

Chapter 1

Overview of Magnesium Metallurgy



Abstract Human beings discovered magnesium compounds as early as the seventeenth century. In later years, the magnesium alloy has been used in our daily life. In this section, we discuss the magnesium mineral resource, magnesium smelting technology, the history of magnesium industry and the comprehensive utilization of magnesium slag. We believe that it is worthwhile to investigate the magnesium and related technology which will make our life better.

Keywords Magnesium · Magnesium mineral · Magnesium industry · Magnesium smelting · Magnesium slag

1.1 Introduction

1.1.1 Properties and Main Uses of Magnesium Metal

Human beings discovered magnesium compounds as early as the seventeenth century. Antoine Lavoisier, a French scientist, theoretically inferred that an ore with unknown composition (ore containing alumina and magnesium oxide) contained a new metal element, but the magnesium could not be extracted using the reducing agents known at that time because of the strong bond between magnesium and oxygen atoms.

Magnesium is a kind of light metal with high chemical activity. There is a huge reserve of magnesium ores widely distributed across the globe. Table 1.1 shows the distribution of elements in the earth's crust. Table 1.2 shows the main physical properties of magnesium. Because it has the advantages of light weight, high specific strength, good ductility, good damping and machinability, a strong electromagnetic shielding effect, good shock absorption, good thermal conductivity and thermal fatigue performance, and is easy to recycle, magnesium is widely used in aviation, aerospace, transportation, electronics, and other fields. The magnesium alloy is far superior to the aluminum alloy in electromagnetic shielding and shock absorption. Compared with fiber-reinforced plastics, the magnesium alloy has lower specific strength but higher specific stiffness. Because of its high chemical activity, magnesium can also be used as a reducing agent in the production processes of refractory metals (Ti, Zr, Be, U, and HF). Because magnesium has an extremely

Table 1.1 Distribution of chemical elements in the earth's crust

Element	Mass content/%	Element	Mass content/%
Oxygen	48.06	Calcium	3.45
Silicon	26.30	Sodium	2.74
Aluminum	7.73	Potassium	2.47
Iron	4.75	Magnesium	2.00
Hydrogen	0.76	Other	0.76

Table 1.2 Main physical properties of magnesium

Melting point/°C	648
Boiling point/°C	1107
Relative density (water = 1)	1.74
Appearance and character	Silver white metallic powder
Solubility	It is insoluble in water and alkali solution and soluble in acid

high affinity with sulfur, it can also be used as a desulfurizer. Magnesium performs unique deoxidation and purification functions in the production of alloy materials that involve Cu, Ni, Zn, and rare earth elements. In addition to being used as a reducing agent of refractory metals and an additive of alloys, magnesium can also be used as a nodularizing agent of nodular cast iron, neutralizer of lubricating oil, and large-capacity energy storage materials. Moreover, magnesium also plays a role in automobiles, electronic communication, aerospace, and other fields thanks to its light weight and ease of processing (cutting and die casting) [1].

Because of the above excellent properties, metal magnesium is touted as “the most promising lightweight engineering metal material in the twenty-first century” [2]. Magnesium and its alloys were first used in the aviation industry during the First World War. Despite its long history of commercial application, the development of magnesium alloys has been slow compared with that of aluminum alloys. Since 2000, the reserves of many traditional metals have been drying up. As governments across the world adopt development strategies based on energy conservation and environmental protection, the superb performance and economic benefits of magnesium and its alloys have attracted extensive attention. Many countries have invested a lot of human and financial resources in the research and development of magnesium-based materials, and the research results have been widely applied in various industrial fields. This is mainly reflected in the following areas: (1) The automobile industry: In response to the increasingly stringent requirements in almost all countries regarding exhaust emission, fuel consumption, and noise, automobile manufacturers seek to replace common components made of steel and lead alloys with ones made of magnesium alloys. As magnesium alloys are 77% lighter than steel and 36% lighter than lead alloys, the use of magnesium alloys can significantly reduce vehicle weight, thus reducing fuel consumption and exhaust emission. At present, North America ranks no. 1 in terms of magnesium alloy consumption in the automobile industry,

