concentrate burners for supplementary heat. Furnace matte, typically containing 47–50 % nickel, is converted to high grade matte in Peirce-Smith converters. Normally, one of three converters is blowing at any time, but two can be operated and enrichment increased to 25 vol% to accommodate production surges /14/.

A double contact acid plant was commissioned in 1996. The plant is of Monsanto Enviro-Chem design and will reduce SO₂ emission to below 200 ppm /15/. Gas from the converters was directed up to the main stack until the acid plant was built.

The flash furnace in Jinchuan is designed by Kalgoorlie. It consists of a flash smelting furnace, waste heat boiler, electrostatic precipitator, acid plant, converter and cleaning furnace for converter slag. Nickel matte production is approximately 21,000 t/a, oil consumption (flash furnace) 21.6 l/t concentrate, power consumption (flash furnace) 144 kWh/t slag, SO₂ concentration at the outlets 9.5–11 % and oxygen enrichment 44–46 % /16/.

4.6.3 DON-process

Outokumpu has been developing the nickel process since the mid eighties /17,18/. The result of this work is the DON Process, which is now commercially applied in Finland and at Fortaleza in Brazil. In the DON process the concentrate is first smelted in the flash smelting furnace to produce high grade matte, slag and gas rich in SO₂, which is conducted to the sulphuric acid plant. Slag is further treated in an electric furnace to recover the nickel content of the slag into an iron rich matte. The two types of matte are subjected to separate leaching processes. This process has been described in Chapter 2.

4.6.4 Inco smelting process

Inco has also been continuously improving its operations /19,20,21/. The SO₂ abatement program, implemented in 1994, has resulted in a considerable reduction in sulphur emissions. The process has been developed so that instead of smelting only separate nickel and copper concentrates, bulk nickel-copper concentrate is processed today. Simultaneously the equipment has been developed.

The matte produced in the smelting stage in the oxygen flash smelting furnace is further converted by Peirce-Smith converters to Bessemer matte. The matte is cooled slowly and the phases rich in nickel and rich in copper are separated. The nickel rich fraction is used for the production of nickel oxide or nickel carbonyl. The copper rich phase, which still contains some nickel, is treated in a sepa-
rate copper reactor and further in a multi purpose Vvessel producing blister copper and nickel-containing slag which is sent back to the nickel smelting circuit.

Sulphur dioxide is recovered from the smelting furnaces and ducted for sulphuric acid manufacture, but the converter gas is vented to the atmosphere. It means that only 60 % about sulphur of the concentrate is recovered.

4.6.5 Roasting and electric smelting

There are still some plants which use roasting and electric smelting. About fifty percent of the sulphur is removed in the process. The end product is Bessemer matte.

Falconbridge modernised its smelting operations in Sudbury, Canada in 1994. Two electric furnaces were replaced by one modernized furnace with considerable improvements in profitability as a result of decreased maintenance costs, reduced personnel requirements, reduced power consumption and lower electrode consumption. The granulation systems were replaced by a new one. After converti, the matte is sent to Kristiansand in Norway for further refining into metallic nickel.

In the process a fluidized bed roaster is employed. The roaster off-gas is fed through cyclones and electrostatic precipitators where 99.5 % of the contained concentrate is collected. The off-gas contains 9 % sulphur dioxide, 0.3 % oxygen and 36 % water. There are also some NOx present. The bed contains predominately hot sand flux and is discharged to the electric furnace. For environmental purposes the acid plant is designed to convert sulphur dioxide and SO3 to sulphuric acid as long as there is a minimum of 5 % of sulphur dioxide in the roaster gas.

Inco’s smelter at Thompson in Canada also uses roasters and electric furnaces.

4.6.6 Comparison of nickel smelting processes

Information from nickel smelters has been collected in Table 9 from the literature available.

High sulphur dioxide recovery is possible in the conventional Flash Smelting- Peirce-Smith converting process. However, the gas stream from the batch-wise Peirce-Smith process fluctuates both by volume and SO2 content and sulphur dioxide recovery is a costly operation because of the size of the acid plant needed. In some countries a sulphur fixation of 90 % of the total sulphur or even less is sufficient today.
Table 9. Comparison of nickel smelters. Abbreviations used: OK = Outokumpu, P-S = Peirce-Smith, WHB = waste heat boiler, FSF = flash smelting furnace, DON = direct Outokumpu nickel flash smelting process.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Concepts</th>
<th>Capacity t/h</th>
<th>Matte production t/a</th>
<th>Production of nickel t/a</th>
<th>O₂ enrichment smelting %</th>
<th>O₂ enrichment converting %</th>
<th>Gas to acid plant SO₂ %</th>
<th>SO₂ emissions t/a</th>
<th>SO₂ emissions kg SO₂ / t (Cu+Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selebi-Phikwe, Botswana</td>
<td>Spray dryers (2), OK flash smelting, P-S converter (3), electric slag cleaning furnace, waste heat boiler, electrostatic precipitator, no acid plant</td>
<td>100</td>
<td>46 000</td>
<td>24.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Madezhda, Norilsk, Russia</td>
<td>Spray dryers (2), OK flash smelting (2), P-S converter, slag cleaning furnaces (2), waste heat boiler, electrostatic precipitator (3), S SO₂ production line for FSF gases, steam from WHB transmitted to turbines in power station</td>
<td>170-180</td>
<td>95 000</td>
<td>35-40</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WMC, Kalgoorlie, Australia</td>
<td>modified OK flash smelting, P-S converter (3), waste heat boiler, electrostatic precipitator, acid plant for FSF gas (1966), waste heat used to generate power with two steam turbines</td>
<td>110</td>
<td>30 000</td>
<td>70-92</td>
<td>19</td>
<td>18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jinchuan, China</td>
<td>Rotary dryer, modified OK flash smelting, converter, waste heat boiler, electric precipitator, acid plant</td>
<td>——45</td>
<td>21000**</td>
<td>44-46</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Harjavalta, Finland</td>
<td>Rotary dryer, OK DON flash smelting, electric furnace for slag cleaning, waste heat boiler, electrostatic precipitator, acid plant</td>
<td>40</td>
<td>30 000</td>
<td>70-92</td>
<td>19</td>
<td>18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fortaleza, Brazil</td>
<td>Steam dryer, OK DON flash smelting, electric furnace for slag cleaning, quench cooling, acid plant</td>
<td>——20</td>
<td>—19000</td>
<td>60-70</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>INCO Copper Cliff, Ontario, Canada</td>
<td>Fluid bed dryer, Inco flash smelting (2), quench, P-S converter (6), steam dryer, copper reactor, fluid bed roasters (2), acid plant and liquid SO₂ plant for flash smelting and Cu reactor gas</td>
<td>——150</td>
<td>127 000</td>
<td>100</td>
<td>24</td>
<td>10-11</td>
<td>230 000</td>
<td>—1000</td>
<td></td>
</tr>
<tr>
<td>Falconbridge, Sudbury, Ontario, Canada</td>
<td>Fluid bed roaster (2), electric furnace, P-S converter (3), slag cleaning for P-S converter slag, spray cooler (2), electrostatic precipitator, acid plant for roaster gas precipitator (3), acid plant for roaster gas</td>
<td>——50 000</td>
<td>45 000</td>
<td>24</td>
<td>6-9</td>
<td>50 000</td>
<td>—500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inco Manitoba, Thompson, Canada</td>
<td>Fluid bed roasting, electric furnace, P-S converter (3)</td>
<td>——81 600</td>
<td>——500</td>
<td>——500</td>
<td>——500</td>
<td>——500</td>
<td>——500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pechenganickel, Russia</td>
<td>Electric smelting, converting, electric slag cleaning</td>
<td>——</td>
<td>——</td>
<td>——</td>
<td>——</td>
<td>——</td>
<td>——</td>
<td></td>
<td>——</td>
</tr>
</tbody>
</table>
Figure 9. Sulphur Dioxide Emissions in Harjavalta between 1950–1997. A. Total emissions. B. Specific emissions /22/.

