

Chapter 13

Nickel

13.1 Introduction

Nickel (Ni) was obtained for the first time by the Swedish chemist A.F. Cronstedt, in 1751, who suggested the name for the element. Although nickel (Ni) is a common constituent of the Earth's crust being more widely distributed than copper, lead and zinc. Nickel has been found in economic quantities only in Canada, New Caledonia, Finland, Russia, Cuba, Griqualand, although other deposits are known. By far the most important of these areas is the Sudbury region of Ontario, Canada. The presence of nickel (and copper) in this region was known as early as 1856. In 1889, the Oxford Copper Co found a separation method for nickel and copper sulphides by taking advantage of their differing solubilities in sodium sulphide. The copper sulphide is readily soluble and nickel sulphide is practically insoluble.

13.2 Sources

Nickel (Ni) is mostly associated with copper and iron compounds in its ore. In nature nickel occurs as oxides, sulphides and silicates forms. The principal ore minerals of nickel are the (I) sulphides: (a) millerite (NiS) and (b) pentlandite [(NiFe)₁₁S₁₀], it is a nickeliferous pyrrhotite mixed with chalcopyrite (Cu₂S, Fe₂S₃) and rocky gangue; (II) hydrous silicate: garnierite [H₂(Mg,Ni)SiO₄]; (III) mixed copper-nickel ore (with nearly equal amount of Cu); (IV) oxide: nickeliferous laterites or Ni-oxide ore; and (V) sea nodules (oxide).

Large deposits are available in Canada and biggest producer of nickel in the world is International Nickel Co (INCO), Canada. INCO contributes for nearly 80% of world nickel production. Total requirement of nickel in India is fully imported.

Apart from above, several tonnes of nodules are scattered across the ocean floor. These nodules, whose principal constituents are Mn (23.86%), Fe (13.8%),

Al (2.86%), Mg (1.66%), Ni (0.98%), Cu (0.52%), Co (0.35%) and siliceous; are collectively termed as *manganese nodules*. In terms of their nickel content, they can also be called *nickel nodules*, since they are a potential source of nickel.

13.3 Extraction of Nickel

Extraction of nickel is more or less similar to that of copper extraction. Basically extraction of nickel from Cu–Ni ore which involves basically three steps:

1. Concentration,
2. Treatment of Ni–Cu sulphide concentrate, and
3. Refining.

13.3.1 Concentration

Flow diagram of nickel extraction is shown in Fig. 13.1. Cu–Ni ore (1.3% Cu, 1.2% Ni) is concentrated by flotation to get bulk Ni–Cu concentrate (7% Cu, 6% Ni), and nickel-ferrous sulphide concentrate (0.9% Ni) as tailing. Again by flotation separating of Ni–Cu sulphide concentrate (10% Ni, 2% Cu, 40% Fe, 30% S) and Cu concentrate (30% Cu, 1% Ni) are done; Cu is recovered from Cu concentrate.

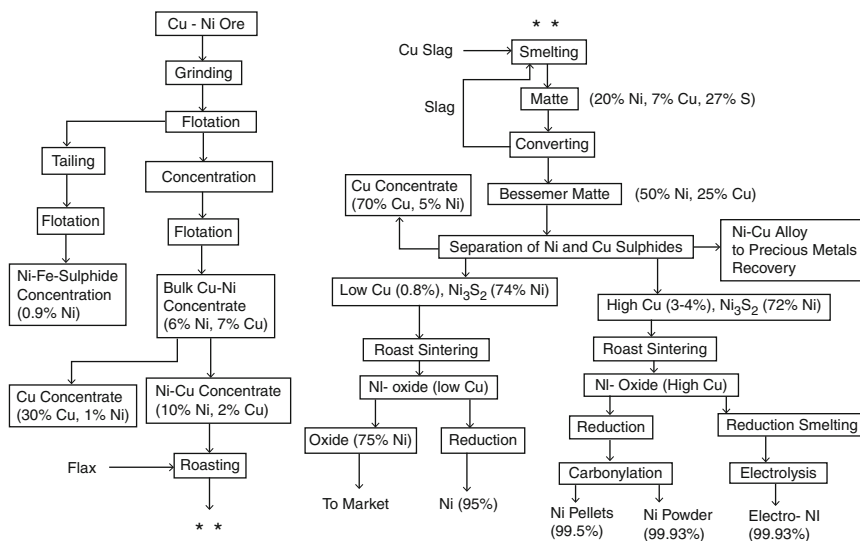


Fig. 13.1 Flow diagram of extraction of nickel

13.3.2 Treatment of Ni–Cu Sulphide Concentrate

Ni–Cu concentrate consists of the sulphides of these metals together with iron pyrite (FeS_2), silica (SiO_2) and small amounts of cobalt (Co), selenium (Se), tellurium (Te), gold (Au), silver (Ag) and metals of platinum (Pt) group. Hence, the treatment is designed to remove impurity and to concentrate nickel, copper and precious metals into matte for further treatment. The treatment consists of the following steps:

- (i) Controlled roasting,
- (ii) Smelting,
- (iii) Converting,
- (iv) Separation of nickel and copper sulphides,
- (v) Roast sintering, and
- (vi) Reduction.