with an annual growth rate of 30%. In China, Shanghai Automotive Company takes the lead in applying magnesium alloys in the production of automobile transmission cases, bringing the annual magnesium consumption to a level higher than 2000 tonnes. (2) Electronic products: Nowadays, electronic products have become necessities in daily life, and electronic products are evolving towards small size and low cost. Compared with traditional engineering plastics that are widely used in electronic products, magnesium alloys have unique advantages in the miniaturization of electronic products thanks to a series of merits, including ease of being made into high-performance thin walls, high strength, and strong impact resistance. Magnesium alloys have been used in producing cases and parts of electronic products, and the market has been growing steadily. (3) Aerospace industry: Because of its light weight, magnesium alloys were used in the aviation industry during the First World War to reduce the weight of aircraft. Today, magnesium alloys are still used in the manufacture of some parts of military and civil aircraft, such as the support structure, which helps improve the dynamic performance of aircraft and reduce the weight. The application scope of magnesium alloys in the aerospace field will be expanded as the properties of magnesium alloys are gradually improved. (4) Other fields: Magnesium alloys have excellent mechanical properties and good formability, and magnesium is one of the essential metal elements of the human body. Thus, magnesium alloys can be used as a medical implant material. Because magnesium is light and comfortable to touch, it is also suitable for producing bicycles, wheelchairs, and other appliances that are used in daily life.

At present, China is the largest producer and exporter of magnesium in the world, accounting for more than 85% of the world's magnesium output. China's magnesium production capacity is highly concentrated in regions with low energy costs, such as Shaanxi, Shanxi, Xinjiang, and Inner Mongolia. As the regulations related to environmental protection become more and more stringent and competition becomes increasingly fierce, some magnesium smelting firms exit the market every year, bringing down the total number of magnesium smelting firms in China. At the end of 2018, there were over 80 magnesium smelting firms in China, most of which have small production capacity. The top ten firms accounted for only 37.7% of the total output, indicating a very low level of concentration in the industry.

According to statistics, China's output of metallic magnesium in 2017 was 912,600 tonnes, and the output in 2018 was 863,000 tonnes, a decrease of 5.44% compared with the same period of the previous year. Figure 1.1 shows the variation of China's magnesium output from 2014 to 2018.

According to customs statistics, China's export volume of metal magnesium in 2018 was 409,800 tonnes, which is a year-on-year decrease of 9.78%; the export amount of metal magnesium in the same year was 1.064 billion US dollars, which is a year-on-year decrease of 2.51%. In 2018, China's import of metal magnesium was 462.35 tonnes, which is a year-on-year increase of 27.83%; the import amount of magnesium in the same year was 12.4201 million US dollars, which is an increase of 44.18% year-on-year. Table 1.3 shows the statistical figures about China's import and export of magnesium from 2010 to 2018.

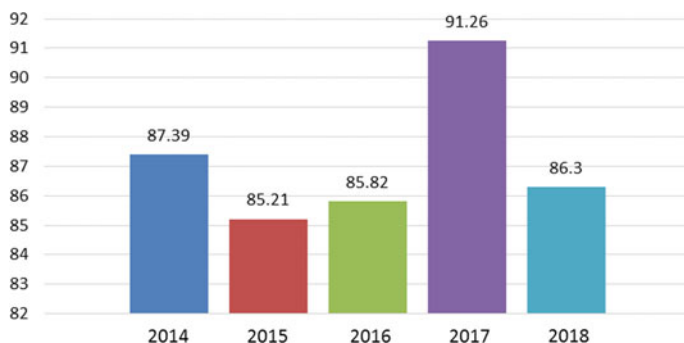


Fig. 1.1 Variations in China's magnesium output from 2014 to 2018 (in 10,000 tonnes)