Figure 9 shows the SO$_2$ emissions in the integrated Harjavalta plant. The upper part of the Figure presents the total emissions and the lower part the specific emissions per tonne of metal produced. Since 1.1.1997 the permit limit is 4,500 t/a. The big decreases in the amount of SO$_2$ are all due to the additional capacity in the acid plant. The double contact acid plant was built in 1994. Since then, the SO$_2$ emissions have decreased from 5,000 tonnes to 3,300 tonnes per year. The decrease from 9,000 to 5,200 tonnes per year in 1991 was due to the change of the drying method of the concentrate. Earlier, the concentrates were dried at a higher temperature, which caused SO$_2$ emissions. In 1997 the specific emission of SO$_2$ was only 16 kg/t metal (Cu+Ni) despite the expansion of copper and nickel production /22/.

Flash smelting is the most energy-efficient process. Electric furnace smelting utilizes large amounts of electrical energy and produces gases which have a low sulphur dioxide content and there is less dust, too. The advantages of the electric furnace are improved platinum group metal recoveries and lower base metal losses to the slag. Thus, the slags can be discarded without further treatment in a slag cleaning furnace as is required in flash smelting /10/.
4.7 Slag cleaning

4.7.1 Electric furnace

Nickel smelting furnace slag is tapped through slag tap holes along launder along the electric furnace. Coke and reverts are added through the furnace roof. Slag from the electric furnace is tapped into granulation and transported to the slag storage area. Matte from the electric furnace is periodically tapped through tapping holes and launder into ladles and transferred by cranes to the Peirce-Smith converters for further treatment.

There are three or six electrodes in the electric furnace to supply energy to the furnace. Electric power is needed for the reduction reactions, heat losses and smelting of reverts. The reductive agent is coke. Electric furnace off-gases are first burned in the incinerator, then cooled and fed through a bag filter to the stack.

4.8 Gas cooling

Table 10 gives a comparative summary of alternatives to gas cooling including advantages, disadvantages and design considerations /23/.

Table 10. Comparison of gas cooling alternatives /23/.

<table>
<thead>
<tr>
<th>Alternatives</th>
<th>Waste Heat Boiler and ESP</th>
<th>Wet System</th>
<th>Spray Chamber and ESP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Cooling</td>
<td>Waste Heat Boiler</td>
<td>Saturation Tower</td>
<td>Spray Chamber</td>
</tr>
<tr>
<td>Gas Cleaning</td>
<td>ESP</td>
<td>Wet Scrubber</td>
<td>ESP</td>
</tr>
<tr>
<td>Advantages</td>
<td>steam generation</td>
<td>Minimum air infiltration</td>
<td>dust segregation</td>
</tr>
<tr>
<td></td>
<td>boiler is a good sulphation</td>
<td>handling cold gas</td>
<td>minimum equipment and</td>
</tr>
<tr>
<td></td>
<td>chamber</td>
<td>high campaign life</td>
<td>capital cost</td>
</tr>
<tr>
<td></td>
<td>reduces heat load and</td>
<td>good in plant</td>
<td>low operating costs/</td>
</tr>
<tr>
<td></td>
<td>gas volume</td>
<td>environment</td>
<td>energy requirements</td>
</tr>
<tr>
<td></td>
<td>dust segregation</td>
<td>reasonable</td>
<td>easy to implement in</td>
</tr>
<tr>
<td></td>
<td>low pressure drop</td>
<td>implementation</td>
<td>retrofit</td>
</tr>
<tr>
<td>Disadvantages</td>
<td>potential tube leaks</td>
<td>minimum dust</td>
<td>no heat removal</td>
</tr>
<tr>
<td></td>
<td>moderate air infiltration</td>
<td>segregation</td>
<td>high air infiltration</td>
</tr>
<tr>
<td></td>
<td>layout difficulties</td>
<td>high energy</td>
<td>high maintenance</td>
</tr>
<tr>
<td></td>
<td>difficult in retrofit</td>
<td>acid pipeline</td>
<td>poor in-plant environment</td>
</tr>
<tr>
<td></td>
<td>need air at WHB inlet for</td>
<td>corrosion</td>
<td>need for air/O2 uptake</td>
</tr>
<tr>
<td></td>
<td>sulphation</td>
<td>no heat removal</td>
<td>for non-rotary process</td>
</tr>
<tr>
<td></td>
<td>high maintenance due to</td>
<td>water usage/effluent</td>
<td>vessels</td>
</tr>
<tr>
<td></td>
<td>build-up at convection section</td>
<td>handling</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>fan noise</td>
<td></td>
</tr>
<tr>
<td>Design</td>
<td>fouling of tubes</td>
<td>need after burning of S/H2S</td>
<td>spray pattern/droplet</td>
</tr>
<tr>
<td>considerations</td>
<td>pluggage of interconnecting</td>
<td>hot/cold interface</td>
<td>evaporation</td>
</tr>
<tr>
<td></td>
<td>flues</td>
<td>build-up</td>
<td>controls</td>
</tr>
<tr>
<td></td>
<td>rapid build-up at WHB</td>
<td>acid-resistant refractory</td>
<td>potential of sticky</td>
</tr>
<tr>
<td></td>
<td>interface</td>
<td>coarse solid separation</td>
<td>dust handling</td>
</tr>
<tr>
<td></td>
<td>rapping systems</td>
<td>venting of weak acid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>expansion between radiation and convection section</td>
<td>tanks</td>
<td></td>
</tr>
</tbody>
</table>
4.9 Dust separation

Non-ferrous metal processing plants use both wet and dry dust, mist or fume collectors at various steps in the gas cleaning process. Following the roaster or smelter, a mechanical dust collector, such as cyclone is utilized to reduce dust loading to a level of about 230 mg/m³ /24/.

