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# Advances and Innovations in Ferronickel-Making

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# Preface

As an important strategic metal, nickel has found extensive application in stainless-steel industry and other fields. Electrolytic nickel is usually used as the feed for the traditional nickel-based stainless-steel production process. However, its production relies on the nickel sulfide ore resource which is gradually depleted. As the supply of nickel sulfide ore can no longer meet the demand of stainless-steel industry, other nickel ore resources, mainly laterite ore, are receiving increasing attentions in producing ferronickel which is now replacing electrolytic nickel as nickel source for the development of stainless-steel industry.

Over the past two decades, the global ferronickel industry has experienced a rapid expansion, as witnessed by the development of the rotary kiln-electric furnace (RKEF) smelting technology for ferronickel-making. Nevertheless, the RKEF process still faces a few intractable problems, such as huge energy consumption and massive discharge of ferronickel slag which causes head-scratching environmental pollution further endangering the survival of ferronickel industry. In China, there exist more rigorous challenges mainly due to the shortage of laterite ore that results in heavy dependence on importation in addition to the above problems. It is urgent to develop fresh processes, methods, and technologies for efficient and sustainable ferronickel-making.

In view of the above problems, the authors of this book and their research team have been wedded to innovating ferronickel-making for nearly twenty years from the aspects of development of new ferronickel production process, innovation of existing processes, value-added utilization of ferronickel slag, etc. For instance, they invented a process for preparing ferronickel from laterite ore by selective solid-state reduction-magnetic separation, allowing decrease of reduction temperature by 500 ºC and cost saving of over 30% in comparison with the traditional RKEF process. They also developed a pioneering technology for regulating slag system of reductive smelting of laterite ore and a novel technology for controlling softening-melting performance of laterite ore, enabling decline of smelting temperature by 100 ºC and electricity saving of 600 kWh per ton of ferronickel. Moreover, they proposed new methods for preparation of forsterite refractory materials and lightweight thermal insulation materials from ferronickel slag, realizing highly efficient value-added utilization of the solid waste. These efforts point to a feasibility to solve the tough problems existing in the process of ferronickel-making. The authors are thus committed to sharing these advances through the present book with readers although it is clearly not comprehensive in its coverage of relevant information.

This book covers six chapters and is organized following the hierarchy of basic research, technological development, and industrial application. Chapter 1 introduces the basic properties and applications of nickel, laterite ore treatment, technological progress, existing problems, challenges, and development trend of ferronickel industry. Chapter 2 presents a novel ferronickel-making process via selective solid-state reduction-magnetic separation of laterite ore, featured by short process, high energy efficiency, and low cost, based on exploration of thermodynamic and kinetic laws of selective reduction and sulfidation of laterite ore with clarification of the growth behavior of ferronickel grains in the process of solid-state reductive roasting. With the much lower operating temperature in comparison with those in traditional ferronickel-making processes, it represents an exciting breakthrough in rational and optimal utilization of low- and medium-grade laterite ore resources for developing ferronickel and stainless-steel industry. Chapter 3 discusses the effects of calcium, magnesium, silicon, aluminum, and ferrous oxide on the properties of slag, from which a new low melting point slag type with diopside and mafic olivine as the main phases and a technology for slag system optimization and regulation centering on controlling FeO content and simultaneous adjustment of quaternary alkalinity are described with the purpose of reducing smelting temperature of electric arc furnace with less power consumption and higher metal recovery. Chapter 4 presents an original technical scheme of reducing the softening-melting temperature of laterite ore with promoted formation of liquid phase based on identification of the relationship between phase transformation and softening-melting property in the roasting process of laterite ore. It also clarifies the formation behavior of low melting point diopside phase during high-temperature roasting from which an innovative technology for regulating the softening-melting performance of laterite ore is presented. The findings denote efforts to improvement of the output and quality of laterite ore sinter and the smelting index of blast furnace, decrease of reduction temperature, acceleration of growth of ferronickel particles, and enhancement of separation of ferronickel in the Krupp–Renn process. Chapter 5 describes in detail the value-added utilization of ferronickel slag for preparing refractory materials and lightweight thermal insulation materials by comprehensively applying a series of techniques including biphasic design, particle gradation, and additive induction to optimize the phase composition, liquid phase generation, and volume/structure of product. Chapter 6 highlights a creative technical route of co-processing stainless-steel pickling sludge, which contains multiple valuable elements and sulfur that hinders its utilization and deteriorates the product quality when recycled as the feed for ferronickel production, with laterite ore via the RKEF process, based on analysis of desulfurization behaviors of the sludge, including thermodynamics, phase transformation, and off-gas emission characteristics during reduction.

The work involved in this book is a part of outcomes of research supported by the Basic Science Center Program, General Program, Youth Programs, and Key Program of National Natural Science Foundation of China (Grants 72088101, 52174288, 51904341 and 51804346, and 51234008, respectively) and the National Natural Science Foundation for Distinguished Young Scholars (Grant 50725416), etc. In the process of technological development and industrial application, it has received generous support from domestic and foreign enterprises such as the Guangdong Guangqing Metal Technology Co., Ltd., Baosteel Desheng Stainless Steel Co., Ltd., and Indonesia SILO Company. The authors hereby express their sincere thanks.

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Changsha, China
October 2022

Tao Jiang

# Contents

## 3 Technology of Slag Formation Control in Electric Furnace Smelting of Laterite Ore . . . . 109

## 4 Softening–Melting Properties of Laterite Ore and Regulation Technology Applied in Krupp–Renn Process and Sintering Process . . . . 179

# Chapter 1
# An Overview of Nickel Utilization from Laterite Ore

**Abstract** Ferronickel is an important alloy and intermediate product for manufacturing many advanced materials with versatile functions, e.g., stainless steel. Its properties and performance are mainly relied on the content of nickel, which is now primarily extracted from laterite ore. This chapter provides an overview of nickel utilization from laterite ore. Based on a brief introduction of properties of metallic nickel, it summarizes the applications of nickel, demand of nickel, resources of nickel, and metallurgical processes of laterite ore, in which the rotary kiln-electric furnace (RKEF) smelting process is dominant for production of ferronickel. Lastly, it discusses the challenges and development of ferronickel-making.

**Keyword** Nickel · Ferronickel-making · Laterite ores · Hydrometallurgical processes · Pyrometallurgical processes · RKEF

Nickel is a kind of silvery white ferromagnetic metal firstly separated by Swedish mineralogist A.F. Cronstedt in 1751. It is in the eighth group of the fourth period in the periodic table of elements, with atomic number of 28, atomic weight of 58.71, density of 8.9 g/cm$^3$ (20 °C), melting point of 1455 °C, and boiling point of 2915 °C. The most stable oxidation state of nickel is +2, but the oxidation valences of +1, +3 and +4 are also well known. The main oxides and sulfide compounds include NiO, $Ni_3O_4$, $Ni_2O_3$, $NiS_2$, $Ni_6S_5$, $Ni_3S_2$, and NiS. In addition, NiO has a melting point of 1650–1660 °C. It is easily reduced to metallic nickel using carbon or carbon monoxide as reducing agent. Ni can react with CO to form $Ni(CO)_4$, which is a colorless liquid with boiling point of 43 °C. $Ni(CO)_4$ decomposes back to nickel and carbon monoxide upon heating to 180 °C.

