

# Overview

Our world is becoming increasingly dependent on nickel, cobalt and platinum-group metals. Ever since Harry Brearley discovered that alloying steel with nickel and chromium produced stainless steel, the demand for nickel has outpaced the global rate of economic growth. Cobalt is a key ingredient in rechargeable batteries, a field that has grown rapidly as a result of mobile phones and other consumer electronic goods, and is bound to grow more with the increased use of electric vehicles. The catalytic properties of the platinum-group elements ensure that the demand for these metals will continue as the demand for automobiles and vehicles grows.

Nickel is mostly used in alloys, for example, in stainless steels, aerospace alloys and specialty steels. Cobalt is also used in specialty alloys, but its largest application is currently in battery chemicals. Platinum-group metals (Pt, Pd, Rh, Ru, Ir and Os) are mostly used as catalysts that minimize emissions from cars and trucks. All of these metals also have many other uses.

Primary production of nickel, cobalt and platinum-group metals in the world in 2009 is shown in Table 1.1. The combined economic value of mining and refining these metals is about US\$ 50 billion per annum.

The purpose of this book is to describe how these metals are produced from the ores that are mined.

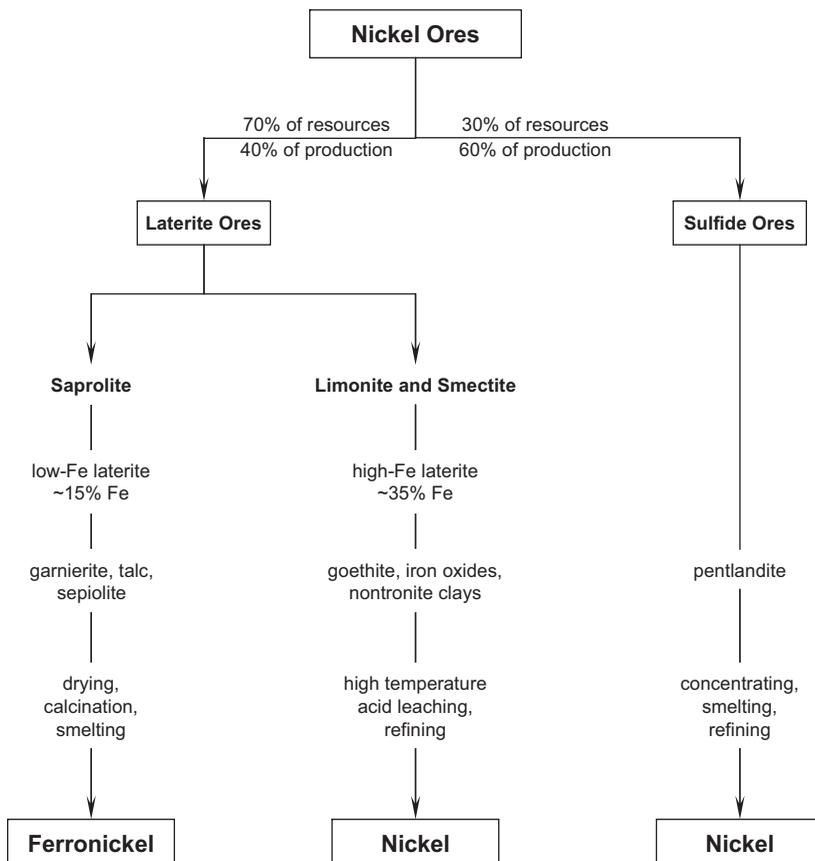
In the next four sections, the most important processes for the production of nickel, cobalt and platinum-group metals and their recycling are presented. An outline of the structure of this book is then given.

## 1.1. EXTRACTION OF NICKEL AND COBALT

Nickel is mined from two types of ores: laterites and sulfides. Although about 70% of the ore reserves are found in laterite ores, only about 40% of the nickel production is from laterites. As shown in Figure 1.1, laterites are mostly used to produce ferronickel, which is used directly in steelmaking. Some laterite ores are used to make melting-grade nickel and nickel matte. Sulfides are refined to produce high-grade nickel.

**TABLE 1.1** Worldwide Primary Production and Value of Nickel, Cobalt and Platinum-Group Metals in 2009

Commodity	Production, tonnes/year	Value, million \$
Nickel, including nickel in ferronickel	1 500 000	30 000
Cobalt	60 000	3000
Platinum-group metals	450	15 000



**FIGURE 1.1** The extraction of nickel and ferronickel from laterite and sulphide ores. Laterite ores occur as saprolite, smectite and limonite layers. Because of their different compositions and mineralogy, they require different methods of extraction. Saprolite, which has a relatively low iron content, is smelted. Limonite and smectite ores, which have a high iron content, are leached and refined. The minerals that represent each type of ore are also shown.



**FIGURE 1.2** Hill-top laterite mine in New Caledonia. The overburden has been removed to expose the saprolite ore, which is mined as shown, upgraded and smelted to ferronickel. The ore delivered to the process plant typically contains about 2% Ni. *Photograph courtesy W.G. Davenport.*

### 1.1.1. Extraction of Nickel and Cobalt from Laterite Ores

Laterites are found mostly in tropical regions and are mined for their nickel and cobalt in countries like Indonesia, the Philippines and Cuba. Sulphides are found mostly in Canada and northern Siberia. Both laterite and sulphide ores are mined for nickel and cobalt when the concentrations exceed about 1.3% Ni and 0.1% Co.

Laterites occur near the surface, and as shown in Figure 1.2, they are mined by surface-mining methods.