Electrostatic precipitators are the most common dust or fume collection devices utilized after the hot dust collector to reduce the dust burden even further. The gases are cooled down to the 420–450°C range prior to the ESP and, in many plants, heat recovery equipment has been found to be profitable. ESPs are typically sized to remove particulates at 98 to 99% efficiency so that the off-gas leaves the ESPs at dust loadings varying from about 20 mg/m³ to 50 mg/m³ /24/.

If arsenic removal from the SO₂ laden gas is necessary, a gas cooling tower is utilized to cool the gases to around 115°C to condense out arsenic fumes. A fabric filter is introduced after this step to remove the arsenic compounds and most of the remaining dust from the gas stream /24/.

The cleaned smelter off-gases enter the gas cleaning section prior to the acid plant.

4.10 Sulphur fixation

Sulphur can be fixed in metallurgical processes by at least one of the following four processes:

- Sulphuric acid production
- Gas scrubbing and gypsum production
- Liquid sulphur dioxide manufacture
- Elemental sulphur production

All of the processes above benefit from high sulphur dioxide concentrations in the gas stream, both economically and in terms of conversion efficiencies. The production of liquid sulphur dioxide and elemental sulphur both require high sulphur dioxide concentrations. Due to the use of oxygen enriched air in the processes this can be easily achieved.

Sulphuric acid production is the most widely used process for two reasons. Firstly it is the easiest and least expensive sulphur fixation method which does not require high sulphur dioxide concentrations in the off-gas. Secondly, the market for sulphuric acid is much larger than for the other products in many locations.

The production of gypsum through the addition of limestone to an ammonium sulphite solution produced from sulphur dioxide, is not as cost effective as sulphuric acid production. It would also require the handling of many tonnes of limestone, which is required as a reagent in the process and subsequently a large amount of gypsum is produced.

The production of liquid sulphur dioxide would provide a good return on investment if there was a large market demand. Elemental sulphur production requires a high sulphur dioxide concentration in the off-gas. The feasibility of such a process requires a local market and the availability of low cost reductant.

The fuel and energy requirements for the fixation of sulphur from low sulphur dioxide concentration streams can be found in Table 11. The primary energy required for any sulphur fixation plant is the energy needed to operate the main blowers that route the gases through the acid plants. The most economical process is the production of sulphuric acid from the continuous gas stream /25/.
Table 11. Fuel and energy requirements for sulphur fixation.

<table>
<thead>
<tr>
<th>Per tonne of SO₂ fixed</th>
<th>Continuous gas stream</th>
<th>Variable converter gas stream</th>
<th>Combined continuous &amp; variable</th>
<th>Ammonia dual alkali scrubbing</th>
<th>Elemental sulphur production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed gas (SO₂ %)</td>
<td>12</td>
<td>5–8</td>
<td>variable</td>
<td>9–12</td>
<td>9–10</td>
</tr>
<tr>
<td>Electric power for main blower and related equipment kWh/tonne</td>
<td>118</td>
<td>219</td>
<td>152</td>
<td>175</td>
<td>350</td>
</tr>
<tr>
<td>Coal for reductant kg/tonne</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>330</td>
</tr>
<tr>
<td>Natural gas, for start-up Nm³/tonne</td>
<td>2.8</td>
<td>3.6</td>
<td>2.5</td>
<td>19.1</td>
<td>22.8</td>
</tr>
<tr>
<td>Acid neutralization Electric power for pumps, etc. kWh/tonne</td>
<td>52</td>
<td>52</td>
<td>52</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Total power required kWh/tonne SO₂ fixed</td>
<td>170</td>
<td>271</td>
<td>204</td>
<td>175</td>
<td>350</td>
</tr>
</tbody>
</table>

4.1 Acid plant

The performance of a metallurgical acid plant is dependent on the performance of the gas cleaning section. If the cleaning system is not effective in removing impurities from the incoming gas, the performance of the contact section will deteriorate. Although the design of wet gas cleaning systems may differ widely, they have the following requirements and features in common:

- Solid contaminants must be removed, giving a final gas quality of 1–2 mg solid/Nm³
- Sulphur trioxide content of the gas must be reduced to a level of 15–25 mg/Nm³
- Fluorides and chlorides must be removed to prevent damage to downstream tower brickwork and converter catalyst
- The gas must be cooled to a temperature of approximately 35–40°C to satisfy the acid plant water balance.

Operating at a gas strength of 14 %, SO₂ reduces the equipment sizes due to the reduced gas volume. It is estimated that the reduction in capital cost is 25 % and the main compressor horsepower is reduced by 40 %, even compared to a plant designed for 10 % gas. Moreover, pumping power will also be reduced by virtue of the lower circulation rates in high efficiency drying and final absorber towers /26/.

One of the opportunities of high gas strength is the excess heat it makes available. In a modern smelter sulphuric acid plant, this heat represents potential income in the form of electrical power /26/.

Sulphur dioxide emissions can be maintained at less than 100 ppm representing 99.95 % collection efficiency of the 14 % SO₂ in the feed gas. Under normal operating conditions SO₂ emissions are in the 30–60 ppm range /11/. As Table 12 shows, increasing enrichment is accompanied by a corresponding decrease in the off-gas volume from the flash furnace. Since matte grade in this example is held constant at 60 %, the gas volume to the acid plant from the the converters does not change /27/.
Table 12. Acid plant size with oxygen enrichment variation (Matte grade at 60 %). FSF = flash smelting furnace.