13.3.2.1 Roasting

Nickel has to be separated from the iron present in the sulphide concentrate; this is similar to copper metallurgy. The concentrate is first partially roasted to selective oxidized of FeS_2 . This is done either in multiple hearth roasters or in a fluidized bed roaster. The later is preferred because of its high output and the rich sulphur dioxide (SO_2) gas stream it generates. During controlled roasting, in the temperature range of 550–600 °C, about 40% of the sulphur is oxidized and enough heat is generated to make the roasting in the fluid bed autogenous process.

13.3.2.2 Smelting

The roasted calcine, which also contains the desired amount of siliceous flux, is smelted in a reverberatory furnace to produce a matte containing nickel and copper sulphides (20% Ni, 7% Cu, 40% Fe, 27% S) and slag containing the gangue and iron oxide (0.3–0.4% Ni, 0.2% Cu, 39% Fe, 35% SiO_2). The converter slags from both nickel and copper converters are charged to the reverberatory furnace. The molten matte is tapped into the ladles and taken to converters.

13.3.2.3 Converting

The matte and flux (SiO_2) is charged in a converter and blowing is done to produce Ni-enriched matte. The blowing is not carried to the metal stage but serves only to oxidize FeS_2 , the formation of a small amount only of metal is allowed to enable this to act as a collector for the precious metals.

The converting is completed at about 1150 °C to produce Bessemer matte (50% Ni, 25% Cu, 0.7% Fe, 21.5% S). The slag (2% Ni, 1.5% Cu, 40% Fe and 25% SiO₂) is returned to the smelting furnace for recovery of nickel and copper.

13.3.2.4 Separation of Ni and Cu Sulphides

Bessemer matte is subjected to a slow cooling process wherein the matte is cooled from its melting point to about 400 °C in a period of 3 days. During slow cooling, first Cu₂S precipitates and grows. At 700 °C, a second phase, namely, a metallic Ni–Cu alloy phase (64% Ni, 16% Cu, 10% S), starts to precipitate. At 575 °C, the third solid phase, Ni₃S₂, starts to precipitate. The slow cooling rate provides the necessary grain growth, so that in subsequent processing the sulphides can be recovered by flotation.

The slow cooled matte is grinded. Before flotation, the Ni–Cu alloy (which contains >95% precious metals) is separated by magnetic separation and sent for the recovery of precious metals. The copper sulphide concentrate produced by flotation, which contains about 70% Cu, 5% Ni and 20% S, is sent to the copper circuit. Nickel sulphite is recovered as a low copper, nickel sulphide (74% Ni, 0.8% Cu, 0.8% Fe and 22% S) and as high copper, nickel sulphide (72% Ni, 3–4% Cu, 0.8% Fe and 21% S).

13.3.2.5 Roast Sintering

Both the nickel sulphide fractions are roasted in fluidized bed roasters at the temperature range 1100–1250 °C to produce granular nickel oxide. The low copper, nickel oxide is marketed directly as nickel oxide or reduced to metal. The high copper, nickel oxide is sent to reduction and refining.

13.3.2.6 Reduction

For low copper, sintered nickel oxide is reduced by H₂ at 350–400 °C:



13.3.3 Refining

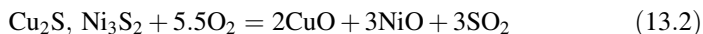
The sinter nickel oxide, containing 75% Ni, can be used as such in the production of steel; but for the production of metallic nickel the oxide has to be reduced and then refined. There are two methods: (1) The Mond process (or Carbonyl process) and (2) Electrolytic process.

13.3.3.1 The Mond Process

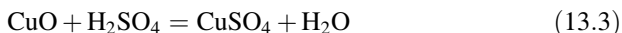
(a) Carbonyl Process

This process is based on the property that nickel possesses of combining with carbon monoxide to form a volatile compound, nickel carbonyl $[\text{Ni}(\text{CO})_4]$ which is stable below 60°C but on heating to 180°C breaks into the original forms.