Metallic nickel has good ductility and toughness, with an elongation of 25–45%. It can be pressed into thin sheets of less than 0.02 mm for forging and rolling various parts. Nickel has excellent oxidation and corrosion resistance performance. The dense oxide film formed on the surface of nickel would prevent its internal oxidation at normal temperature in humid atmosphere. Nickel can resist corrosions of fluorine, alkaline water, and organic substances and dissolve slowly in dilute acid. The surface of nickel is passivized in strong nitric acid solution, preventing further corrosion.

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## 1.1 Applications of Nickel

Nickel is an indispensable metal in high-tech field. It is mainly used as an alloying element for production of stainless steel, high-temperature alloy steel, high-performance special alloy, and nickel-based plating materials (Fig. 1.1) [1]. Nickel can alloy readily with many other metals, including chromium, iron, copper, and cobalt. This allows for a wide variety of alloys that demonstrate outstanding resistance to corrosion and scaling, exceptional high-temperature strength, and other unique properties. For example, the copper-nickel alloys are featured by unique combination of strong resistance to corrosion, good thermal conductivity, and low macro-organism attachment in marine environments [2, 3]. They are applied in the fields of offshore oil and gas exploration, ship building, desalination, and power generation [4, 5]. The nickel–cobalt alloy is a kind of permanent magnetic material and is widely used in the field of electronic remote control, atomic energy industry and ultrasonic technology [6–8]. Besides, in chemical industry, nickel and its alloys are usually used as catalysts for hydrogenation reactions.

Nickel can also be used as anticorrosive coating on ceramic pigments and metal surfaces [9] and its demand proportion reached 7%. The nickel plating provides a unique combination of corrosion and wear resistances [10, 11]. It is used to increase brightness, lustre, appeal, and adhesion properties for subsequent coating layers.

Nickel foam and hydrogen storage metal, which are synthesized by nickel and rare earth, are widely used in the production of Ni–MH and Ni–Cd batteries due to the hydrogen absorption ability of nickel [12, 13]. More significantly, because of the increase of electric vehicles and the popularity of Ni-rich ternary cathode materials (e.g., NCM 811) for lithium batteries [14, 15], the nickel demand is expected to grow significantly [16]. The consumption of primary nickel in ternary Li-ion batteries was about 230 kilotons in 2021. This value is expected to reach 900 kilotons by 2030. The proportion of nickel demand for batteries is estimated to increase from 7% in 2021 to 35% by 2030, making batteries the second-largest application of nickel after stainless steel.

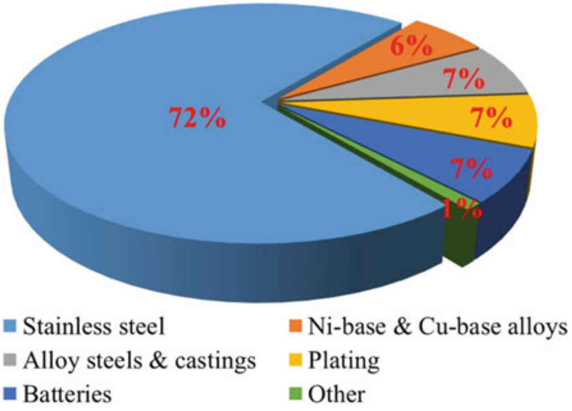

**Fig. 1.1** Applications of primary nickel worldwide in various fields [1]

**Table 1.1** Properties of various series of stainless steel

| Classification | Crystalline structure | Magnetism | Corrosion resistance | Machinability |
|---|---|---|---|---|
| 200 series | Austenite | No | Mediate | Good |
| 300 series | Austenite | No | Excellent | Excellent |
| 400 series | Ferrite/Martensite | Good | Good | Mediate |

More than two thirds of global nickel production is used to produce stainless steel [17]. As an alloying element, nickel enhances steel properties such as formability, weldability and ductility, and corrosion resistance in certain applications [18]. It is widely used in civil products, building decoration and other industries. According to its main chemical composition, stainless steel can be divided into chromium stainless steel (400 series), chromium-nickel stainless steel (300 series), chromium manganese nitrogen stainless steel (200 series) [19, 20]. The main properties of various series of stainless steel are listed in Table 1.1.

Nickel promotes the formation of austenite and optimizes the crystal structure of steel, improving the plasticity, weldability, and toughness of stainless steel. The addition of nickel to plain carbon steel results in the transformation of crystal structure from body centered cubic (BCC) structure to face centered cubic structure (FCC), namely the austenistic structure. Except for nickel, carbon, nitrogen, manganese, and copper are also austenite-forming elements.

There are two opposite effects in stainless steel. Ferrite forming elements continuously form ferrite, while austenite forming elements incessantly form austenite. The final crystal structure of stainless steel depends on the relative quantity of these elements [21, 22]. There is a competitive relationship between chromium and austenite forming elements in the formation of crystal structure of stainless steel because chromium is a ferrite forming element. Therefore, the magnetic properties of 400 series stainless steel are good due to the fact that both iron and chromium are ferrite-forming elements. As the nickel content increases, the amount of austenite will gradually increase until all ferrite structures are transformed into austenite structures to form 300 series stainless steel. Duplex stainless steels have a mixed microstructure of austenite and ferrite in equal amount when the amount of nickel is decreased by half. At present, austenitic stainless steel accounts for 70% of stainless steel. The best-known types are type 304 with 8% nickel and type 316 with 11% nickel.

## 1.2 Demand of Nickel

The global production and consumption of primary nickel have increased continuously in the past decade. Figure 1.2 shows that the global consumption of primary nickel was 1.47 million tons in 2010 and increased to 2.93 million tons in 2021, with the growth rate of 100% [23, 24]. On the other hand, the production of nickel reached 1.44 million tons in 2010, reaching 2.79 million tons in 2021, with an increase of

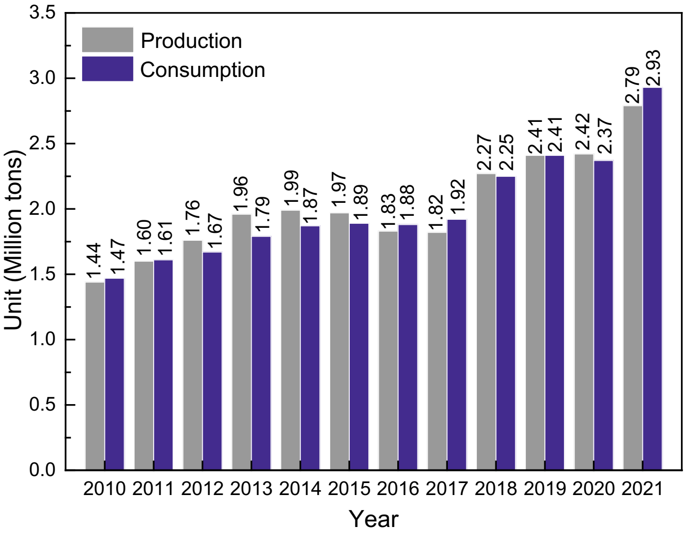

**Fig. 1.2** Global production and consumption of primary nickel in 2010–2021

more than 93% from 2010. From 2015 to 2017, the annual output of primary nickel decreased slightly from 1.97 million tons to 1.82 million tons. The nickel production was higher than the consumption globally in 2012–2015, leading to the slight decreases of nickel production in 2016 and 2017.