Laterites are complex ores formed by the weathering of ocean floor that has been pushed up by tectonic forces. This weathering, which has occurred over millions of years, has resulted in a profile of different minerals from the surface to the bedrock. Three nickel-bearing layers are commonly identified within this profile<sup>1</sup>:

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1. The classification of the laterites is often unclear and inconsistent. *Limonite* is a mineralogical term, and *saprolite* is a textural rock term. Many of the ores encountered in extractive metallurgy are referred to by host, such as sulfide or oxide. However, the variable nature of laterites makes this difficult.

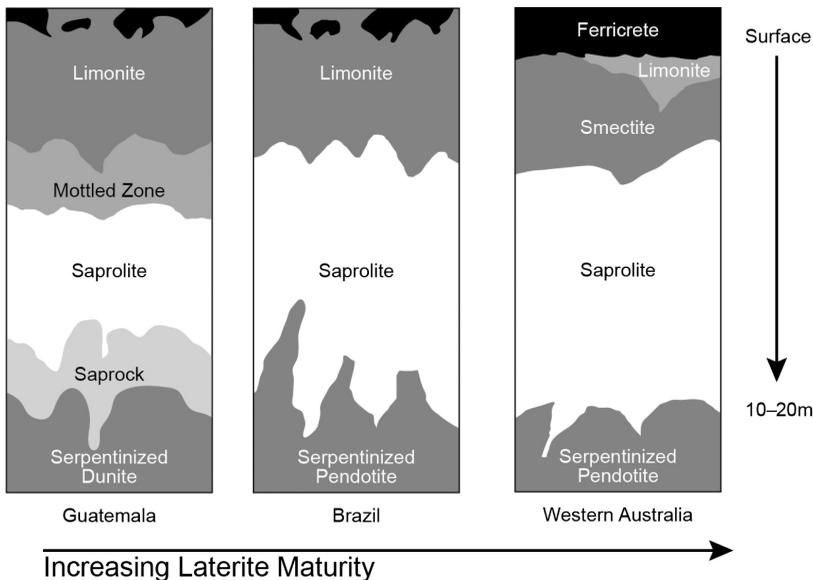
- (a) limonite, which occurs near the surface;
- (b) smectite layer, which also occurs near the surface; and,
- (c) saprolite layer, which occurs below the limonite and smectite layers.

There may be several other identifiable layers, such as ferricrete and a mottled zone, in the laterite profile. These layers are shown in Figure 1.3.

The limonite layer consists of a mixture of minerals that have a high iron and low MgO content. One group of minerals is limonite or hydrated iron oxides,  $\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$ . Nickel substitutes for iron in these minerals (Carvalho-e-Silva *et al.*, 2003). The generic formula of goethite,  $(\text{Fe},\text{Ni})\text{OOH}$ , is used to represent limonite ores in chemical reactions.

A layer of smectite clay, such as nontronite, is found in some deposits, for example, at Murrin-Murrin in Western Australia.

The saprolite layer is below the limonite layer. The saprolite ores have a low iron and a high MgO content. Because it is further from the surface, it is less



**FIGURE 1.3** Laterite profiles from different climatic zones and maturity of weathering (Harris & Magee, 2003, Freyssinet 2005). Each layer is 2–5 m thick. Rain and vegetative acids have leached MgO and  $\text{SiO}_2$  from the original igneous peridotite rock – enriching the leached layers in iron, nickel and cobalt. Dissolved nickel has also percolated down into the saprolite layer, where it is most concentrated. The natural leaching process is most advanced at the top and least at the bottom (million and 10 million years). The unleached peridotite rock is ocean floor that has been pushed above sea level by tectonic forces. Most of New Caledonia (for example) is made up of peridotite ocean floor rock – which explains why this region is such an important source of nickel. Diagram after Harris and Magee (2003), courtesy of CM Solutions (Pty) Ltd.

weathered, or chemically altered, than limonite. The minerals found in this layer are magnesium hydroxysilicates,<sup>2</sup> such as chysotile,  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ . The generic formula of garnierite,  $(\text{Mg}[\text{Ni},\text{Co}]_3\text{Si}_2\text{O}_5(\text{OH})_4$ , is used to represent saprolite ores in chemical reactions.

The identification of these layers in the laterite ore body is important because different methods of extraction are used. There are two main routes for processing laterites: smelting to produce ferronickel and leaching and refining to produce nickel metal. The iron content of limonite and smectite ore is too high for it to be economically smelted, while the MgO content of the saprolite ore is too high for it to be leached economically. Thus, the method of extraction is matched to the type of ore.

Both saprolite and limonite ores, which typically contain 1.3%–2.5% Ni and 0.05–0.15% Co, are upgraded before metallurgical treatment. This upgrading of the mined ore rejects hard, precursor rock using the techniques of mineral processing, such as crushing, grinding and screening. The precursor rock is generally low in nickel and cobalt. The nickel content of the ore might be doubled during upgrading.

### *Method of Extraction from Saprolite Ore*

Saprolite ores are mostly smelted to ferronickel, which typically contains 30% Ni and 70% Fe, for use in stainless steel and other ferrous alloys. A schematic diagram of this processing route is shown in Figure 1.4. Cobalt is present in the ferronickel in small amounts but it is not of any economic value to end-users.

A small amount of saprolite ore is smelted to sulphide matte by adding sulphur during processing. Most of this matte is made into alloying-grade nickel by oxidation and then by reduction roasting. Some of this matte is refined hydrometallurgically to high-purity nickel and cobalt.