As the nickel oxide sinter contains small amounts of sulphur and metallic elements which reduce the efficiency of the subsequent processing. So it is first given a preliminary oxidized roasting. Temperature of 750°C is maintained and a flow of air admitted to oxidize the sulphur and metals.



Then calcine, high copper, nickel oxide, is leached with dilute H_2SO_4 , the leaching removes large part of the copper as copper sulphate and left a residue of NiO .



This copper sulphate is filtered to remove the undissolved nickel oxide, the copper sulphate recovered by crystallization.

NiO is reduced to finely divide metallic nickel by an atmosphere of water gas (36% CO and 52% H_2) at $350\text{--}400^\circ\text{C}$. To ensure efficient reduction two reducers are operated in series, the partially reduced material is conveying from the bottom of the first to the top of the second. The passage through each reducer takes about 4 h.



At the comparatively low temperature carbon monoxide plays very little part in the reduction, this is mainly carried out by the hydrogen. The result of the greater activity of hydrogen [reaction (13.4)] is to yield an exit gas which after removal of the water is very rich in carbon monoxide and thus suitable for the formation of nickel carbonyl in the next operation.

It is then cooled, passed on to volatilizer, where at a temperature of about $40\text{--}90^\circ\text{C}$, the active nickel is exposed to a flow of carbon monoxide gas to form gaseous nickel carbonyl $[\text{Ni}(\text{CO})_4]$, which is carried out in the gas stream. The material passes through eight volatilizers in series; the process takes place in several days. This is a slow process.



This gas $[\text{Ni}(\text{CO})_4]$ is then passed through a tower containing nickel shots (4 – 6 mm diameter) at 180°C and the compound nickel carbonyl is decomposed into metallic nickel and carbon monoxide (because nickel carbonyl is stable below 60°C).



Close control of temperature is necessary because at 200 °C some carbon and carbon dioxide are formed by decomposing carbon monoxide in presence of nickel, which act as a catalyst. This carbon is absorbed by metallic nickel.



Decomposed metallic nickels are deposited on the nickel shot and increase its size to form nickel pellet. Time taken for pure nickel pellet to build-up, 10 mm diameter, is approximately 3 months. This nickel, containing <0.06% Fe and <0.09% Cu as impurities, is considered as pure metal.

(b) INCO Pressure Carbonylation Process

An elevated pressure of about 70 atmospheres is used. Higher pressure aids the reaction and permits higher operating temperature (180 °C). Under this conditions, carbonyls of iron, nickel and cobalt [Fe(CO)_5 , Ni(CO)_4 and $\text{Co}_4(\text{CO})_{12}$] are formed. Ni(CO)_4 is recovered by fractional distillation and later converted to metallic nickel in a pellet decomposer or a powder decomposer.

13.3.3.2 Electrolytic Process

Sintered Ni oxide is first reduced to metal by reduction smelting in presence of carbon and Ni–Si flux (assisting deoxidation):

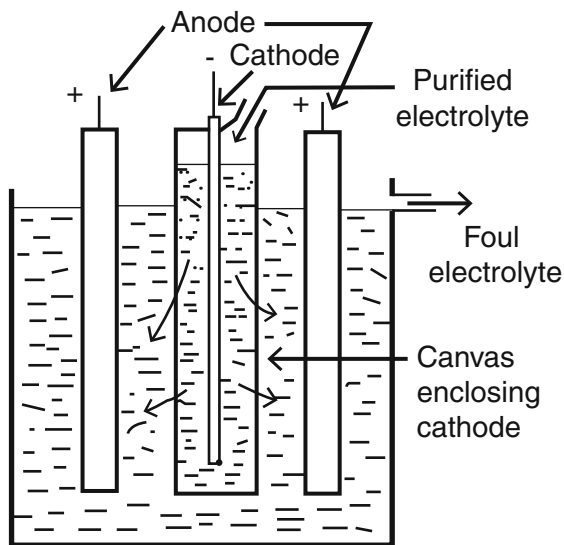


Crude nickel metal is then cast into anodes, which contain 95% Ni, 2% Cu, 0.75% Fe, and 0.7% S. Cathodes are produced in a somewhat similar to that are used in the preparation of electrolytic copper starting sheets. Thin nickel sheets are produced in starter cells.