The global consumption proportion of primary nickel is shown in Fig. 1.3. The countries with large proportions of nickel consumption include China (53%), America (8%), Japan (7%), South Korea (4%), Italy (4%), Germany (3%), and India (3%). Among them, the nickel consumption in China accounts for more than half of the global primary nickel consumption. It is mainly attributed to the rapid development of infrastructure construction, which consumes large amounts of stainless steel (Fig. 1.4). Apart from China, the countries with large nickel consumption are mainly developed countries. The developing countries consume little primary nickel. Evidently, the nickel demand and stainless steel consumption have a close correlation (Figs. 1.3 and 1.4). The global demand for primary nickel is expected to increase continuously considering economic development of developing countries with more investment in infrastructure.

As shown in Fig. 1.5, the nickel production gradually increased from 330 in 2010 to 736 thousand tons in 2013 in China, with an average annual growth rate of more than 40%. Since 2014, the nickel production in China has decreased due to the overseas investment of Chinese enterprises in the construction of ferronickel production lines. In recent years, the nickel consumption has shown an obvious growth trend in China. The nickel consumption was 590 thousand tons in 2010 and increased to 1542 thousand tons in 2021, with a growth rate of nearly 161%. The nickel output has been unable to meet the primary nickel demand for stainless steel

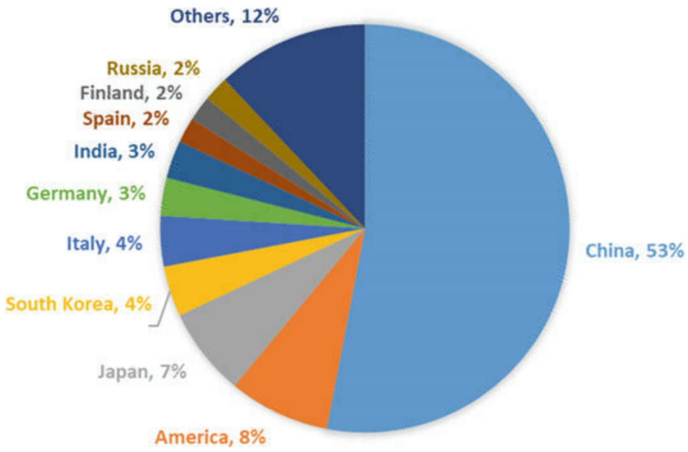

**Fig. 1.3** Consumption proportion of crude nickel around the world

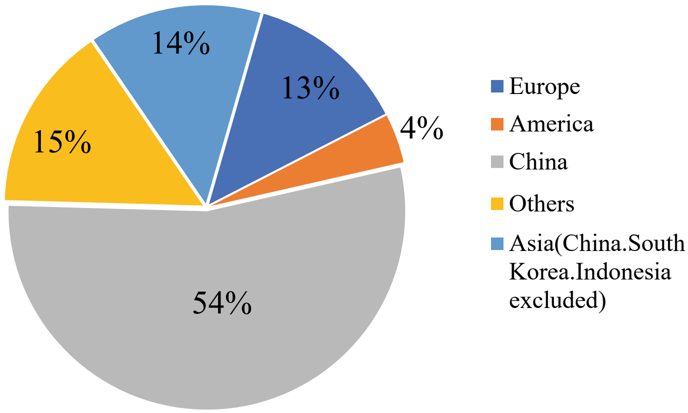

**Fig. 1.4** Distribution of stainless steel production around the world in 2021

production. From 2010 to 2019, the average annual nickel import accounted for more than 30% of the primary nickel consumption. Especially, in 2021, the decline in domestic production brought the nickel import to 865 thousand tons, more than half of the domestic consumption that year. According to Figs. 1.2 and 1.5, the global nickel consumption from 2010 to 2017 maintained at approximately 900 thousand tons per year, except for China. Evidently, the demand of primary nickel in China drives the global nickel production and consumption.

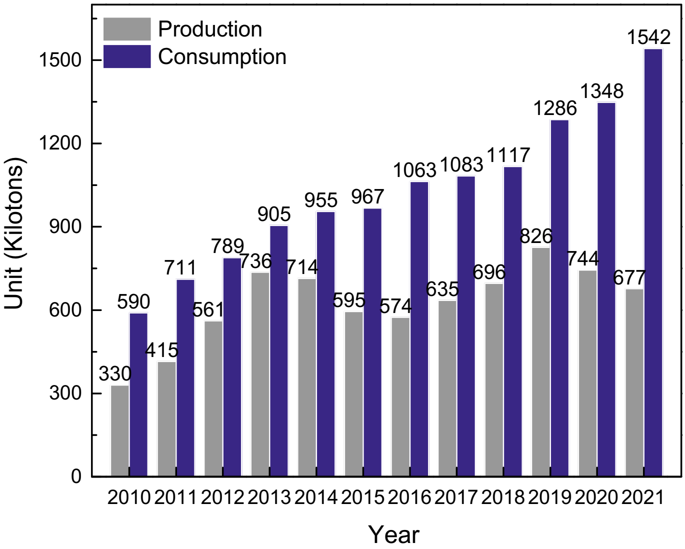

**Fig. 1.5** Production and consumption of primary nickel in China in 2010–2021

## 1.3 Resources of Nickel

There are abundant nickel resources in the world. Nickel exists in the form of natural ferronickel alloy in the core of the earth but it cannot be extracted. The available nickel resources in the world include three main types, namely nickel sulfide ores, laterite ores, and submarine manganese nodules. Compared with nickel sulfide ores and laterite ores, the submarine manganese nodules have not been used effectively due to the limitation of mining technology and high cost. According to the statistics of the United States geological survey in 2021, the global proven land-based nickel reserves are about 96 million tons and the total nickel resources are approximately 130 million tons. They are mainly distributed in Australia, Brazil, New Caledonia, Russia, Cuba, Indonesia, South Africa, Philippines, China, and Canada (Fig. 1.6) [25]. Among them, the countries located near the equator have the most abundant nickel resources, particularly, laterite ores (Fig. 1.6). Indonesia and Australia have 21 and 19 million tons of nickel reserves, respectively, accounting for approximately 42% of the global reserves. The sum of nickel reserves in the top ten countries accounts for approximately 90% of the global reserves, indicating uneven distribution of nickel resources.