Table 1.3 Statistical figures about China's import and export of magnesium from 2010 to 2018

Year	Import amount/USD	Import volume/kg	Export amount/USD	Export volume/kg
2010	\$5,042,727	1,021,566	\$1,062,226,022	383,980,095
2011	\$6,198,693	1,182,031	\$1,239,150,801	400,076,252
2012	\$4,792,884	694,501	\$1,157,021,413	371,084,410
2013	\$3,721,902	396,831	\$1,187,366,008	411,122,706
2014	\$9,387,038	1,325,233	\$1,171,995,186	434,996,136
2015	\$9,535,648	1,623,543	\$1,006,675,498	405,435,198
2016	\$11,433,999	736,283	\$852,234,148	356,536,970
2017	\$8,614,564	361,683	\$1,058,038,865	454,191,109
2018	\$12,420,097	462,348	\$1,031,497,935	409,788,162

It is estimated that the total demand for magnesium in China's metallurgical industry will be 278,200 tonnes in 2018, the demand in the metal processing fields (castings, die castings, and profiles) will be 156,400 tonnes, and the demand in other fields will be 12,000 tonnes. According to the data in recent years, the demand for metal magnesium has been increasing year by year, and the domestic supply and demand have reached a balance. Figure 1.2 shows the actual consumption and supply-demand balance of magnesium in China from 2014 to 2018.

1.2 Magnesium Mineral Resources

1.2.1 Global Distribution of Magnesium Mineral Resources

Magnesium resources are abundant and widely distributed in the world. Magnesium is one of the most abundant light metal elements on earth. Among all of the natural

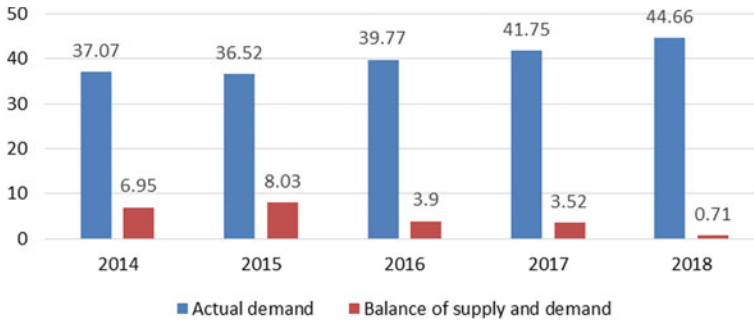


Fig. 1.2 Actual consumption and supply-demand balance of magnesium in China from 2014 to 2018 (in 10,000 tonnes)

elements on earth, magnesium ranks no. 8 in terms of content. The content of magnesium in the earth's crust is 2%, and by content, magnesium in seawater ranks no.3. Although magnesium is rich in nature and it is one of the most widely distributed elements in the earth's crust (ranking no. 8), it can only exist in nature in the form of compounds because of its high chemical activity. There are more than 200 kinds of ores that contain magnesium compounds, but only a few can be used as raw materials for magnesium smelting.

Magnesium is widely distributed across the world, and magnesium salt resources are extremely rich worldwide; they are available mainly in the forms of solid mineral resources and liquid mineral resources. Solid mineral resources mainly include magnesite, dolomite, serpentine, talc, brucite, and a small amount of other sedimentary minerals. Liquid mineral resources mainly exist in sea water, natural salt lake water, brine, etc., that occupy a large portion of the earth's surface. Liquid mineral resources are virtually inexhaustible. Natural brine can be regarded as a kind of recyclable resource, and so, the amount of magnesium minerals mined by humans will be regenerated in a relatively short time. Although more than 60 minerals contain magnesium, the majority of magnesium used in the world comes from dolomite, magnesite, brucite, carnallite, and olivine, followed by seawater bittern, salt lake brine, and underground brine. The current reserves of magnesium minerals can fully meet the human demand for magnesium, and there will not be shortage of supply in the foreseeable future. Table 1.4 shows the distribution of various types of magnesium mineral resources in the world [3].