<table>
<thead>
<tr>
<th>Oxygen enrichment</th>
<th>35 %</th>
<th>49 %</th>
<th>55 %</th>
<th>65 %</th>
<th>70 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate smelted t/d</td>
<td>2424</td>
<td>2424</td>
<td>2424</td>
<td>2424</td>
<td>2424</td>
</tr>
<tr>
<td>Matte t/d</td>
<td>1486</td>
<td>1486</td>
<td>1486</td>
<td>1486</td>
<td>1486</td>
</tr>
<tr>
<td>Oxygen t/d</td>
<td>343</td>
<td>405</td>
<td>420</td>
<td>436</td>
<td>442</td>
</tr>
<tr>
<td>FSF process gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume kNm3/h (wet)</td>
<td>43.7</td>
<td>28.3</td>
<td>24.7</td>
<td>20.4</td>
<td>18.9</td>
</tr>
<tr>
<td>SO2 %</td>
<td>19.6</td>
<td>30.2</td>
<td>34.6</td>
<td>41.7</td>
<td>45.2</td>
</tr>
<tr>
<td>FSF process gas to acid plant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume kNm3/h (wet)</td>
<td>78.8</td>
<td>53.5</td>
<td>47.6</td>
<td>40.6</td>
<td>38.0</td>
</tr>
<tr>
<td>SO2 %</td>
<td>10.9</td>
<td>16.0</td>
<td>17.9</td>
<td>21.0</td>
<td>22.4</td>
</tr>
<tr>
<td>Peirce-Smith converter process</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas (avg.) to acid plant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume kNm3/h (wet)</td>
<td>175.1</td>
<td>175.1</td>
<td>175.1</td>
<td>175.1</td>
<td>175.1</td>
</tr>
<tr>
<td>SO2 %</td>
<td>4.9</td>
<td>4.9</td>
<td>4.9</td>
<td>4.9</td>
<td>4.9</td>
</tr>
<tr>
<td>Avg. process gas to acid plant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume kNm3/h (wet)</td>
<td>253.8</td>
<td>228.6</td>
<td>227.7</td>
<td>215.8</td>
<td>213.2</td>
</tr>
<tr>
<td>SO2 %</td>
<td>6.8</td>
<td>7.5</td>
<td>7.7</td>
<td>8.0</td>
<td>8.1</td>
</tr>
<tr>
<td>Converter scheduling</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume kNm3/h (wet)</td>
<td>366.3</td>
<td>341.0</td>
<td>335.1</td>
<td>328.1</td>
<td>325.5</td>
</tr>
<tr>
<td>Acid plant capacity, 10 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Design factor, kNm3/h (wet)</td>
<td>400.4</td>
<td>375.1</td>
<td>369.2</td>
<td>362.2</td>
<td>359.6</td>
</tr>
<tr>
<td>Relative capital cost factor</td>
<td>104 %</td>
<td>100 %</td>
<td>99 %</td>
<td>97.9 %</td>
<td>97.5 %</td>
</tr>
</tbody>
</table>

4.12 Tail and secondary gas cleaning and scrubbing

Acid plant installations with tail gas scrubbing are becoming common /10/. Secondary emissions are gases and dust from tap holes, transfer pots, etc. It is possible to control these emissions to contain sulphur less than 0.1 % of the input to the smelter. In addition, it is necessary to capture the dust emissions. To achieve such levels, a myriad of exhaust vents, blowers and auxiliary equipment must be added, which further increase the energy consumption. Table 13 shows some energy requirements needed for the control of fugitive emissions.

These fugitive emissions come from feed handling equipment, dryer, furnaces, matte and slag granulation systems etc. They can be treated with bagfilters and scrubbers. One possibility is to use calcium hydroxide Ca(OH)2, which has a high surface area as an absorbing agent. The reaction product is recirculated several times to exploit it as far as possible. The end product is a mixture of dust, calcium sulphate as well as additive residue and it is fed to the flash smelting furnace. Cleaned gas dust contents of less than 1 mg/Nm3 can be achieved in the cleaned off-gas from the connected baghouse /4/.

Table 13. Energy requirements for control of fugitive emissions /25/.

<table>
<thead>
<tr>
<th>Smelter Area</th>
<th>Design Capacity of exhaust fan, Nm3/h</th>
<th>Total Annual energy consumption, kWh/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate and flux receiving and handling</td>
<td>377 000</td>
<td>1 080 000</td>
</tr>
<tr>
<td>Smelting furnace, hood, ladle pits, launder covers, etc.</td>
<td>187 000</td>
<td>750 000</td>
</tr>
<tr>
<td>Slag return launder hood</td>
<td>374 000</td>
<td>220 000</td>
</tr>
<tr>
<td>Total power required for fugitive emission control for smelter area alone</td>
<td>2 050 000</td>
<td></td>
</tr>
</tbody>
</table>
All environmental control equipment must be continuously monitored to ensure compliance.

### 4.13 Waste acid and water treatment

The weak acid generated in the gas cleaning section contains typically 1-20 % H$_2$SO$_4$. Halides will be present as HCl (10–1,000 ppm) and HF (10–1,000 ppm including H$_2$SiF$_6$). The acid may also contain metals such as copper, zinc and iron (individually up to 2,500 ppm), mercury (up to 1,900 ppm) and lead (up to 50 ppm). Arsenic may be present up to levels of 10,000 ppm. Other elements, such as aluminium, nickel, chromium, cadmium, bismuth, antimony, etc. may also be present depending on the contaminants present in the smelter feed. The weak acid will also be saturated with SO$_2$ (typically between 2,000 and 5,000 ppm depending on the SO$_2$ strength)/28/.

A typical method for removing arsenic from dilute sulphuric acid is to add a ferric salt and an oxidant to precipitate ferric arsenate at a pH value of between 2.5 and 3.0 (<0.5 % H$_2$SO$_4$).

The main part of selenium will be volatilized during roasting. Under oxidising conditions, selenium will enter sulphuric acid as selenious acid. However, it is rapidly reduced to elemental selenium. Selenium is recovered from the weak acid by filtering.

The weak acid can be used in hydrometallurgical leaching processes. If this is not possible, the common treatment for weak acid effluent is lime neutralization. This produces large amounts of gypsum, which is frequently contaminated with potentially toxic metal compounds and therefore must be stored or disposed of. The advantage of this approach is that it is well established and uses relatively straightforward equipment. The acid passes into reaction vessels into which lime slurry is added to form soluble calcium sulphate and insoluble hydroxides of metals such as lead, zinc and copper. Air and a ferric salt may be added to promote the precipitation of ferric arsenate. The presence of ferric ions also assists in the removal of mercury. Fluorides will be precipitated as calcium fluoride but chlorides will remain in solution. The slurry is thickened and the overflow is discharged to the environment. In order to achieve optimum performance of the neutralisation system, it is important to maintain pH control and monitor and control the ratio of certain components/28/.

The disadvantage of the neutralisation process is that the gypsum which is produced is usually not of a quality high enough to be sold. Therefore the gypsum product has traditionally been stored.

However, in many locations, the storage space is limited and there is concern that the potentially toxic contaminants in the gypsum may leach to the groundwater. Therefore, there is a growing tendency to encapsulate the gypsum into the furnace slag either via external addition of the gypsum to the molten slag or by recycling the gypsum sludge to the smelting furnace/28/.