About 130 million tons of nickel resources with an average nickel content of 1% or more have been proved. Among these nickel resources, nickel sulfide ores account for about 40% and laterite ores account for about 60%. The former is mainly distributed in Canada, Russia, Australia, China and South Africa. Its deposit areas include the Kambalda nickel deposit in Australia, Kola peninsula and Siberia Norilsk nickel

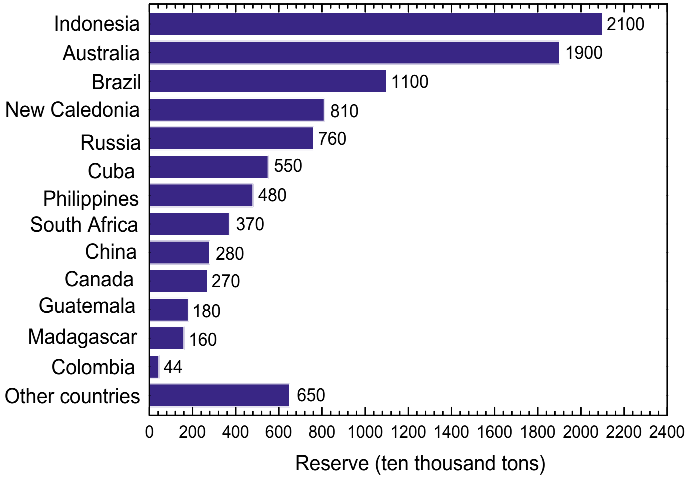

**Fig. 1.6** Reserves of nickel resources in the world [25]

deposits in Russian, Sudbury, and Manitoba Thompson nickel deposits in Canada, and Jinchuan nickel and Panshi nickel deposits in China [26–28].

The laterite ores in the world are mainly distributed near the equator, including Indonesia, Brazil, New Caledonia, Cuba, Philippines, and Myanmar. Their large mines include New Caledonia nickel mines, Orient nickel mines in Cuba, Molucca and Sulawesi nickel mines in Indonesia, Palawan nickel mines in Philippines, Queensland nickel mines in Australia, Bannan nickel mines in Dominica, and Rajema nickel mines in Greece.

The reserves of nickel in China are 2.8 million tons, ranking ninth in the world (Fig. 1.6). By comparing the quantity of nickel resources with the consumption of crude nickel in recent years (Figs. 1.5 and 1.6), it is shown that the nickel reserves in China are unable to meet the long-term national demand, which is the main reason for its huge import of nickel resources and intermediate products, such as ferronickel and nickel sulfates. According to the distribution of nickel mineral resources, the sulfide nickel resources are abundant, and their quantity accounts for more than 90% of the total nickel resources in China. Gansu province of China has the largest nickel sulfide ores, accounting for about 62% of total nickel reserves. The main mining areas are Jinchuan mine, Kratonk mine and Huangshan mine. Jinchuan mine is rich in nickel, behind Sudbury mine in Canada, ranking second in the world.

On the other hand, the laterite ores in China are deficient and the amount of laterite ores only accounts for about 10% of the total resources. In China, there are still problems of low nickel grade and high mining cost in laterite deposits. Because of large stainless steel consumption, China needs to import a huge number of laterite ores from Indonesia, Australia, and Philippines every year to develop stainless steel production. China imported most of laterite ores from Indonesia before the country issued the policy of restricting the export of nickel ores in 2014. In recent years,

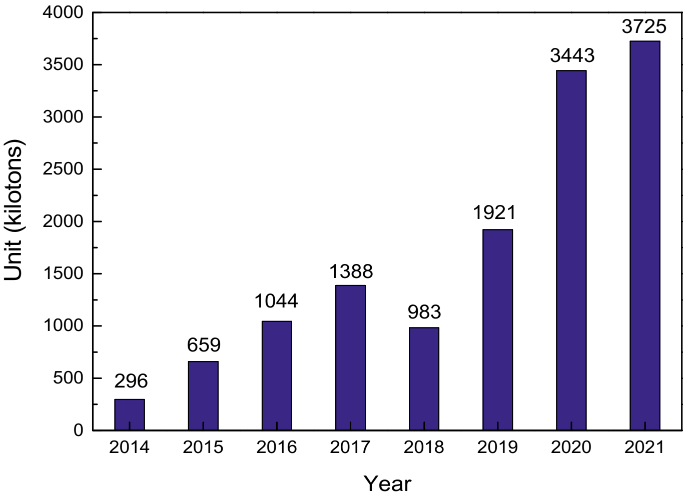

**Fig. 1.7** Import of ferronickel in China since 2014–2021

a part of laterite ores has been imported from Philippines. Besides, many Chinese enterprises built ferronickel production plants in Indonesia. As a result, the amount of ferronickel imported from Indonesia has markedly increased since 2015. The import of ferronickel was only 296 kilotons in 2014, while this value increased to 1388 kilotons in 2017 (Fig. 1.7). After the Indonesian government relaxed the restrictions on the export of nickel resources again in 2017, the import of laterite ores from Indonesia was increased. Conversely, the import of ferronickel was decreased in 2018. Unfortunately, Indonesia issued the policy of restricting the export of laterite ores in 2019. The ferronickel imports reached the highest value of 3725 kilotons in 2021, with about 84% (3118 kilotons) from Indonesia.

## 1.4 Metallurgical Processes of Laterite Ore

Due to the limited treatment technology of laterite ores, sulfide ores were the main source of global nickel production for quite a long time in the past. High-grade sulfide ores were used as raw materials to produce high-quality nickel products. With gradual depletion of sulfide ores, it is difficult to meet increasing demand of raw materials. Thus, it is important to make full use of laterite ores with low cost. Compared with sulfide ores, laterite ores are more abundant and easier to be exploited. Many kinds of valuable metals, such as cobalt, iron, magnesium and chromium, are associated with laterite ores. The comprehensive recovery of these valuable metals can improve the utilization efficiency of the resources. In recent years, the development of laterite ores has made rapid progress. According to statistics, the amount of crude nickel derived from laterite ores has surpassed the amount derived from sulfide ores in 2010, opening a new chapter for the use of laterite ores in nickel production [29].

Generally, laterite ore deposits can be divided into three different layers from top to bottom, namely, limonite layer, transition layer and saprolite layer [30, 31], as shown in Figs. 1.8 and 1.9. Due to long-term weathering and eluviation, the nickel grade of limonitic laterite ore is the lowest while the iron grade is the highest. Nickel mainly exists in goethite in the form of lattice substitution [32, 33]. The saprolite laterite ore has the highest nickel grade and lower iron grade. Iron mainly exists in the form of silicates, such as serpentine [34, 35]. The nickel and iron grades in the transition layer are between the limonite and saprolite layers and they mainly occur in goethite, hematite, and silicates.

The contents of cobalt, magnesium, silicon, aluminum, and chromium in laterite ore are also different (Fig. 1.9). The extraction and separation of these elements require different metallurgical methods. The limonitic laterite ore is relatively suitable for extracting valuable metals such as nickel and cobalt by hydrometallurgy due to its low contents of magnesium and silicon and high content of cobalt. However, the saprolitic laterite ore has high content of nickel and low content of iron and it is more suitable for ferronickel production using pyrometallurgical methods. For laterite ore in the transition layer, both pyrometallurgical and hydrometallurgical processes may meet the production requirements.