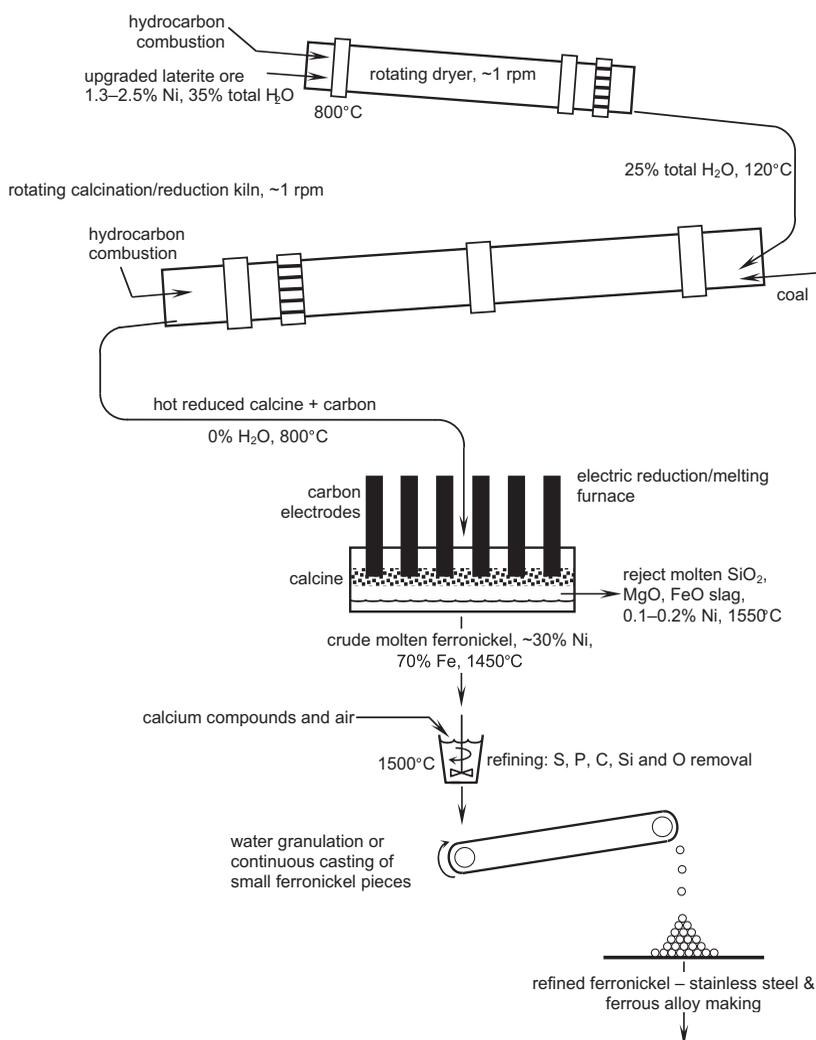
### *Method of Extraction from Limonite Ore*

Limonite ores are mostly leached with hot sulfuric acid at a temperature of about 250°C and a pressure of about 40 bar. A schematic diagram of the process is given in Figure 1.5. Nickel and cobalt are recovered from the pregnant solutions by the following steps:

- (a) purification by precipitation and concentration of the solution by redissolution;

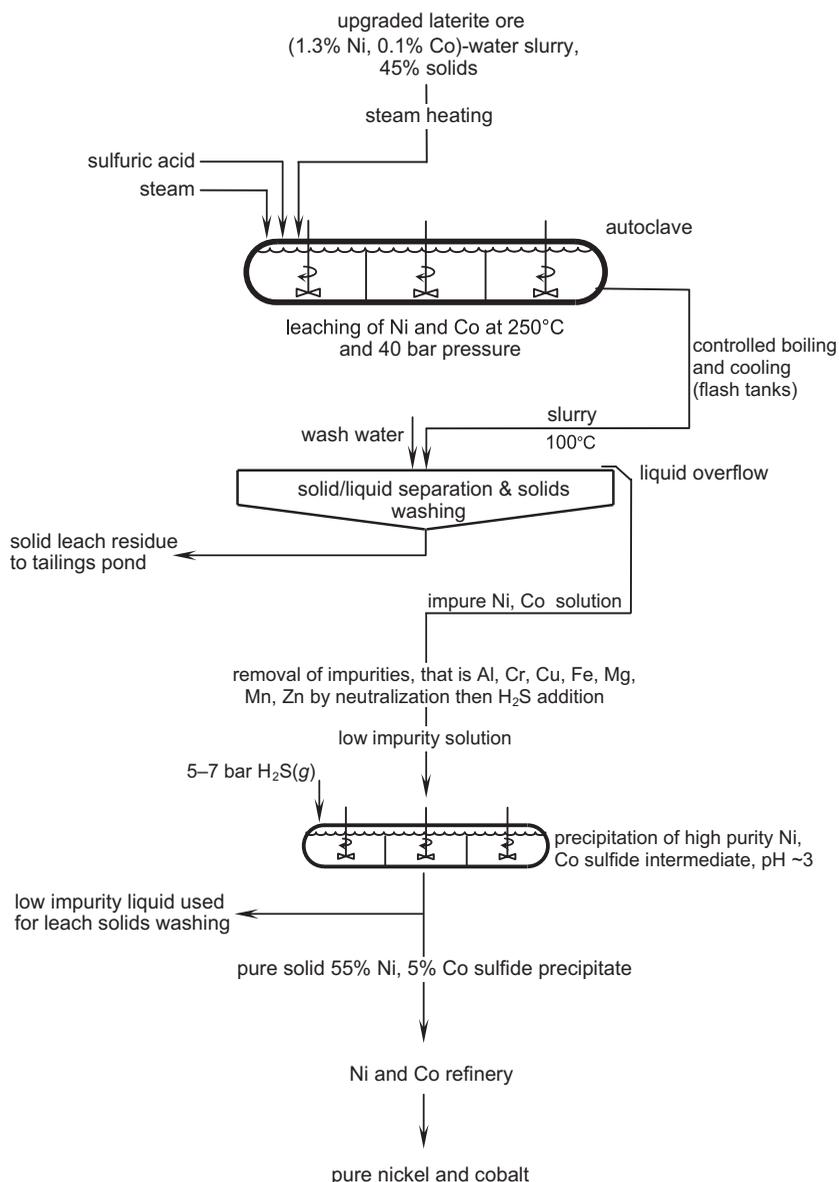
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2. Examples of minerals found in the saprolite layer are as follows: (i) minerals of the serpentine group, like chysotile (lizardite),  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ , and nepouite,  $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ; (ii) talc,  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ , and willemseite,  $(\text{Ni},\text{Mg})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ; (iii) clinocllore,  $(\text{Mg},\text{Fe})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$ , and nimite,  $(\text{Ni},\text{Mg},\text{Al})_6(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_8$ ; and, (iv) sepiolite,  $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ , and falcondite,  $(\text{Ni},\text{Mg})_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ .



**FIGURE 1.4** Representative flowsheet for smelting moist 1.5%–2.5% Ni and low-iron saprolite ore to ferronickel containing 20%–40% Ni and 80%–60% Fe. Reduction is production of metal by removing oxygen from the oxide mineral, for example,  $\text{NiO} + \text{C} \rightarrow \text{Ni} + \text{CO}$ . Ferronickel electric furnaces are round (15–20 m diameter) or rectangular (10 m wide, 25–35 m long). They each produce 100–200 tonnes of ferronickel per day. Drying kilns are typically 4 m diameter  $\times$  30 m long. Calcination/reduction kilns are typically 5 m diameter  $\times$  100 m long.

- (b) separation of nickel and cobalt in solution is often carried out by solvent extraction; and finally,
- (c) hydrogen reduction or electrowinning from solution to produce 99.9% pure nickel and cobalt.



**FIGURE 1.5** Representative flowsheet for high-temperature sulphuric acid laterite leaching. The feed is mainly limonite, an ore that is low in magnesium. The product is high-purity nickel-cobalt sulphide precipitate, 55% Ni, 5% Co and 40% S, ready for refining to high-purity nickel and cobalt. A leach autoclave is typically 4.5 m diameter  $\times$  30 m long with six stirred compartments. It treats about 2000 tonnes of solid feed per day.

### *Rationale for the Method of Extraction*

Saprolite ore is smelted for the following reasons:

- (a) saprolite contains little iron (15%), so it produces nickel-rich ferronickel (20%–30% Ni); and,
- (b) saprolite contains considerable MgO (20%), which consumes excessive sulphuric acid if it is leached.

Limonite ore is leached in sulphuric acid for the following reasons:

- (a) goethite in the limonite ore dissolves efficiently in hot sulphuric acid and, if the temperature is sufficiently high, iron, which constitutes about 40% of the ore, precipitates as hematite or jarosite; and,
- (b) limonite ore has a low content of MgO, usually less than 3% in the ore, which means that the consumption of sulphuric acid is sufficiently low.

A major research thrust is to develop a process that is ‘omnivorous’, that is, it can treat both limonite and saprolite ores (Duyvensteyn, Wicker, & Doane, 1979; Harris & Magee, 2003; Steyl *et al.*, 2008).

### **1.1.2. Extraction of Nickel and Cobalt from Sulphide Ores**

Sulphide ores were mostly created by (i) the intrusion of molten magma from the mantle into the crust of the earth; and, (ii) the formation of localized metal-rich sulphide ore bodies by sequential solidification and/or hydrothermal leaching and precipitation.

The source of the sulphur in these ore bodies is either from the magma itself or from the pre-existing rock where it was present as sulphate.

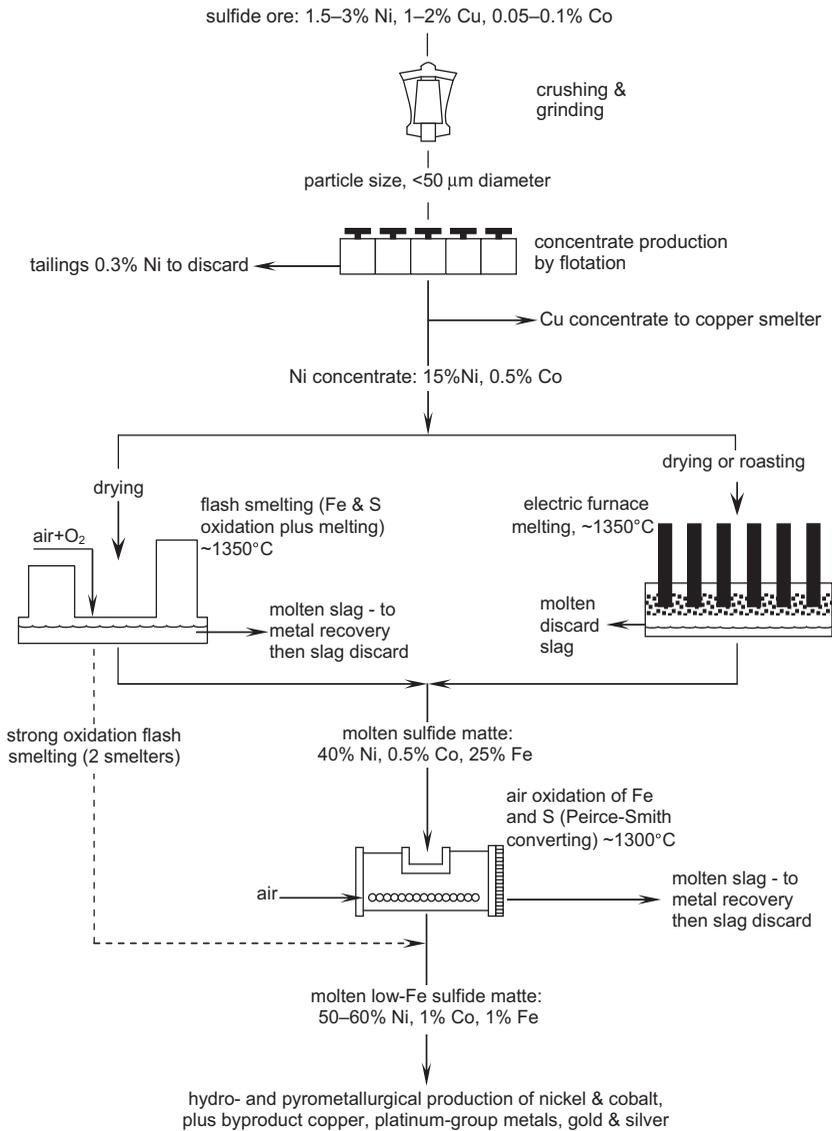
The most common nickel mineral in these ores is pentlandite,  $(\text{Ni,Fe})_9\text{S}_8$ . The atomic ratio of nickel to iron in pentlandite ranges between 0.34 and 2.45. Most often, though, it is about 1.15. Common minerals that accompany pentlandite are pyrrhotite,  $\text{Fe}_8\text{S}_9$ , and chalcopyrite,  $\text{CuFeS}_2$ . Cobalt and platinum-group elements are also present, either dissolved in the pentlandite or present as distinct minerals.