Many plants have an effluent treatment plant which can treat the acidic discharges, process water and contaminated site water. The metals are precipitated with sodium hydroxide or lime. The sludge formed is routed to clarification basins. The filtered overflow can be let to the waterways. The metal precipitates can be fed to the smelting furnace.
4.14 Leaching of nickel matte

Refining is the final operation to decrease to an acceptable level those impurities that would have an adverse effect on metal or alloy performance and that are not readily eliminated during the proceeding extractive processes. The refining operation is generally considered separate from the extractive process, and in many cases the two plants are far away from each other so that the crude metal has to be shipped to the refinery for final treatment.

Unlike copper refining, where only one basic process is used, nickel refining is much more complicated. Nickel producers can choose from several processes. Some of these processes are used in different combinations. The type of refining that is used to purify the crude metal depends upon the impurities to be removed, the desired purity of the refined metal product and the source of energy most economically available.

4.14.1 Ammonia pressure leaching

Sherrit has developed a hydrometallurgical process for sulphidic raw materials, which is based on ammoniacal oxygen pressure leaching. In the subsequent refining process part of the nickel is recovered as powder using hydrogen reduction and the rest as nickel/cobalt sulphide precipitate. The sulphur content of the concentrate is recovered as ammonium sulphate and iron as residue with impurities. The process has been commercially used by Sherrit itself, but is today used only for matte and precipitates and by Western Mining for matte in the Kwinana refinery.

In the process (Figure 10) the finely ground matte (or precipitate) is leached in ammoniacal ammonium sulphate solution at 80–95°C under 850 kPa air pressure in two-stage countercurrent process in autoclaves. Nickel, cobalt and copper are dissolved as soluble ammonia complexes, while sulphide is oxidised to form a series of soluble thio salts. Iron is oxidised, too. The leach solution is boiled to distil off the free ammonia and elemental sulphur or SO2 is added to precipitate copper. Copper is sold to the copper smelter. The ammoniacal nickel sulphate solution is oxidised under pressure. In the final step of the process, nickel is precipitated from the solution as metal powder by hydrogen reduction.

4.14.2 Atmospheric acid leaching

The atmospheric acid leach process for the treatment of high-copper, low-sulphur nickel matte was developed by Outokumpu for the Harjavalta plant. The process was in use before the modernisation of the plant in 1995. This process is also in use in Zimbabwe. The process flow sheet is shown in Figure 11. The ground matte is leached at 80°C in acidic sulphate solution in a three-stage countercurrent leach circuit. Nickel, which is largely present in the low-sulphur matte as metallic nickel, dissolves in the first stage leach by reaction with sulphuric acid and with soluble copper, which is cemented from solution as copper metal. Most of the remaining nickel and some of the copper are leached in the second and third stages, which operate under increasingly oxidising and acidic conditions. The solution from the first leaching stage is a copper-free nickel sulphate solution, while the residue from the third stage is enriched in copper relative to nickel.
The atmospheric leach residue is treated in a pressure leach under mildly oxidising conditions at 160°C, in which nickel is extracted selectively, leaving a low nickel, high copper sulphide residue which can be treated in the copper smelter. The Zimbabwean plants recover copper by electrowinning from the second stage leach liquor and recycle to leach residue to nickel smelter.

Cobalt is separated from the nickel sulphate solution by adding a nickel(III)-hydroxide slurry to precipitate cobalt as cobalt(III)hydroxide. The nickel(III)-hydroxide is produced by electrolytic oxidation of nickel(II)hydroxide, formed by neutralizing purified nickel sulphate with sodium hydroxide. Nickel is recovered from the purified nickel sulphate solution by electrowinning.

Figure 11. The conventional Outokumpu refining process /1/.
4.14.3 Acid pressure leaching

The acid pressure leaching process for the treatment of high-copper nickel mattes was developed by Sherritt Gordon during the 1960s and is currently operated by all platinum producers in the Republic of South Africa.

The acid pressure leaching is normally carried out in brick- and lead-lined horizontal multicompartment autoclaves at $135–160^\circ\text{C}$ and oxygen partial pressures of $140–350\text{ kPa}$. The major advantage of this process for the platinum producers is that very high extractions of nickel, copper and sulphur can be obtained. The extractions are typically over 99.9%, so that the leach residue is a high-grade platinum group metal concentrate. The process flow sheet differs significantly for the various operations. The nickel products also differ widely.

4.14.4 Chloride leach process

Nickel matte refining processes based on leaching in chloride solution in the presence of chlorine gas have been developed and successfully commercialized by Falconbridge at Kristiansand in Norway and by SLN at Le Havre-Sandouville in France. Leaching of matte is carried out at atmospheric pressure at the boiling point of the leaching solution, about $110^\circ\text{C}$. Chlorine, which is recovered from the electrolysis cells, is sparged directly into the leach tanks. In the SLN process the leachant is the iron(III)chloride solution recovered from an iron removal step, whereas in the Falconbridge process the leachant is a solution of copper and nickel chlorides recycled from the copper residue treatment circuit. The flow sheet of the Falconbridge process is shown in Figure 12.

Granulated nickel copper mattes from the Falconbridge smelter in Ontario and from BCL in Botswana are leached with chlorine in a nickel copper chloride solution in a train of agitated tanks.

The leach slurry is heated to $140–145^\circ\text{C}$ in autoclaves to promote the precipitation of copper and the dissolution of nickel. The discharge from the autoclave is further treated with fresh matte to reduce the copper concentration. Iron, which is largely dissolved in the chlorine leach, is precipitated by oxidation with chlorine and hydrolysis with nickel carbonate. Cobalt is extracted from the nickel chloride solution by solvent extraction and, after purification of the strip solution, is recovered as high-purity cathode by electrowinning. The nickel chloride raffinate is diluted and purified further by treatment with chlorine and nickel carbonate to remove the remaining traces of impurities. High-purity nickel is recovered by direct electrowinning as cathode.

Copper is extracted from the chlorine leach residue by roasting it in a fluidized-bed roaster to convert the copper sulphide and elemental sulphur to copper oxide and sulphur dioxide. Sulphur dioxide is converted to sulphuric acid. The calcine is leached in sulphuric acid and copper is recovered by conventional electrowinning.

The calcine leach residue undergoes further chloride leaching to recover nickel and copper in solution for recycling to the leach circuit leaving the platinum group metals in an upgraded concentrate.

In the SLN process, in which the feed matte is produced from laterite ore contains virtually no copper. Iron is removed as ferric chloride by solvent extraction. Part of the ferric chloride strip solution is recycled to the chlorine leach. Cobalt chloride is extracted and sold as solution for cobalt recovery elsewhere. Nickel is recovered from the purified solution as high-purity cathode by electrowinning.
4.14.5 New Outokumpu nickel refining process

In the new DON-process two different types of matte are produced, -the flash smelting furnace (FSF) matte and the electric furnace (EF) matte. The two types of matte are subjected to separate leaching processes (Figure 7). The finely ground Flash Smelting Furnace matte is leached in the FSF-matte leaching circuit with the aid of oxygen and sulphuric acid. Sulphuric acid is recycled from nickel electrowinning.