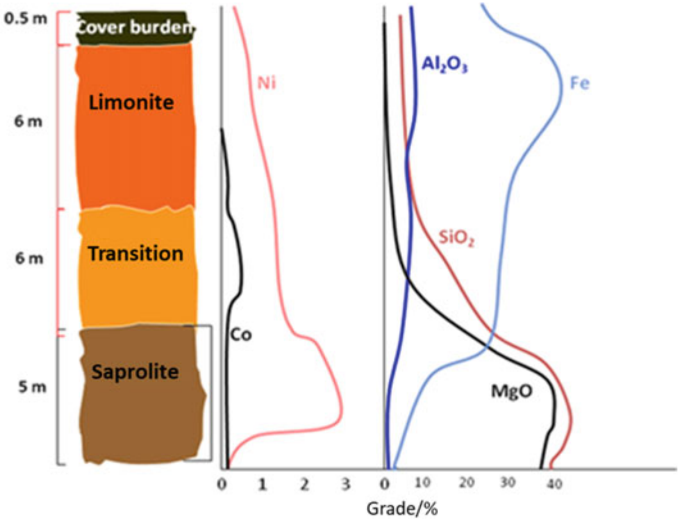

**Fig. 1.8** Schematic illustration of distribution and chemical composition of laterite ore deposits

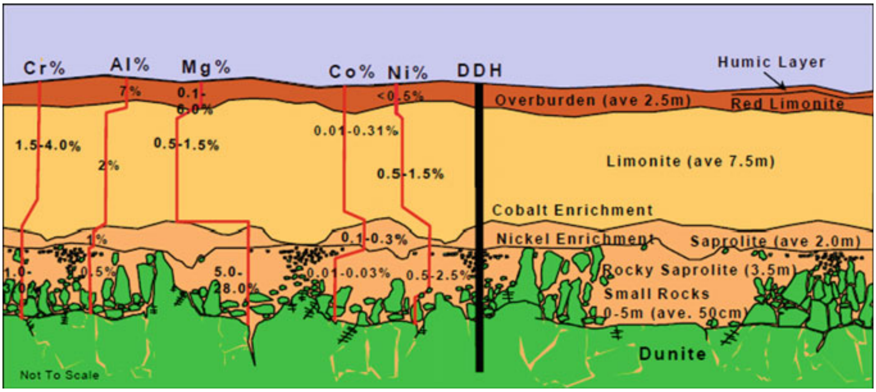

Fig. 1.9 Profile of the Remu laterite ore in the Papua New Guinea [31]

## 1.4.1 *Hydrometallurgical Processes*

### 1.4.1.1 High-Pressure Acid Leaching (HPAL) Process

The high-pressure acid leaching (HPAL) process of laterite ore was developed in the 1950s. The flowsheet of the HPAL process is shown in Fig. 1.10. The metal elements, including nickel, iron, and cobalt, are selectively leached at high temperature and high pressure. The leaching of nickel and cobalt reach nearly 95%, while most of the impurity components such as iron and aluminum retain in the leaching residue [36, 37]. The components are dissolved in sulphuric acid at leaching temperature of 245–265 °C and pressure of 4–5 MPa (Eqs. 1.1–1.9). The iron and aluminum ions in the solution are hydrolyzed at high temperature and pressure and then transformed into hematite and hydrated alunite (Eqs. 1.10 and 1.11), resulting in the selective leaching of nickel/cobalt over iron/aluminum [38–40]. A recent study reported that the leaching percentages of nickel and cobalt were 97% and 96%, respectively, while that of iron was less than 1%, with sulfuric acid concentration of 250 kg/t, liquid/solid ratio of 3 mL/g, leaching temperature of 250 °C, and leaching time of 1 h [41]. In addition, the leached silicon precipitated when it was cooled (Eq. 1.8). The remaining impurities such as iron and aluminum in the lixivium were precipitated and separated by adjusting pH value, while nickel, cobalt, and magnesium entered the leachate. When sulfidizing agents or alkalis were added, the sulfides or hydroxides were precipitated and the products $(Ni, Co)(OH)_2$ or (Ni, Co)S could be obtained.

$$NiO + H_2SO_4 = NiSO_4 + H_2O \tag{1.1}$$

$$CoO + H_2SO_4 = CoSO_4 + H_2O \tag{1.2}$$

$$FeO + H_2SO_4 = FeSO_4 + H_2O \tag{1.3}$$

$$\begin{aligned} Co_2O_3 \cdot MnO_2 + 4FeSO_4 + 5H_2SO_4 = {} & 2CoSO_4 + MnSO_4 \\ & + 2Fe_2(SO_4)_3 + 5H_2O \end{aligned} \tag{1.4}$$

$$2FeOOH + 3H_2SO_4 = Fe_2(SO_4)_3 + 4H_2O \tag{1.5}$$

$$Al_2O_3 \cdot 3H_2O + 3H_2SO_4 = Al_2(SO_4)_3 + 6H_2O \tag{1.6}$$

$$MgCO_3 + H_2SO_4 = MgSO_4 + H_2O + CO_2 \tag{1.7}$$

$$MgO \cdot SiO_2 + H_2SO_4 = MgSO_4 + H_2SiO_3 \tag{1.8}$$

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2 \tag{1.9}$$

$$Fe_2(SO_4)_3 + 3H_2O = Fe_2O_3 + 3H_2SO_4 \tag{1.10}$$

$$3Al_2(SO_4)_3 + 14H_2O = 2(H_3O)Al_3(OH)_6(SO_4)_2 + 5H_2SO_4 \tag{1.11}$$

The high-pressure acid leaching process of limonitic laterite ore has been successfully adopted by MOA (Cuba), Bulong, Cawse, Murrin Murrin and Ravensthorpe plants (Australia), Coral Bay and Taganito plants (Philippines), Ramu plant (Papua New Guinea), Ambatovy (Madagascar) and other enterprises [42–44]. It has some advantages in extracting nickel and cobalt from limonitic laterite ore, despite a few problems. At present, the process is mainly used to treat limonitic laterite ore with high iron content and low silicon and magnesium contents. Generally, the magnesium content is required to be less than 5%. The main reason is that high magnesium content in the raw material leads to large acid consumption and high cost of magnesium separation in the subsequent leaching solution [45, 46]. Due to the strict production conditions of high temperature, pressure and corrosion, the process needs special facilities (such as titanium alloy autoclave), greatly increasing the investment and production costs [36]. On the other hand, along with the generation of hematite, hydrated alunite, and calcium sulfate (Eqs. 1.9–1.11), scales are easily formed inside the autoclave during leaching [47]. Removing the scales needs to stop the autoclave, which affects the operation of the production. On the other hand, because of the high iron content in limonitic laterite ore, for every ton of nickel leached, over 100 tons of acidic iron-containing residues are generated in the HPAL plants. These residues are typically discharged into deep seas, causing marine pollution. In view of this fact, the tailings pond should be constructed in the new HAPL production lines.