Among the magnesium resources, magnesite is the principle magnesium mineral with value in industrial applications. According to the data released by the United States Geological Survey (USGS) in 2015, the world's proven reserves of magnesite minerals amount to 12 billion tonnes, among which 2.4 billion tonnes are exploitable reserves. Countries with rich reserves of magnesium minerals include Russia (650 million tonnes, accounting for 27%), China (500 million tonnes, accounting for 21%), and South Korea (450 million tonnes, accounting for 19%). The largest and highest-quality magnesite deposit in the world is located in Dashiqiao, Liaoning Province, China. Table 1.5 shows magnesite reserves of countries.

Table 1.4 Distribution of magnesium mineral resources

Mineral	Molecular formula	Magnesium content	Countries with the largest reserves
<i>Magnesium silicate</i>			
Serpentine	$3\text{MgO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$	26.3	Former Soviet Union, Canada
Olivine	$(\text{MgFe})_2\cdot \text{SiO}_4$	34.6	Italy, Norway
Talc	$3\text{MgO}\cdot 4\text{SiO}_2\cdot 2\text{H}_2\text{O}$	19.2	USA, Spain
<i>Magnesium carbonate</i>			
Magnesite	MgCO_3	28.8	China, India, USA
Dolomite	$\text{MgCO}_3\cdot \text{CaCO}_3$	13.2	China, the former Soviet Union, the United States
<i>Magnesium chloride</i>			
Bischofite	$\text{MgCl}_2\cdot 6\text{H}_2\text{O}$	12.0	China, the former Soviet Union, the United States
Carnallite	$\text{MgCl}_2\cdot \text{KCl}\cdot 6\text{H}_2\text{O}$	8.8	
<i>Magnesium sulphate</i>			
Magnesium sulfate	$\text{MgSO}_4\cdot \text{H}_2\text{O}$	17.6	
Jarosite	$\text{MgSO}_4\cdot \text{KCl}\cdot 6\text{H}_2\text{O}$	9.8	The former Soviet Union, China, the United States
Polyhalite	$\text{MgSO}_4\cdot \text{K}_2\text{SO}_4\cdot 2\text{CaSO}_4\cdot 2\text{H}_2\text{O}$	4.0	Germany
Anhydrous jarosite	$2\text{MgSO}_4\cdot \text{K}_2\text{SO}_4$	11.7	
Albite	$\text{MgSO}_4\cdot \text{NaSO}_4\cdot 4\text{H}_2\text{O}$	7.0	China

1.2.2 Distribution of Magnesium Mineral Resources in China

China is one of the countries with the most abundant magnesium resources in the world, with total reserves accounting for 22.5% of the world's total. China has many varieties of magnesium mineral resources, including magnesite, dolomite, and salt lake magnesium salt, and they are widely distributed across the country. The magnesium minerals that have been mined and used include dolomite, magnesite, carnallite, and potassium magnesium salts in Qarhan, Qinghai Province. There are 27 mining areas with proven magnesite reserves in China, and these are distributed in 9 provinces (regions). Liaoning Province ranks no. 1 in terms of magnesite reserves, accounting for 85.6% of the country's total. Liaoning, Shandong, Tibet, Xinjiang, and Gansu, also have large magnesite reserves.

At present, the proven dolomite reserves in China amount to 4 billion tonnes, the magnesite reserves are about 3.47 billion tonnes, and the prospective reserves of magnesium salt resources in salt lake areas are more than 8 billion tonnes (the

Table 1.5 Magnesite reserves of countries in the world (100 million tonnes)

Country	Reserve
U.S.A	0.1
Australia	0.95
Austria	0.15
Brazil	0.86
China	5
Greece	0.8
India	0.2
Korea	4.5
Russia	6.5
Slovakia	0.35
Spain	0.1
Turkey	0.49
Other countries	3.9
Global total	23.9

magnesium salt reserve in Qarhan Salt Lake in Qinghai Province is about 4.82 billion tonnes) [3]. The total magnesium resources of China account for 22.5% of the world's total, ranking no.1 in the world [4–6].