Sulphide ores that are mined for nickel and cobalt typically contain 1.5%–3% Ni and 0.05%–0.1% Co.

### *Concentration, Smelting and Converting to Matte*

The sulphide ores are concentrated, smelted and converted to metal-rich matte. A schematic diagram of this process is shown in Figure 1.6. The processing steps are as follows:

- (a) the valuable minerals in an ore are concentrated by froth flotation of crushed or ground ore; and,



**FIGURE 1.6** Main processes for extracting nickel and cobalt from sulphide ores. Parallel lines indicate alternative processes. The dashed line indicates a developing process. The compositions are for ores from Sudbury, Canada.

- (b) this concentrate is smelted and converted into an even richer, low-iron sulphide matte.

Representative concentrations before and after each of these steps are given in Table 1.2.

**TABLE 1.2** The Change in Concentration with Each Step of the Extraction Process

Element	In mined ore, %	After concentration, %	After smelting and converting, %
Ni	1.5–2.5	10–20	40–70
Co	0.05–0.1	0.3–0.8	0.5–2

### *Production of Nickel and Cobalt from Matte*

Nickel and cobalt are mostly recovered from low-iron matte by the following steps:

- the matte is leached using either chlorine gas in a chloride solution, oxygen in an ammonia solution or oxygen in a solution of sulphuric acid;
- the pregnant solution is purified;
- separate nickel and cobalt solutions are produced, usually by solvent extraction; and,
- high-purity nickel and cobalt are produced from the solutions either by electrowinning or by hydrogen reduction (see Figure 1.7).

Several other processes are also used, for example, carbonyl refining and electrolytic refining.

## 1.2. EXTRACTION OF COBALT FROM COPPER–COBALT ORES

Cobalt (but not nickel) also occurs in the copper–cobalt oxide ores from the Central African Copperbelt. These ores typically contain about 3% Cu and 0.3% Co.

The main cobalt mineral is heterogenite [CoOOH]. Copper occurs as chrysocolla [CuOSiO<sub>2</sub>·2H<sub>2</sub>O] and malachite [CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>]. Some sulphide ores are also mined. The main gangue minerals are siliceous dolomite [MgCO<sub>3</sub>·CaCO<sub>3</sub>] and quartz (SiO<sub>2</sub>).

Cobalt and copper metals or chemicals are produced by the following hydrometallurgical steps:

- reductive leaching using sulfur dioxide gas or sodium metabisulphite as a reductant;
- solid/liquid separation and clarification of the solution;
- separation of copper from cobalt by solvent extraction;
- purification of the aqueous solution;



**FIGURE 1.7** Nickel briquettes produced from powder obtained from the hydrogen reduction of nickel in solution (see Chapter 27). An important alternative process is electrowinning, which is discussed in Chapter 26. Photograph by M. Fox, courtesy of Impala Platinum.

- (e) precipitation of cobalt hydroxide or electrowinning of cobalt; and,
- (f) copper electrowinning.

### 1.3. EXTRACTION OF PLATINUM-GROUP METALS FROM SULFIDE ORES

Virtually all of the production of platinum-group metals is from sulphide ores. A small amount is produced from alluvial deposits of metallic platinum in Russia (Kendall, 2004).

Platinum-group elements occur mainly in or near sulphide minerals in an ore deposit. They are typically dissolved in pentlandite  $[(\text{Ni},\text{Fe})_9\text{S}_8]$ , or present as distinct mineral grains, for example, as braggite  $[(\text{Pt},\text{Pd})\text{S}]$ . The minerals containing platinum-group elements are often attached to or occluded by grains of pentlandite, pyrrhotite  $[\text{Fe}_8\text{S}_9]$  and chalcopyrite  $[\text{CuFeS}_2]$ . The platinum-group elements are extracted by the following process steps:

- (a) crushing and grinding of the ore;
- (b) production of a bulk sulphide concentrate that is rich in platinum, predominantly by froth flotation;

- (c) smelting and converting of the concentrate to matte; and
- (d) refining of platinum-group metals from the matte by hydrometallurgical techniques.