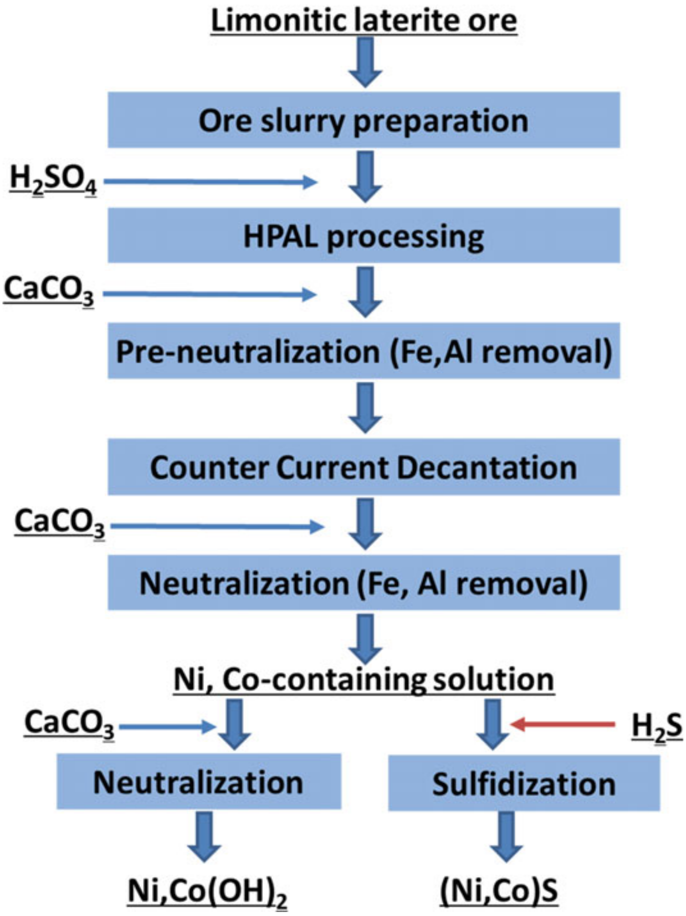

**Fig. 1.10** Flowsheet of the HPAL process

### 1.4.1.2 Atmospheric Acid Leaching (AL) Process

In view of the shortcomings of the HPAL process, the technology of acid leaching at atmospheric pressure to treat limonitic laterite ore has attracted widespread attention [48]. Compared with HPAL, the atmospheric acid leaching (AL) process is simpler with advantages of lower energy consumption and less strict requirement for apparatuses [32, 49]. Hydrochloric acid, sulfuric acid, and nitric acid are commonly used in this process. However, since nickel mainly exists in the form of lattice substitution in the goethite, leaching of nickel depends on the dissolution of goethite [50, 51], which is difficult to dissolve under atmospheric condition, resulting in a low nickel leaching percentage (40–60%) [52, 53]. Moreover, the dissolved iron ions cannot form hematite precipitation under this condition, causing poor leaching selectivity of nickel over iron. The leaching ratio of Ni to Fe is close to 1 [32, 52].

Adding some reducing agents (such as thiosulfate, hydrosulfite, and $SO_2$) and acids (such as citric acid and oxalic acid) can strengthen the dissolution of goethite, promoting nickel leaching (Eqs. 1.12–1.17) [53–55]. It was found that the leaching percentages of iron and nickel in laterite ore increased from 45% to 85% with the sulfuric acid concentration of 0.72 M at leaching temperature of 90 °C for 6 h with the addition of 0.3 M $SO_2$ [52]. Besides, due to the strengthened leaching of Co-doped manganese oxides, Co leaching should also be promoted after adding the reducing agents (Eq. 1.18). However, because of the simultaneous increase in the amount of leached iron, the leaching of nickel and iron also kept a linear relationship, which had a negative impact on the separation of nickel and iron in the subsequent solution.

$$2FeOOH + SO_2 + H_2SO_4 = 2FeSO_4 + 2H_2O \tag{1.12}$$

$$2FeOOH + S_2O_4^{2-} + 4H^+ = 2Fe^{2+} + 2HSO_3^- + 2H_2O \tag{1.13}$$

$$2FeOOH + 4H^+ + S_2O_4^{2-} = 2FeHSO_3^+ + 2H_2O \tag{1.14}$$

$$8FeOOH + S_2O_3^{2-} + 14H^+ = 8Fe^{2+} + 2SO_4^{2-} + 11H_2O \tag{1.15}$$

$$14FeOOH + C_3H_8O_3 + 28H^+ = 14Fe^{2+} + 25H_2O + 3CO_2 \tag{1.16}$$

$$2FeOOH + H^+ + 5HC_2O_4^- = 2Fe(C_2O_4)_2^{2-} + 4H_2O + 2CO_2 \tag{1.17}$$

$$(Mn, Co)O_2 + SO_2 + H_2SO_4 = MnSO_4 + CoSO_4 + H_2O \tag{1.18}$$

#### 1.4.1.3 Combined HPAL-AL Leaching Process

The combined HPAL-AL leaching process is mainly applied to the treatment of limonitic and saprolitic laterite ores simultaneously [48]. Firstly, HPAL is used to treat the limonitic laterite ore and then the leachate is used for leaching saprolitic laterite ore at atmospheric pressure. The leaching residue derived from AL can be circulated for HPAL. The process utilizes the dissolution of magnesium-containing minerals in the saprolitic laterite to neutralize the excessive acid in the high-pressure leaching solution to adjust the pH value of the solution without adding other alkaline agents. Also, nickel and cobalt can be leached from saprolitic laterite ore using residual acid in high-pressure leaching solution, thereby improving the overall nickel recovery with lower production cost.

#### 1.4.1.4 Reductive Roasting-Ammonia Leaching Process

To improve nickel leaching, some processes based on roasting followed by leaching have been developed [56–58]. They mainly include reductive roasting-ammonia leaching, reductive roasting-acid leaching, oxidative roasting-acid leaching, chlorinating roasting-water leaching, and sulfate roasting-water leaching.

Among these processes, the reductive roasting-ammonia leaching process (also known as the Caron process) has been used in industry. It has been applied in the Yabula refinery of QNI in Australia and the Nicaro smelter in Cuba [59, 60]. The laterite ore is selectively reduced at 600–700 °C. The nickel and cobalt oxides are reduced to the metallic state, while iron oxides are transformed into magnetite and wüstite (Eqs. 1.19–1.22). In addition, $NH_3$ and $CO_2$ are introduced into the leaching solution to leach the metallic nickel and cobalt in the form of ammoniac complex ion, while iron, magnesium and other impurities remain the leaching residue [61, 62]. However, in this process, the comprehensive recovery of nickel is about 75–80% and the recovery of cobalt is only 40–50%.

$$\mathrm{NiO} + \mathrm{CO} = \mathrm{Ni} + \mathrm{CO_2} \tag{1.19}$$

$$\mathrm{CoO} + \mathrm{CO} = \mathrm{Co} + \mathrm{CO_2} \tag{1.20}$$

$$6\mathrm{FeOOH} + \mathrm{CO} = 2\mathrm{Fe_3O_4} + 3\mathrm{H_2O} + \mathrm{CO_2} \tag{1.21}$$

$$2\mathrm{FeOOH} + \mathrm{CO} = 2\mathrm{FeO} + \mathrm{H_2O} + \mathrm{CO_2} \tag{1.22}$$

#### 1.4.1.5 Reductive Roasting-Acid Leaching Process

The process of reductive roasting followed by acid leaching is similar to that of reductive roasting-ammonia leaching process, in which nickel and cobalt in laterite ore are selectively reduced to the metallic state by reduction, and hematite is reduced to magnetite and wüstite [63, 64]. Nickel and cobalt in the metallic state are easily dissolved in a diluted acid solution, increasing leaching of nickel and cobalt within shorter leaching time. A limonitic laterite ore (TFe 50.88 wt% and NiO 0.38 wt%) was reduced at 700 °C in the gas of 30 vol.% CO/(CO + $CO_2$) for 90 min. The leaching percentage of nickel in the reduction product was 93% after leaching using 0.05 mol/L $H_2SO_4$ at temperature of 70 °C for 60 min [65]. The iron retained in the leaching residue was mainly in the form of magnetite, which could be used for iron-making after magnetic separation.