Leaching is done in three steps which are countercurrently connected: atmospheric copper removal, nickel atmospheric leach and nickel pressure leach. In the first leaching stage nickel is leached as sulphate with the aid of copper cementation. Iron is oxidised to iron oxide, which precipitates. The solution is filtered and routed to solvent extraction. In the second atmospheric leach nickel and copper are leached from the residue, at the same time iron is kept precipitated. The solution is returned to the cementation step.

The residue from the atmospheric leaching subsequently undergoes selective and total pressure leaching steps. In the selective leaching autoclave, nickel is dissolved and copper precipitated as copper sulphide. Iron is also dissolved. In the total leaching autoclave the rest of nickel and a part of copper sulphides are leached. The solution from FSF-matte pressure leaching is fed to EF-matte atmospheric leaching for iron removal. The leaching residue from the pressure leaching is copper sulphide which is introduced to the copper smelter for copper and precious metals recovery.

The finely ground granulated electric furnace matte is leached in the EF-matte leaching circuit. In this process nickel, copper and cobalt are leached and iron is precipitated in a controlled way.

The EF-matte leaching contains two leaching steps. In atmospheric leaching nearly all iron dissolves first and then precipitates as oxide. The solution from the atmospheric leaching is sent for iron removal. The rest of the dissolved iron is precipitated in an autoclave under highly oxidising conditions. The solution is conducted to the FSF-matte first atmospheric leaching. The iron oxide precipitate is fed to the nickel Flash Smelting Furnace. The residue from the atmospheric leaching is leached with pressure leaching as completely as possible. The iron oxide residue left is fed to the nickel Flash Smelting Furnace. The solution goes back to the atmospheric leaching.
The nickel raw solution from the leaching is cleaned with solvent extraction. Cobalt is extracted from the solution. Cobalt powder is produced by hydrogen reduction. Nickel is produced from the purified solution both by electrowinning and by hydrogen reduction.

4.14.6 Comparison of the nickel leaching processes

The leaching processes described have both advantageous and disadvantageous features. The selection of the process depends on many factors; the impurities in the matte, the energy price etc. Of course, if there is an acid plant on the site, it is obvious to use sulphate leaching.

Most difficulties arising from the leaching process used affect the working environment. Chlorine handling requires strict safety precautions. In particular, it is necessary to maintain a good working atmosphere in the nickel tankhouse by ventilation and by keeping the thousands of individual anode hoods tight to avoid escape of chlorine gas. The copper sulphide residue fed to the fluidised bed roasters still contains much nickel. To avoid exposure to nickel oxide dust, the roasting operation must be extensively automated and the dust removed from the area by permanent sprinkling and collection systems.

The conventional Outokumpu leaching system is attractive because it does not require hazardous chemicals such as chlorine or hydrogen sulphide. Sulphate electrowinning, however, produces acid mist, requiring good ventilation in the tank house.

The sulphuric acid pressure leach requires careful design, operation and maintenance of all pressure operations to ensure safety in the plant area. Great care is also required in the handling of ammonia used for neutralisation and particularly of hydrogen used for reduction at high pressure.

In the ammonia leach process careful design, operation and maintenance is also required to ensure safety. In the areas where the leaching solution with excess of free ammonia is filtered, adequate hooding of the equipment and sufficient ventilation in the building has to be provided to keep ammonia concentrations within the permissible limit in the work area.

4.15 Nickel electrowinning

Electrowinning differs from electorefining in that it is used to recover nickel from a leach liquor and can therefore be carried out with an insoluble anode, since the only function of the anode is to transfer electrons from the electrolyte to the external circuit. The electrowinning of nickel is practised commercially with both pure sulphate and pure chloride electrolytes. In the sulphate system the anodes are made of chemical lead or antimonial lead, which have a relatively long life in sulphate solutions, although soluble in chloride solutions. In the highly corrosive chloride system, dimensionally stable anodes, made by coating a titanium substrate with a platinum group metal oxide, are used.

The principal anodic reaction in the sulphate system is the decomposition of water to produce gaseous oxygen. The main cathodic reaction is the deposition of nickel ions to form nickel atoms on the cathode. The overall cell reaction is:

$$2\text{NiSO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{Ni} + 2\text{H}_2\text{SO}_4 + \text{O}_2$$

The sulphuric acid generated at the anode is utilised by recirculating the anolyte to the leach circuits. In the chloride system the principal anodic reaction is the
oxidation of chloride ion to chlorine gas. The overall reaction is thus the decomposition of nickel(II)chloride to metallic nickel and chlorine gas:

\[
\text{NiCl}_2 \rightarrow \text{Ni} + \text{Cl}_2 \quad (2)
\]

The chlorine liberated at the anode is recycled for use in the leach circuits. In practice some decomposition of water also occurs to yield small quantities of hydrogen at the cathode and oxygen at the anode.

### 4.15.1 Electrowinning from sulphate electrolytes

In a sulphate electrowinning system, the cathodes are suspended in bags, even though the nickel sulphate solution is purified before it enters the tankhouse. The cathode must still be protected from the anolyte, which is strongly acidic due to anodic generation of hydrogen ions. A high concentration of hydrogen ions at the cathode would result in the formation of hydrogen gas which is formed in preference to nickel deposition, thus seriously reducing the current efficiency of the cell.

Treatment of the electrowinning anolyte or spent electrolyte varies depending on the type of leaching circuit used. In the Outokumpu process, almost all anolyte can be recycled to the leaching circuit, where the acid is neutralised in leaching nickel from matte, thus replenishing the nickel content of the solution. Only a small bleed is taken out of the circuit to control the concentration of sodium sulphate, which would otherwise build up to unacceptable levels. In the Sherritt acid pressure leaching process, a much larger bleed of solution is required to maintain the sulphur balance.

### 4.15.2 Electrowinning from chloride electrolytes

In the Falconbridge chloride electrowinning system, the dimensionally stable anodes are enclosed in a polyester diaphragm bag to contain the chlorine gas generated in the anode reaction, and channel it to a vacuum hood fitted to the top of the anode. Ducts, connecting the top of the hood with a manifold that runs alongside the tank, allow the withdrawal of both chlorine and anolyte by suction. The purified solution is fed at one end of the cell, and the solution level is held constant by maintaining a small overflow at the other end, while the greater portion of the electrolyte is withdrawn as anolyte with the chlorine gas.