A schematic diagram of the process is shown in Figure 1.8.

### 1.3.1. Matte Leaching

The matte from the smelting and converting of platinum-group element concentrates contains about 0.3% total platinum-group elements (PGE). This matte is leached in sulphuric acid with oxygen to produce an undissolved solid residue containing about 60% total PGE. The solid residue, sometimes called a bullion concentrate, is the feed to the platinum-group metal refinery.

### 1.3.2. Refining of Platinum-Group Metals

The first step in the refining of platinum-group metals is the dissolution of the solid residue, described in Section 1.3.1, which contains about 60% platinum-group metals, in hydrochloric acid using chlorine as the oxidant. This dissolves all the precious metals except silver. In other words, Pt, Pd, Rh, Ir, Ru and Au dissolve. Osmium forms osmium tetroxide,  $\text{OsO}_4$ , which is volatile and is captured from the gas phase.

The platinum-group elements are separated and purified into the different metals by the following steps:

- (a) sequential removal of each element from the leach solution by processes such as precipitation, solvent extraction, ion exchange and vaporization;
- (b) purification of each element in solution by a similar set of processes; and
- (c) forming the metal by ignition or reduction.

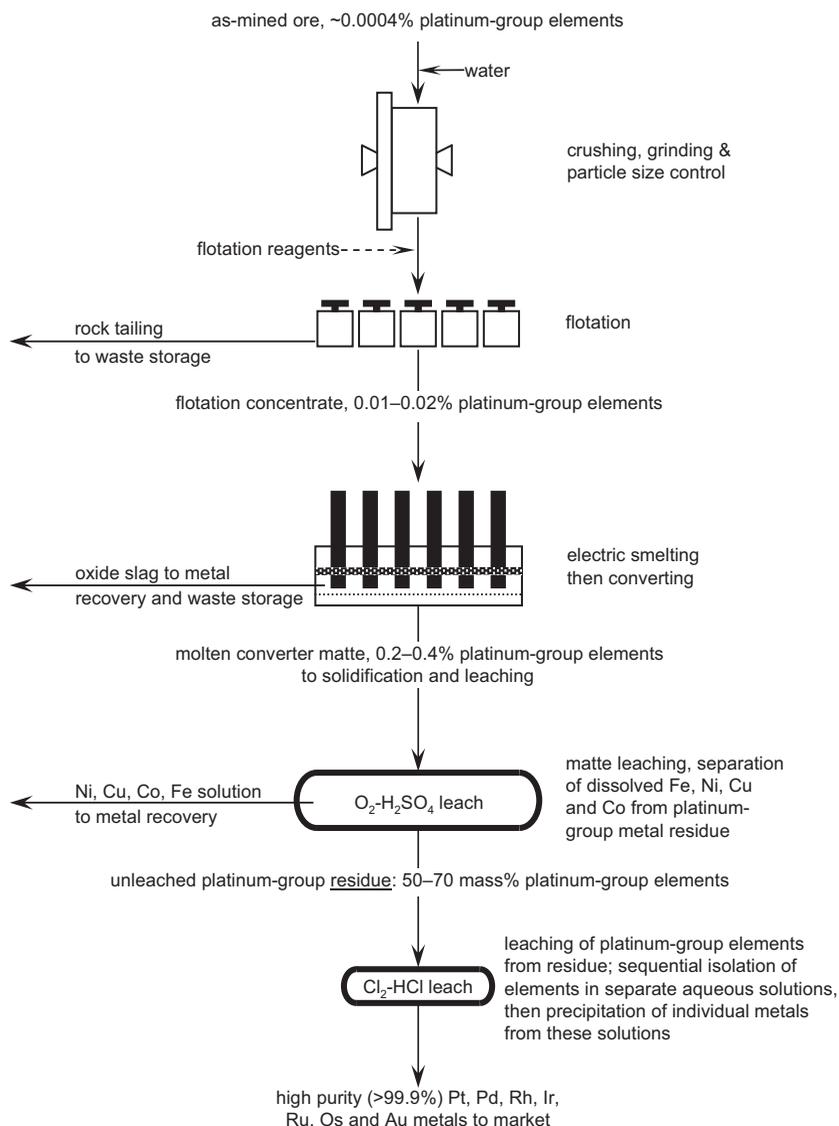
The purities of the product metals from a platinum-group metal refinery are typically between 99.9% and 99.99%.

## 1.4. RECOVERING NICKEL, COBALT AND PLATINUM-GROUP METALS FROM END-OF-USE SCRAP

About 40% of nickel consumption, 20% of cobalt consumption and 30% of platinum-group metal consumption comes from recycled end-of-use scrap.