#### 1.4.1.6 Oxidative Roasting-Acid Leaching Process

The oxidative roasting-acid leaching process is an alternative method. Its mechanism is different from that of the reductive roasting-acid leaching process. The goethite in laterite is dehydrated during roasting, and the specific surface area of the minerals is improved after roasting at 250–400 °C [63, 64]. The purpose of strengthening leaching of nickel and cobalt under the atmospheric pressure can be realized, depending on the change of the crystal structure and specific surface area of minerals [65, 66]. In the process of transformation from goethite to hematite (Eq. 1.23), the increase of activation energy of iron leaching leads to the decrease of iron leaching, eventually improving the selective leaching of nickel and cobalt. Compared with direct acid leaching, the leaching percentage of nickel increased from 67.1% to 92.7% while that of iron decreased from 78% to 32.5% after oxidative roasting at 400 °C, followed by leaching at 50 °C for 1 h with HCl concentration of 4 mol/L [67]. Garces-Granda et al. also reported an increase in the leaching percentage of nickel from 15.8% to 98.0% after roasting at 430 °C for 2 h (leaching temperature: 25 °C, time: 48 h, and HCl concentration: 3.2 M) [68]. However, due to uniform distribution of Ni in the structure of iron oxides, there was simultaneous dissolution of Ni and Fe.

$$2\mathrm{FeOOH} = \mathrm{Fe_2O_3} + \mathrm{H_2O} \tag{1.23}$$

#### 1.4.1.7 Sulfatizing Roasting/Chloridizing Roasting-Water Leaching Process

Through roasting with additives, the phase composition in laterite ores can be modified to improve their solubility in aqueous solution for higher leaching efficiency of nickel, cobalt, and other metals [69].

The principle of sulfatizing roasting-water leaching is basically the same as that of chloridizing roasting-water leaching. At certain temperature and atmosphere, the main metal components in laterite ores are transformed into water-soluble sulfate or chloride by using sulfur-containing or chlorine-containing additives. Concentrated sulfuric acid or sulfates (such as ammonium sulfate, ammonium bisulfate and sodium sulfate) are used as the additives in sulfatizing roasting in the temperature range 200–500 °C [70, 71]. Generally, chloride salts including sodium chloride and magnesium chloride are used in chloridizing roasting and its roasting temperature is higher than that of sulfatizing roasting, reaching about 700–1000 °C [72–74]. Li et al. used a mixture of NaCl and $\mathrm{MgCl_2 \cdot 6H_2O}$ as the additive for leaching of nickel, cobalt, and iron. Their leaching percentages were 87%, 58%, and 53%, respectively, after roasting at 900 °C, followed by water leaching [72]. The results showed that leaching of nickel and cobalt could be improved significantly. However, the leaching percentage of iron was also increased. In addition, the emission of hydrogen chloride gas during roasting would pose potential environmental risks.

#### 1.4.1.8 Phosphoric Acid Leaching Process

As mentioned above, because of the high iron content in limonitic laterite ore, the selective leaching of nickel/cobalt over iron is a critical problem in hydrometallurgical processes. There are two feasible approaches: (i) limiting the dissolution of iron-bearing minerals and (ii) re-precipitation of the dissolved iron ions during leaching. In general, the limited dissolution of iron-bearing minerals results in a low leaching percentage of nickel, making it more feasible to re-precipitate the dissolved iron ions. In the above leaching processes, only the HPAL process can achieve re-precipitation of the dissolved iron ions and selective leaching of nickel and cobalt over iron. However, in this process, large amounts of acidic iron-containing residues are discharged into deep seas, causing marine pollution. The AL processes also produce large amounts of unutilized iron-residues while removing iron from lixivium by precipitation. This means that recovering iron components is important during the hydrometallurgical processing of laterite ore for cleaner production.

Recently, it was reported that phosphoric acid could be used as a leaching agent for processing limonitic laterite ore [75, 76]. Based on the differences in the solubility of phosphates, nickel and cobalt were leached (Eqs. 1.24–1.28) and iron phosphate was prepared simultaneously during leaching (Eqs. 1.29 and 1.30). This process could realize efficient leaching of nickel and cobalt, as well as a superior selective leaching of nickel and cobalt over iron. The related results showed that 98.7% of nickel and 89.8% of cobalt were leached from the roasted limonitic laterite ore (at 400 °C for 60 min) under the optimized leaching conditions (phosphoric acid concentration of 3 mol/L, leaching temperature of 90 °C, leaching time of 180 min, and liquid/solid ratio of 10 mL/g). Meanwhile, 98.3% of iron was converted into insoluble $FePO_4{\cdot}2H_2O$ [75]. By using another similar approach to with phosphoric acid, the leaching percentages of Ni, Co, and Fe were 99.2%, 81.8%, and 0.54%, respectively, in a 3 mol/L $H_3PO_4$ liquor at 130 °C for 2 h [76]. Compared with high-pressure leaching, the temperature required was decreased by 115–125 °C and the hydrothermal pressure was only 0.2–0.27 MPa. Furthermore, because of the simultaneous precipitations of $Fe^{3+}$ and $Al^{3+}$, a lamellar Al-doped iron phosphate, ($FePO_4{\cdot}2H_2O$), as leaching precipitate was obtained at the (Fe + Al)/P molar ratio of 1.0 and purity of 99%, which could be used as the anode material for $LiFePO_4$ batteries after removing impurities. The process eliminated the generation of acidic residues and realized value-added utilization of iron in limonitic laterite ore.

$$NiO + 2H_3PO_4 = Ni^{2+} + 2H_2O + 2H_2PO_4^- \tag{1.24}$$

$$CoO + 2H_3PO_4 = Co^{2+} + 2H_2O + 2H_2PO_4^- \tag{1.25}$$

$$Fe_2O_3 + 6H_3PO_4 = 2Fe^{3+} + 3H_2O + 6H_2PO_4^- \tag{1.26}$$

$$NiO + 2H_2PO_4^- = Ni^{2+} + H_2O + 2HPO_4^{2-} \tag{1.27}$$

$$CoO + 2H_2PO_4^- = Co^{2+} + H_2O + 2HPO_4^{2-} \tag{1.28}$$

$$Fe_2O_3 + 6H_2PO_4^- = 2Fe^{3+} + 3H_2O + 6HPO_4^{2-} \tag{1.29}$$

$$Fe^{3+} + PO_4^{3-} + 2H_2O = FePO_4 \cdot 2H_2O \tag{1.30}$$

#### 1.4.1.9 Microbiological Leaching

The aim of microbiological or biological leaching process is to use the oxidation or reduction functions of microorganisms to oxidize or reduce certain mineral components in laterite ores to achieve the purpose of separating valuable components (Eq. 1.31) [77–79]. The components are oxidized or reduced, depending on the characteristics of microorganisms to achieve selective separation in the process. Compared with the HPAL and AL leaching processes, the use of biological leaching at room temperature takes longer time, even several months.

$$6FeOOH + S + 10H^+ = 6Fe^{2+} + SO_4^{2-} + 8H_2O \text{ (bacterial)} \tag{1.31}$$

### *1.4.2 Pyrometallurgical Processes*

Although a lot of studies of hydrometallurgical processes have been carried out for processing of laterite ores with low energy consumption, the hydrometallurgical technology is used in only a small proportion of enterprises for crude nickel production due to its limited scale and long production process. In contrast, pyrometallurgy can meet the demand of stainless steel industry for nickel through large-scale industrial production. At present, more than 70% of the global nickel production is based on pyrometallurgy, including the matte smelting process, rotary kiln reduction process, blast furnace smelting process and rotary kiln-electric furnace smelting process.