1. Dolomite

China is also rich in magnesium-bearing dolomite, with proven reserves of more than 4 billion tonnes. Dolomite resources are found in all provinces and regions of China, especially Shanxi, Ningxia, Henan, Jilin, Qinghai, and Guizhou. Dolomite deposits can be divided into hydrothermal type and sedimentary type according to their properties. Hydrothermal deposits have been widely developed in eastern Liaoning region and Jiaodong region, and sedimentary deposits are mainly distributed in Shanxi, Henan, Hunan, Hubei, Guangxi, Guizhou, Ningxia, Jilin, Qinghai, Yunnan, and Sichuan provinces [7].

Most dolomites are secondary sediments that resulted from the metasomatic process between a magnesium-containing solution and limestone. Only in high salinity lakes can thick dolomites and primary sedimentary dolomites be formed directly. Dolomite is a compound salt mineral composed of magnesium carbonate and calcium carbonate. The theoretical mass fraction is 21.7% dolomite, 30.4% CaCO_3 , and 47.9% CO_2 [8], and the mass ratio of CaO to MgO is 1.394. In natural dolomite minerals, the mass ratio of CaO to MgO is in the range of 1.4–1.7, the relative density is 2.8–2.9 $\text{g} \times \text{cm}^{-3}$, and the Mohs hardness is 3.4–4. Dolomite crystals are hexagonal, their common color is white with a tint of yellow or brown, and they have a glass luster.

Because dolomites contain impurities, their chemical and physical properties may vary. The structures of dolomites can be roughly divided into two types [9, 10]: one

is a hexagonal rhombic structure, and the other is an amorphous network structure. Compared with dolomites that have a network structure, the calcined dolomites with a hexagonal rhombic structure are easy to grind, do not stick to the grinder, have low reaction activity [11], and are brittle. The dolomites with an amorphous network structure retain the structural characteristics of dolomite after calcination, have low lattice energy, and have lower heat absorption than dolomites with hexagonal rhombic structure during thermal decomposition. Because of these properties, the calcination time of dolomites with an amorphous network structure is much shorter than that of dolomites with a hexagonal rhombic structure.

Dolomites are widely distributed in the world. In addition to China, the major producers of dolomites are Switzerland, Italy, North England, and Mexico. When dolomite is used as a raw material for magnesium smelting, the thermal reduction method is usually used. Dolomites can also be used in building materials, ceramics, the chemical industry, and other fields.

China is also rich in magnesium-bearing dolomites, with more than 4 billion tonnes of proven reserves and 208 explored mining areas. The dolomite resources are widely distributed across the country. Almost all provinces and regions in China have dolomite mines, represented by Hunan, Sichuan, Shandong, Hebei, Shanxi, Liaoning, Jilin, and Inner Mongolia. At present, most of the deposits have been exploited. According to the Overall Plan of Mineral Resource Exploitation in Shanxi Province (2016–2020), the retained reserves of magnesium minerals (magnesium dolomite) in Shanxi Province were 845 million tonnes by the end of 2015, accounting for 30% of the country's total and ranking no. 1 in China. In recent years, Shanxi Province has developed a circular industrial chain of using the exhaust gas of a blue coal (a kind of clean coal produced using high-quality coals mined from the mines in Fugu, Shenmu, and other places in Shaanxi Province) production facility to produce ferrosilicon and then using ferrosilicon to reduce metal magnesium, achieving great cost savings. Consequently, the raw magnesium output of Shaanxi accounted for 62% of China's total, and the share of Shanxi Province declined to 14%.