### 4.16 Hydrogen reduction to nickel powder

Nickel is recovered as a pure metal powder from nickel sulphate leach solutions by chemical reduction with hydrogen under pressure in several hydrometallurgical nickel refineries. Precipitation of the metal is carried out with an ammonia-nickel sulphate solution having a molar ratio of ammonia to nickel of 2:1, so that the acid generated in the reduction reaction is neutralised by reaction with ammonia to form ammonium sulphate.

The reduction process is operated at 200°C at a hydrogen pressure of 3 Mpa in autoclaves. The solution is processed batchwise, with the powder particles growing as successive layers of nickel are reduced onto seed particles, from up to sixty batches of nickel-bearing feed solution. After each reduction or densification the powder is allowed to settle, and the depleted solution is decanted off and replaced by fresh feed solution.
The nickel precipitation can occur on any metal surface, and in the absence of suitable seed particles most of the deposition occurs on the vessel walls as a solid plate. When suitable seed particles such as fine nickel powder are available, most of the nickel deposits on these particles, but even so, a minor but significant amount of nickel still plates on the walls, and must be releached periodically. Normally this plating leach is carried out after each cycle of 50–60 densifications, and the leach liquor produced is used to prepare the seed particles for the subsequent densification cycle.

Seed particles are produced by adding an aqueous solution of iron(II)sulphate to the plating leach liquor to form a finely divided precipitate of ferrous hydroxide, and applying a hydrogen overpressure of 2.5 Mpa at 115°C. Under these conditions the nickel deposits onto the nuclei of ferrous hydroxide to form very fine particles of nickel metal, which provide the seed particles for densification. Once the seed particles are formed, subsequent nickel deposition occurs autocatalytically on the surface of these particles, in preference to the vessel walls.

The reduction reaction is selective for nickel from a solution containing 50 g/l Ni and 1 g/l Co until the nickel content drops to about 1 g/l. Reduction is normally stopped at this point. The remaining metals from the solution are precipitated with hydrogen sulphide and the barren solution is evaporated to crystallise ammonium sulphate for sale.

At the end of the densification cycle when the powder has reached the desired particle size and density, the whole contents of the autoclave are discharged. The powder is drawn from the tank, washed with water and dried. The powder is either marketed as such or is converted to briquettes by mixing with an organic binder and pressing in briquetting rolls.

This process of recovering nickel powder from solution can be used in combination with ammonia pressure leaching, acid pressure leaching, the Outokumpu DON-process and with the Caron process for treating laterites.
In the last chapter the various process steps in the pyrometallurgical nickel production were discussed. It seems easy to conclude that there is no unambiguous best available technique. The best available technique consists of optimised unit processes. These unit processes must be designed in such a way that they are compatible. All particulate and gaseous emissions must be kept in strict control.

The best available technique consists of the following process units:

- The concentrates are stored in warehouses.
- The concentrates are dried in multicoil steam dryers.
- A loss-in-weight feeding system is used to feed the concentrate into the flash smelting furnace.
- The DON process is used to smelt the concentrate.
- The resulting mattes are refined using the process best suited for the plant in question.
- The gas stream from the furnaces is conducted to a modern double contact acid plant for the manufacture of sulphuric acid.
- Process and environmental control is well maintained.

The use of the DON process brings a number of benefits:

- lower investment and operation costs when converting is eliminated
- low investment and operating cost of the smelter and acid plant because of continuous operation of the flash smelting process. The gas stream from the smelter is stable and high sulphur recovery can be achieved in a modern acid plant.
- the sulphuric acid plant can be smaller than with the conventional process
- gas flow and the amount of tailings are smaller
- the working conditions in the smelter improve as the SO$_2$-rich gas does not escape from ladles and converters during blow interruptions. Transportation of molten material in ladles between the flash smelting furnace, converter and electric furnace is eliminated.
- the amount of reverts is only a small part of the previous amount.
- high recovery of nickel and especially cobalt and precious metals is boosted by elimination of unnecessary molten material circulations
- the flash smelting furnace yields a low iron matte from unconventional raw materials
- no matte and slag recycling between converters and electric furnace, facilitating optimisation of operation
- one continuous SO$_2$-gas stream. The operation of the acid plant improves and SO$_2$-emissions are reduced
- no ladle transfer resulting in minimal fugitive and dust emissions and improved in-plant hygiene
- no need for excess fuel, because the chemical energy content of the concentrate is utilised in smelting
- improved metal recoveries compared to the old process, owing to the elimination of internal recirculations
- optimisation of the process concept and operation mode
— flexibility to treat a wide range of raw materials. It must be kept in mind that the effect of the raw material is significant and influences the selection of the process. Even small variations in raw material composition may change the competitiveness. The contents of harmful constituents as well as the contents of valuable by-products have significance. Arsenic, which can be found in large quantities in some ores requires special treatment in metallurgical processing.

The most important by-product is cobalt and in some cases it plays the determining role in the profitability. Platinum group metals are typically found in nickel raw materials. If they have a significant impact on profitability, the traditional smelter-refinery route is favoured.
Emerging Techniques

It is quite difficult to determine the difference between available and emerging techniques. In this study “available” means that an operating company, following issue of a commercial invitation to tender for a metallurgical engineering design contractor for the construction of a full scale plant, could expect to receive an offer capable of acceptance, including technical and commercial performance guarantees. If such an offer was unlikely to be forthcoming the process/plant should be considered as “emerging”. The emerging techniques have, however, been tested on pilot scale and the results and process calculations seem promising.

The totally new processes are all hydrometallurgical leaching processes followed by solution purification and electrowinning or hydrogen reduction to produce the metal.

The main reason to start development has been the aim to reduce production costs. However, the differences in raw materials make it difficult to alternative processes, because the site-specific factors and by-product credits alone play a significant role.

Currently, there are three new plants, Murrin Murrin, Cawse and Bulong, under construction or at the commissioning stage in Australia, which all represent somewhat different process concepts.

6.1 Leaching of sulphides

6.1.1 Pressure leaching

Pressure leaching has been applied by Sherritt as noted before.

A new development is Activox leaching, which has been proposed for the Yakabindie project. This comprises fine grinding and low temperature low pressure (100°C, 10 bar) leaching, which is claimed to be considerably less costly than the high pressure applications. The process has been successfully pilot tested.

6.1.2 Bioleaching

Bioleaching has been commercially applied for the leaching of refractory gold ores and concentrates in reactors and copper ores in heaps. Its application to nickel sulphide concentrates has been developed by Billiton together with Mintek in South Africa. The resulting process is known as Bionic /29/. The process has been successfully pilot tested, but no commercial plant is under construction yet.