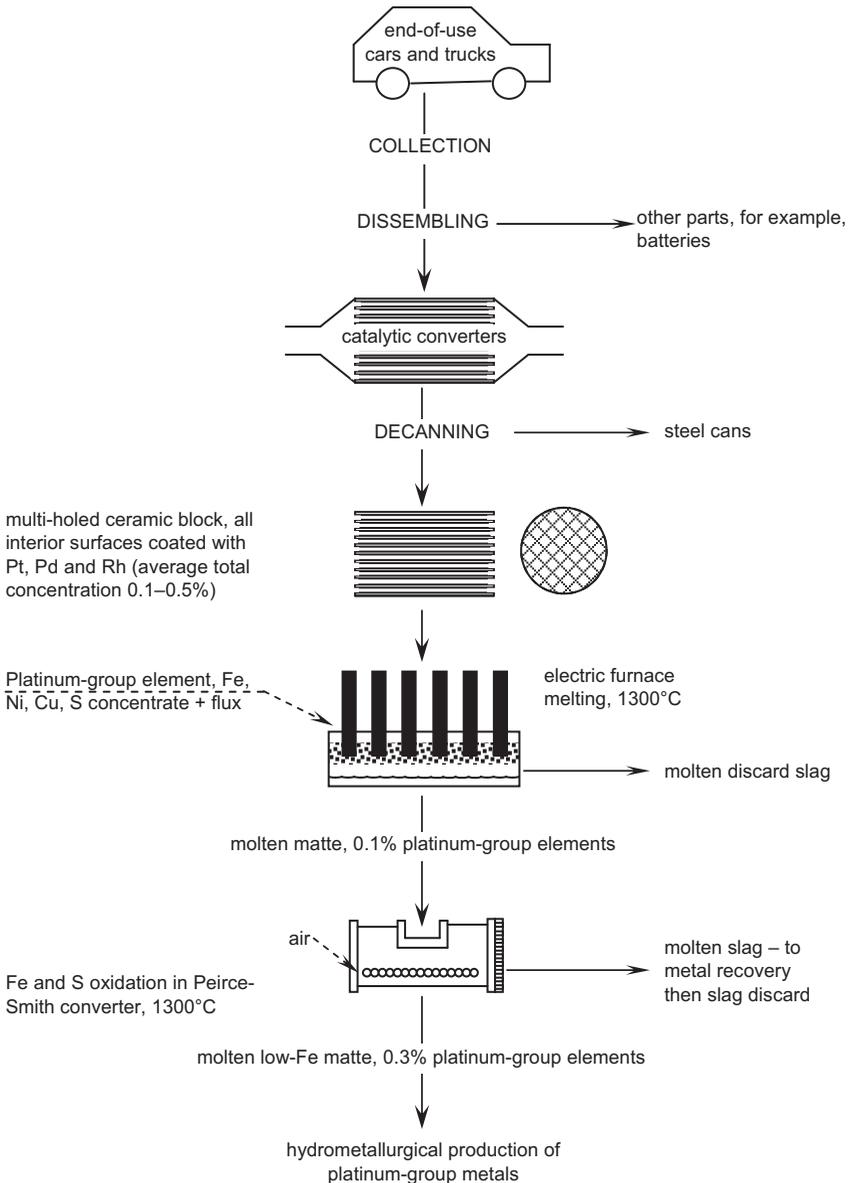
Production of these metals from scrap has the advantage that it slows the depletion of the earth's resources, uses less energy than metal production from ore, avoids the production of mine waste products and slows the usage of valuable land for wasteland fills.

Most recycled nickel and cobalt are recovered by recycling alloy scrap. It is made into alloy similar in composition to the scrap.



**FIGURE 1.8** Generalized flowsheet for producing pure platinum-group metals and gold from ore in South Africa. The major steps are concentrate production, matte production, residue production and high-purity metal production. The numerical values are from Jones (2004) and Jones (2006).

More complex, dilute scrap is often smelted along with sulphide concentrate to make matte, which is subsequently refined to high-purity nickel, cobalt and platinum-group metals. Figure 1.9 shows a recycle flowsheet, using platinum, palladium and rhodium automobile catalyst recycle as an example.



**FIGURE 1.9** A schematic flowsheet for the recycle of catalytic converters from cars and trucks. The platinum-, palladium- and rhodium-coated ceramic blocks are treated in a primary smelter along with concentrates containing platinum-group metals. The numerical values are for South African practice. Car and truck catalysts are also recycled through purpose-built secondary smelters, which are discussed in Chapter 38.

Complex scrap is also smelted to metallic alloy in purpose-built secondary (scrap) smelters. This alloy is then refined to high-purity metals.

## 1.5. ORGANIZATION OF MAJOR THEMES AND TOPICS

The extractive metallurgy of each of the metals is discussed in four parts expressing the major themes of this book:

- Part I Nickel;
- Part II Cobalt;
- Part III Platinum-Group Metals; and,
- Part IV Recycling.

Each of these parts begins with a chapter on the major producers, markets, prices and costs of production. The topics within each of these are organized along the lines of the methods of extraction. The arrangement of topics within each theme is shown in Figures 1.10–1.12.

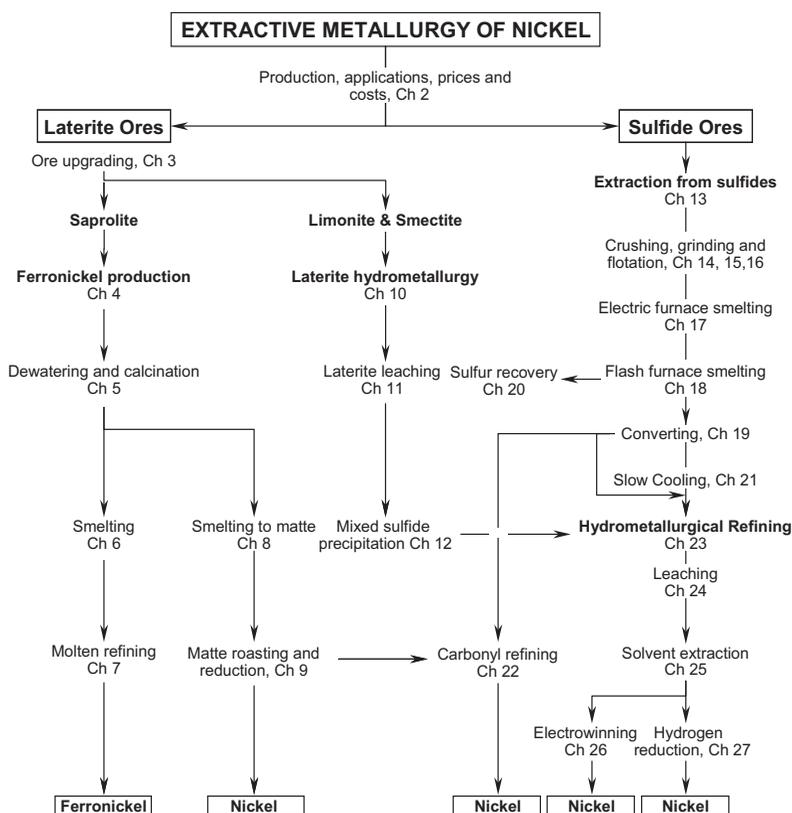


FIGURE 1.10 Organization of the topics describing the extractive metallurgy of nickel.