Because dolomite can be used as a refractory material, electrical insulation material, chemical building material, advanced ceramic material, and sealing material, it has the potential of being used widely in various fields. China has huge reserves of high-quality dolomite with a potentially wide application scope, and the magnesium alloy products that are developed with dolomite as a raw material play an important role in China's economic and social development.

The composition of dolomite varies depending on place of origin. Table 1.6 shows the compositions of dolomite ores mined from several typical dolomite mining areas.

At present, all of the dolomite mines are open-pit mining, and most of them supply building materials for residents. The Baiyunan dolomite deposit in Nanjing, Jiangsu Province is the first deposit to have been exploited, and it has developed into a large-scale mine with a high level of mechanization. The dolomite ores are high quality, and more than 50% of the ores have a MgO content higher than 20% and a SiO₂ content less than 2%. With an annual mining capacity of over one million tonnes, the mine mainly supplies dolomite to serve as a refractory material and flux in the

Table 1.6 Compositions of dolomite ores mined from several typical dolomite mining areas in China

Place of origin	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Loss on ignition
Great Stone Bridge	0.32	0.39	0.89	30.28	21.72	47.08
Wulong Spring	0.03	0.05	0.34	31.75	20.02	47.10
Lacao Mountain, Guyang	1.53	0.14	0.75	30.10	19.48	46.13
Yutian	0.27	0.10	0.03	30.52	21.91	46.80
Zhoukoudian	0.55	0.08	0.16	29.06	21.93	46.24
Zhen'an, Shaanxi Province	1.90	0.58	0.58	30.00	21.00	46.94
Zhenjiang	1.17	0.37	0.18	30.80	21.16	47.07

production processes of Baoshan Iron and Steel Company and Ma'anshan Iron and Steel Company.

In the late 1980s, dolomite was used as a raw material for magnesium smelting in silicothermic magnesium smelting plants, and magnesium smelting plants usually use magnesium ores mined from nearby mines. To date, there is still no unified quality standard for dolomite that is used in magnesium smelting. Before a newly-built magnesium smelting plant is put into operation, it is necessary to carry out lab-testing on the quality of dolomite ore to be used in the magnesium smelting process because the ore quality has a great impact on the technical and economic indicators of magnesium production. First, the chemical composition of the ore should meet the requirement of $\text{MgO} > 20\%$, $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 \leq 1\%$, $\text{SiO}_2 \leq 1\%$, and $\text{Na}_2\text{O} + \text{K}_2\text{O} \leq 0.1\%$. Second, the structural characteristics of the ore should be considered. The ore structure has a certain influence on the magnesium smelting processes, such as calcination and ball making.

With the rapid development of silicothermic magnesium smelting plants in recent years, the consumption of dolomite mineral resources also increased. In 1992, the total consumption in China was about 100,000–130,000 tonnes, and this figure reached 650,000–7,150,000 tonnes in 2007, which is a 65-fold increase.

2. Magnesite mineral

According to the data released by USGS in 2015, the global magnesite output in 2014 was 6.97 million tonnes, which is an increase of 60,000 tonnes over the same period of the previous year. China is the biggest producer of magnesite, accounting for 70.3% of the world's total. China has a large magnesite reserve, second only to that of Russia. Most of China's magnesite reserves are concentrated in large deposits in a few regions. There are 27 mining areas with proven magnesite reserves in China, and these are distributed in 9 provinces (regions). Liaoning Province ranks No. 1 in terms of magnesite reserves, accounting for 85.6% of the country's total. In addition to Liaoning Province, there are also large magnesite reserves in Shandong, Tibet, Xinjiang, and Gansu (Table 1.6). Table 1.7 shows proven reserves of magnesite minerals in China from 2015–2017.