#### 1.4.2.1 Matte Smelting Process

The nickel matte smelting process has been applied since 1920s and it was the first pyrometallurgical process of laterite ore in industrial production [80, 81]. By adding sulfur, sulfide ore or gypsum into laterite ore, the low-grade nickel matte ($Ni_3S_2{\cdot}FeS$) is generated when the smelting process is carried out at 1500–1600 °C in blast furnace or electric arc furnace. Then, the high nickel matte with nickel grade more than 40%

is produced by converter blowing. The quantity of nickel matte produced by laterite ores is about 120 kilotons per year in the world (calculated by metal nickel).

The basic principle of nickel matte smelting is that the ore melts into liquid phase and the metal components including Ni, Co, and Fe react with sulfiding agents after reduction, forming mixed melt of nickel, cobalt, and iron sulfides, also named low-grade nickel matte [82]. The advantages of this process are simple equipment, mature technology, and adjustable products. After roasting and desulfuration, high-grade nickel matte can be used for direct reduction and preparation of crude nickel for stainless steel production. It can also be used as a feed for refining nickel by the atmospheric carbonyl method to produce nickel pellets and nickel powder. In addition, the matte can be made into anode plate to produce cathode nickel by electrolytic refining. However, there are also some problems in the matte smelting process, such as high energy consumption, heavy pollution, and poor nickel recovery (about 70% in the whole process). At present, the main factories that use this process are Anbo smelter in New Caledonia and Thorocco smelter in Sulawesi, Indonesia.

#### 1.4.2.2 Rotary Kiln Reduction-Physical Separation Process

The laterite ore is dried, crushed, screened, and then mixed with flux and reducing agent in a certain proportion to form agglomerates. The agglomerates are dried and reduced in a rotary kiln. The calcines are then cooled by water quenching, crushed, and screened for magnetic or gravity separation to obtain ferronickel nuggets or powders [83, 84]. The whole process in the rotary kiln could be divided into three stages, including the drying stage, reduction stage, and growth stage of ferronickel particles, as shown in Fig. 1.11. The temperature of drying is generally lower than 800 °C, leading to the evaporation of the crystal water in the feeds. The reduction of nickel oxides and iron oxides take place in the reduction stage at 800–1250 °C. The ferronickel particles generated in the reduction stage are fully aggregated and remain in the molten or semi molten state at 1250–1450 °C [85–87].

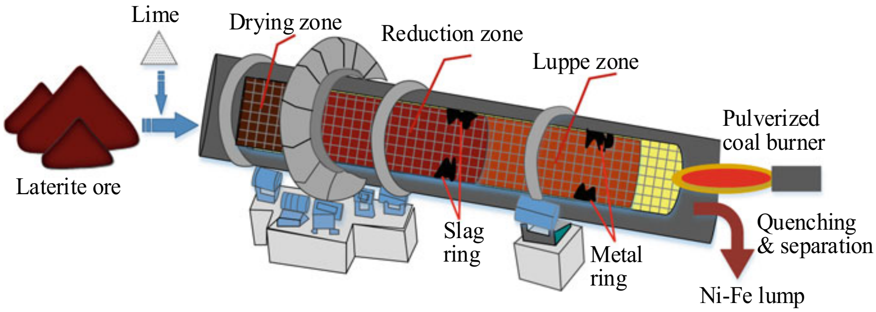

**Fig. 1.11** Flowsheet of the rotary kiln reduction-physical separation process

The ferronickel production by the rotary kiln reduction-physical separation process has the advantages of short process and low energy consumption, mainly due to the use of coal as both heat source and reductant. About 80–85% of the total energy consumption is provided by coal. It is the most economical way to deal with high-grade saprolitic laterite ore. This process was originally developed from the Krupp-Renn process for ironmaking in Germany. In 1930s, Nippon Yakin Kogyo Co. Ltd. in Japan firstly used this process to produce ferronickel from laterite ores and is still running [88, 89]. The company is equipped with five rotary kiln production lines, which use high-grade laterite ore (more than 2 wt% Ni), limestone as desulfurizer, and anthracite as reducing agent. The annual output of ferronickel is about 15–20 kilotons (calculated by nickel metal).

Due to the obvious advantages of rotary kiln reduction-physical separation process, many ferronickel plants in China are developing or have already put into production of rotary kiln lines. Chaoyang Heavy Building Materials Machinery Manufacturing Co., Ltd. has successively carried out the tests and production of ferronickel in rotary kilns in Qiqihar and Jiangsu province, obtaining ferronickel products containing more than 10% of nickel. In 2013, Chengde Nickel Industry Co. Ltd. established four rotary kiln lines in Guangxi province. Desheng Stainless Steel Co. Ltd. of Baosteel group carried out the technical transformation project of direct reduction of ferronickel by rotary kiln in Fujian Luoyuan No. 2 Crude Refinery and the trial production was carried out in 2016. The overall nickel recovery could reach 90%. Shanghai Pan-Pacific Group has built two production lines in North Maluku province to produce ferronickel products (nickel grade: 10–13%). The second stage of Dafeng Port (Indonesia) of Heshun Nickel Industry Co., Ltd. plans to build six rotary kiln reduction lines in Sulawesi, Indonesia, which is expected to produce 150 kilotons of ferronickel per year.

#### 1.4.2.3 Blast Furnace (BF) Smelting Process

The technological process of producing nickel pig iron (NPI) by smelting laterite ore in blast furnace is basically the same as that of modern BF smelting for producing pig iron from iron ores [29], as shown in Fig. 1.12. Initially, the laterite ore is crushed, mixed with flux and fuel, and then sintered in a sintering machine. The resulting sinter is smelted in BF to produce NPI. The process is usually applied for treatment of high iron and low magnesium limonitic laterite ore (nickel grade of 0.7–1.2 wt%) and the nickel grade of NPI is kept at 1–3 wt% to produce 200 series stainless steel. At the beginning of the twenty-first century, many private enterprises in China started to use small-scale BF (50–150 $m^3$) to produce NPI [34, 35]. Due to the rapid increase of stainless steel demand in the early 2010s, this process has been developed in China. It turned into a typical NPI production process with Chinese characteristics.

Due to the restrictions of Chinese government policy, the small-scale BF has been shut down gradually in recent years. However, because the blast furnace smelting process has the advantages of mature technology, large production capacity, and low requirements for raw materials, some ferronickel plants still use this process