The basic idea is to dissolve nickel sulphides with the aid of iron and sulphur oxidising bacteria so that the nickel yield into the solution is high and the residue is acceptable for disposal to tailings. Iron must be precipitated from the solution obtained. For the further solution treatment, ion exchange or solvent extraction can be applied followed by electrowinning or hydrogen reduction to produce nickel metal or powder. Alternatively, the metals can be recovered by traditional precip-
itation methods. Sulphur is fixed as gypsum by neutralizing the part of the solution which is not circulated back to the bioleaching stage.

### 6.1.3 Chloride leaching

Cominco has been working for a long time on chloride leaching in sulphate solution of copper concentrates and subsequent recovery of metallic copper. The proposed CESL process has been successfully pilot tested, but no commercial application exists still. The same process has been investigated and pilot tested with the aim of applying it to nickel.

Intec in Australia has long been developing a chloride based process for copper concentrates as an alternative to traditional smelting. The company proposes the same concept for nickel concentrates, too.

### 6.2 Leaching of laterites

#### 6.2.1 Atmospheric leaching

QNI in Australia applies a process (Caron process) where the laterite is first roasted under reducing conditions using multiple-hearth roasters. The calcine is subjected to ammoniacal leaching which is followed by solvent extraction to separate cobalt and nickel. Cobalt is precipitated as sulphide while nickel is first precipitated as carbonate which is then further calcined to oxide and reduced to metallic nickel by hydrogen.

A similar type of reductive roasting and ammonia leaching to produce nickel metal and cobalt by-products is used for laterites from New Caledonia and by Nicaro and Punta Gorda in Cuba and Tocantins in Brazil.

#### 6.2.2 Pressure leaching

The pressure leaching of laterites with sulphuric acid is principally a simple and straightforward process. The temperature, pressure and other parameters may vary from case to case to achieve the best possible metallurgical conditions depending on the ore and products in question and other objectives. The resultant solution is purified either by modern solvent extraction methods or by traditional precipitation methods. The final solution is used for nickel recovery by electrowinning or hydrogen reduction.

Commercially, this process has been used by Moa Nickel S.A. in Cuba since 1959. The temperature of the leaching autoclaves is between 230 and 260 °C. Hydrogen sulphide is used to selectively precipitate nickel and cobalt sulphides which are sent for further metal recovery by Sherritt in Canada.

The Cawse Nickel Project in Australia, which is currently under construction, will use pressure leaching at 250°C. The solution will be neutralised so that iron precipitates. Nickel and cobalt will be precipitated and releached with ammonia. Solvent extraction will be used to separate nickel and cobalt. Metallic nickel will be produced by electrowinning and cobalt precipitated as cobalt sulphide.

The Murrin Murrin Nickel Cobalt Project, which is also under construction, applies sulphuric acid pressure leaching at 255°C and 43 bar. After separating the leach residue nickel and cobalt are precipitated as mixed sulphide, which is releached in autoclaves with oxygen. Cobalt and nickel are separated by solvent
extraction and finally both nickel and cobalt are recovered as metal powders using hydrogen reduction.

The process to be used in Bulong also applies pressure acid leaching, but the solution purification does not include an intermediate precipitation. Instead, the solution from the leaching stage is purified directly by solvent extraction and the separated cobalt and nickel solutions are passed on to electrowinning to recover the metals as cathodes.

6.2.3 Chloride leaching

As an alternative to pressure leaching of laterites, atmospheric chloride leaching has been proposed and investigated. The advantages of chloride leaching are the high yields and avoidance of pressure leaching.
Executive Summary

The variety of raw materials and products as well as the availability of different unit technologies result in a number of different process alternatives depending on the raw material and product. It is typical for the nickel industry that the processes are in many cases tailored for specific types of raw material. This is not the case with copper and zinc, the raw materials of which are typically fairly homogeneous and of the same type, allowing rather standard processes to be used.

Traditionally, refined nickel has been produced from sulphidic ores and ferronickel from saprolitic laterites. The development of new technologies and the differences between individual ores have made the picture even more complicated. The development of new hydrometallurgical processes has made it possible to produce refined nickel from limonitic laterites at competitive cost and simultaneously recover cobalt.

There are two types of nickel processing techniques. In pyrometallurgical processes the ores or concentrates are smelted in furnaces and the metals are separated from the slag and further refined. Pyrometallurgy is mainly used in the treatment of sulphidic concentrates and high nickel-containing laterites. Hydrometallurgical treatment is mainly used in the treatment of low nickel-containing laterites and in the refining of matte or concentrates.

In Finland, nickel is produced by the pyrometallurgical Direct Outokumpu Nickel (DON) Flash Smelting process from sulphidic concentrates. The key feature in the process is the fact that high grade nickel matte is produced without converting and two different types of matte are produced. The mattes are then leached by hydrometallurgical processes.

The main remaining waste from the process is the slag which has to be stored on site. Liquid effluents from the process result from the cooling water system, the sulphuric acid plant attached to the smelter and from the wet gas cleaning system. The wet gas cleaning system produces a weak acid and collects arsenic, mercury, selenium and fine dust particles containing other impurities. In the nickel refining plant, wet scrubbers are used to wash the gases before they are routed to the stack. The major environmental challenge results from the release of SO₂ and particulate emissions.

The best available technique to produce nickel from sulphidic concentrates consists of the following process units:

- Indoor storage of concentrates.
- The concentrates are dried in multicoil steam dryers.
- A loss-in-weight feeding system is used to feed the concentrate into the flash smelting furnace.
- The DON process is used to smelt the concentrate.
- The resulting mattes are refined using the process best suited for the plant in question.
- The gas stream from the furnaces is channelled to a modern double contact acid plant for the manufacture of sulphuric acid.
- The plant is equipped with an efficient process and environmental control system.
Literature


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The aim of this BAT report is to identify available techniques for the reduction of emissions and energy use in the primary nickel production in Finland.

In Finland, nickel is produced by the pyrometallurgical Direct Outokumpu Nickel (DON) Flash Smelting process from sulphidic concentrates. Flash smelting takes place without any external fuel addition, i.e. the chemical energy of the concentrate is utilised for smelting. The key feature in the process is the fact that high grade nickel matte is produced without converting and two different types of matte are produced. The mattes are then leached by hydrometallurgical processes.

The main remaining waste from the process is the slag which has to be stored on site. Liquid effluents from the process result from the cooling water system, the sulphuric acid plant and from the wet gas cleaning system. In the nickel refining plant, wet scrubbers are used to wash the gases. The major environmental challenge results from the release of SO₂ and particulate emissions.
Suomalainen asiuntijaraportti parhaimmista käytettävissä olevista tekniikoista nikkelin tuotannossa

Tässä BAT raportissa esitellään menetelmät, joita käyttämällä voidaan vähentää päästöjä ja energian kulutusta primäärisessä nikkelin tuotannossa Suomessa.


### Tiivistelmä

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