Table 1.7 Proven reserves of magnesite minerals in China from 2015–2017

Mineral	Unit	2015	2016	2017	Forecast resources
Magnesite	Ore, 100 million tonnes	29.7	30.9	31.15	131.4

Table 1.8 Global magnesite output (1000 tonnes) in the period of 2013–2014

Country	2013	2014
U.S.A	10	5
Australia	130	130
Austria	220	200
Brazil	140	150
China	4900	4900
Greece	100	115
India	60	60
Korea	70	80
Russia	370	400
Slovakia	200	200
Spain	280	280
Turkey	300	300
Other countries	130	150
Global total	6910	6970

For various reasons related to policies, the output of magnesite in other countries is far less than that in China. Table 1.8 shows the global magnesite outputs (1000 tonnes) in the period of 2013–2014.

Magnesite is the main raw material used for smelting metal magnesium. It is a carbonate mineral with a trigonal system. Its molecular formula is MgCO_3 , and its theoretical composition in mass fractions is: 47.81% MgO and 52.19% CO_2 . Magnesite minerals have two structures: an amorphous structure and a crystalline structure. The former has no luster, and the latter belongs to the hexagonal system, which has a glassy luster. The color of magnesite is mostly white or light yellow and sometimes light red, but the color is brown when the magnesite contains iron. When magnesite is used as a raw material for magnesium smelting, either an electrolysis method or silicothermic method can be used. Magnesite can also be used as a refractory material, building material, and chemical raw material.

Magnesite belongs to the calcite group and is a carbonate mineral. Its main component is MgCO_3 , and it often contains impurities such as CaCO_3 , FeCO_3 , MnCO_3 , Al_2O_3 , and SiO_2 . With the presence of impurities, magnesite often turns into calcium magnesite, iron magnesite, manganese magnesite, aluminum magnesite, silica magnesite, and so on. Magnesite crystal is rare. It belongs to the trigonal system. Magnesite can be divided into two types according to its mineral characteristics: crystalline magnesite and amorphous magnesite. The aggregates are usually

dense blocks or grains, exhibiting grayish white, white, light red (containing Co), or yellowish brown (containing Fe) colors. Their density is in the range of $2.9\text{--}3.1 \text{ g} \times \text{cm}^{-3}$, and their hardness is in the range of 3.5–4.5.

At present, the proven reserves of magnesite in the world are about 13 billion tonnes. China's total reserve of magnesite accounts for 1/4 of the world's total, with the proven reserves reaching 3.1 billion tonnes and the retained reserves being 3.0 billion tonnes. Both the proven reserves and retained reserves of China rank no. 1 in the world [12]. The reserves of other major magnesite-producing countries are: the former Yugoslavia: 14 million tonnes; Greece: 30 million tonnes; Brazil: 40 million tonnes; North Korea: 3 billion tonnes; Canada: 60 million tonnes; the United States: 70 million tonnes; Austria: 80 million tonnes; India: 100 million tonnes; the Czech Republic: 500 million tonnes; New Zealand: 600 million tonnes; the former Soviet Union: 2.2 billion tonnes [13]. In China, 27 magnesite deposits distributed in 9 provinces and autonomous regions have been identified. A large portion of reserves is concentrated in Laizhou, Shandong Province (286 million tonnes) and the southern part of Liaoning Province (2.569 billion tonnes). The aggregate reserves of these two regions are 2.855 billion tonnes, accounting for 95.2% of the country's total. In contrast, the aggregate reserves of Sichuan, Qinghai, Tibet, Anhui, Gansu, Xinjiang, and Hebei are only 145 million tonnes, accounting for 4.8% of the country's total. The major magnesite production firms are located in Yexian County (Shandong Province) and Dashiqiao and Haicheng (Liaoning Province). As China is the biggest producer and exporter of magnesite resources in the world, there is a strong demand for China's magnesite in the international market. China's magnesite-producing firms have a strong competitive advantage in the international even through their magnesite production processes are not very advanced. However, we should also have a clear understanding that China still lags far behind some developed countries in the utilization of magnesite resources, wasting a lot of ore resources [14].