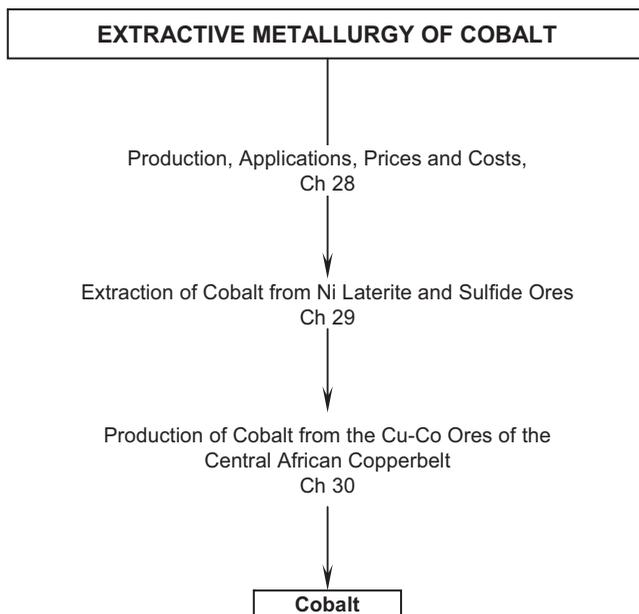


FIGURE 1.11 Organization of the topics describing the extractive metallurgy of cobalt.

The extractive metallurgy of nickel is the most complex of the themes of this book since there are two major ore types, the laterites and the sulfides, different marketable products and a variety of process routes to these marketable products. For the most part, the description is a part-by-part comparison, that is, the details of a single process step are compared across different operations. In addition, there are four short chapters that provide an overview so that sight of the entire process is not lost in the details of the parts. The organization of these topics is shown in Figure 1.10.

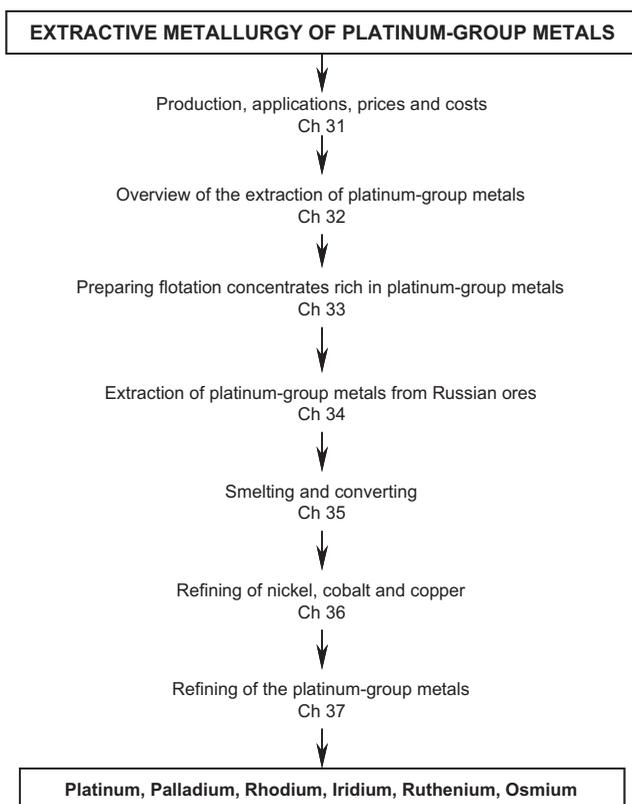
Cobalt is produced in conjunction with nickel, and a separate discussion of cobalt in this context is not warranted. However, a significant amount of cobalt originates from the copper ores of the Central African Copperbelt. The organization of these topics in this theme is shown in Figure 1.11.

The extractive metallurgy of the platinum-group metals is the penultimate theme of this book. The organization of the topics on the extraction of these metals is shown in Figure 1.12.

The final theme of the book is concerned with recycling. The recycling of nickel, cobalt and platinum-group metals is described in Chapter 38.

## 1.6. SUMMARY

Nickel and cobalt are produced from laterite and sulphide ores. Cobalt is also produced from Central African copper-cobalt ores.



**FIGURE 1.12** Organization of the topics describing the extractive metallurgy of platinum-group metals.

Platinum-group metals, that is, Pt, Pd, Rh, Ir, Ru and Os, are predominantly extracted from sulfide ores from South Africa and Siberia. Their extraction always involves smelting followed by hydrometallurgical refining.

Nickel is mostly used in stainless steels; cobalt is used mainly in aerospace alloys and platinum-group elements are used in emission reduction catalysts for cars and trucks. All of these metals also have many other uses.

Significant quantities of nickel, cobalt and platinum-group metals are recovered by treating recycled end-of-use scrap. High-quality alloy scrap is usually melted to form a new alloy of similar composition. Complex and low-purity scrap is usually smelted and then hydrometallurgically refined.

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