Electrolysis is carried out in concrete tanks, solution of nickel sulphate and chloride containing about 60 gm of Ni^{2+} per litre, 95 gm of SO_4^{2-} per litre, 35 gm of Na^+ per litre, 55 gm of Cl^- per litre and 16 gm of H_3BO_3 per litre are used as electrolyte. Electrolysis is carried out at 60 °C at a current density of 170 A/m². On passage of current, nickel is dissolved from the anodes and is deposited on the cathode starting sheet. To prevent the deposition of copper and iron, the cathodes are enclosed in a canvas cover, which is tightly woven in order that a hydrostatic head of 25–50 mm is maintained over the level in the tank; thus ensuring a constant outward flow of electrolyte through the canvas (as shown in Fig. 13.2).

Actually nickel ions, set free at the anode, are not carried directly to the cathode but along with the copper and iron ions in solution flow continuously out of the tank

Fig. 13.2 Electro-refining of nickel



as foul electrolyte. The foul electrolyte is free from copper by agitation with active nickel powder, the copper is cementing out. Vigorous agitation is done by passing air, oxidizes the iron which is precipitates as $\text{Fe}(\text{OH})_3$. Small amount of chlorine gas is passed to ensure oxidation to form precipitates of $\text{Fe}(\text{OH})_3$. Cobalt is removed as cobalt hydroxide by further chlorine gas oxidation. At this stage cobalt is removed; further removal of impurities, such as arsenic and lead, are taking place. The purified solution (contains 0.01 gm of Co per litre, 0.001 gm of Cu per litre, 0.004 gm of Fe per litre, 0.0002 gm of As and Pb each per litre) is then passed to the cathode compartment. When deposition is complete the cathodes are withdrawn, washed and either marketed in sheet form or melted and cast into ingots and shots (99.93% Ni, 0.05% Co, 0.005% Cu, 0.002% Fe, 0.001% S, 0.0002% As and 0.001% Pb).

13.4 Properties

The atomic weight of nickel is 58.69 and specific gravity of 8.88, melting point and boiling point are 1445 °C and 3075 °C respectively. Nickel is a divalent, non-toxic metal, has FCC structure; Nickel is strong and ductile metal and has high corrosion and heat resistance metal (important property). It is ferro-magnetic in nature. Nickel can be readily cold or hot worked, welded and machined. It retains its strength to an excellent degree at high temperatures and its ductility and toughness as well as strength at sub-zero temperatures. Another feature is the retention of its mechanical properties at high temperature. Nickel is dissolved in acids but it does not react with

alkali (important property) i.e. high corrosion resistance to alkalis. It is one of the important alloying elements. It forms binary and ternary alloys with many metals which are used for resistance to corrosion and heat.

13.5 Applications

Nickel in its commercial pure (99.5), wrought and cast forms has wide and important industrial application due to good mechanical and special physical properties which it combines with good resistance to corrosion. Nickel is non-toxic, so it is used extensively in manufacture of food handling equipments. The ductility of nickel is also of a high order especially in the hot rolled condition, and the combination of strength and ductility, it can be used in many constructional and mechanical applications.

Nickel and chromium are two strategically important alloying elements that are being increasingly consumed in the fields of chemical processing, space research, and nuclear reactor etc. Many uses of nickel are dependent on the combination of the properties of strength and ductility, which are the metal possesses. Nickel is also a valuable alloying constituent in more than 3000 commercial alloys which find wide applications, principally for their mechanical properties and resistance to corrosion and heat. Pure nickel acts as catalyst in many reactions: (a) cracking of natural gas ($\text{CH}_4 \rightarrow \text{CO} + \text{H}_2$); and (b) hydrogenation of vegetable oil.

Stainless steels, which contain a high percent of Ni (8%) and Cr, are known for outstanding resistance to high temperature oxidation and strong chemicals such as alkalis. Ductile nickel alloyed steels (up to 5.25% Ni) are used in various structural applications. Electric heaters and thermocouples use heat resistance alloys made of Ni, Fe and Cr. Due to non-toxic nature, nickel is used extensively in the manufacture of food handling equipment and in plant for the processing of pharmaceutical products.

Nickel forms so many non-ferrous alloys:

1. Inconel (80% Ni, 13% Cr and 7% Fe), resistance to corrosion at high temperature; it is used in petroleum refining, dairy, fruit juice, alkali, edible oil industries.
2. Monel (67% Ni, 30% Cu with Mn, Fe) for its good corrosion resistance and strength; it can be used in food, chemical, petroleum industries, hospital and kitchen equipment, marine service etc.
3. Cupronickel (30% Ni, 70% Cu), corrosion resistance, it can be used as heat exchanger tubes, steam turbine blades, coinage.
4. German silver (10–30% Ni, 5–30% Zn, 1–10% Pb and rest Cu), workability, corrosion resistance; ornamentation, jewellery, food equipment, musical and dental instruments.