Magnesite deposits can be divided into four types: hydrothermal metasomatism, metamorphosed sedimentary, vein filling, and weathered residual. The most important industrial type of deposit is the metamorphosed sedimentary type, which is also the type that is most intensively exploited by domestic and foreign firms. Deposits of this type are bigger than the other types, with reserves ranging from a few millions tonnes to hundreds of millions tonnes. Moreover, the deposits are mostly planar or have the shape of a lens, with dozens of layers. The ore quality is excellent, and the content of MgO is in the range of 35–47%. The magnesite resources in China are characterized by shallow burial, good quality, and large-scale deposits, and the proportion of carbonates can reach 96%. Among the 27 magnesite mining areas in China, there are 11 large-scale deposits with a reserve equal to or larger than 50 million tonnes. The aggregate reserve of these mining areas accounts for 95% of the country's total. Relevant data show [15] that among the retained reserves of magnesite mineral, ores of high quality (super class and class 1) account for more 37.58%. Table 1.9 shows the compositions of ores mined from major magnesite mineral areas in China.

It can be seen from the data in the above table that once the magnesite ores in the magnesite mines in Liaoning, Shangdong, Sichuan, and other provinces are mined,

Table 1.9 Compositions of ores mined from major magnesite mineral areas in China (%)

Component		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Loss on burning
Liaoning	Haicheng super class	0.17	0.12	0.37	0.50	47.30	51.13
	Haicheng Xiafangshen	0.26	0.06	0.27	0.45	47.30	50.99
	Dashiqiao class-1 mine	1.90	0.47	0.50	1.14	45.80	48.87
	Huaidong section of Qingshann Mine	0.66	–	–	0.73	46.91	–
	Yingkou Class-1 mine	1.13	0.21	0.33	0.33	47.14	50.97
Shandong	Yexian West Mine class-1 Mine	0.90	0.18	0.55	0.37	47.00	51.11
	Yexian West mixed class	4.95	1.39	0.93	0.86	44.08	47.33
	Yexian East mixed class	3.87	0.59	0.58	0.75	46.43	48.21
Sichuan	Ganluo Yandaii	0.24	–	–	4.30	44.41	–
	Hanyuan Guidai	0.10	–	–	0.80	46.91	–
Dahe, Xingtai, Hebei Province		0.30	–	–	3.94	42.53	–
Biegai, Subei, Gansu		0.25	–	–	4.58	43.81	–

they can be used as MgO after roasting. In China, most of the magnesite mines are operated in the open-pit mining mode. For the magnesite ores mined from the Haicheng and Dashiqiao magnesium mines, the electrolysis method can be used for magnesium smelting. Haicheng magnesium mine is located in Pailouling, which is southeast of Haicheng City, Liaoning Province. In the mining area, there are super high-quality magnesite deposits in the Xiafangshen, Jinjiapu, and Wangjiapu areas. This mining will last 25 years, and the ores of class-1 and super class quality account for 50–55% of the total. The production capacity of this magnesite mine is 1.7 million ton/year, the stripping amount is 2.8 million ton/year, the total annual excavating and stripping amount is 4.5 million ton/year, the average stripping-to-excavating ratio is 0.85, the mining recovery rate is 92%, the annual labor productivity of mining workers is 5948.9 ton/person, and the unit mining cost is 26.73 yuan/ton.

3. Carnallite

Carnallite is an aqueous complex salt composed of MgCl₂ and KCl, and its molecular formula is KCl·MgCl₂·6H₂O. Theoretically, the contents of MgCl₂, KCl, and H₂O are 34.5%, 26.7%, and 38.8%, respectively. The molar ratio of MgCl₂-to-KCl is 1. Carnallite belongs to the orthorhombic system. Pure carnallite is white. Because natural carnallite minerals contain impurities, such as NaCl, NaBr, MgSO₄, and FeSO₄, they exhibit various colors, including pink, yellow, gray, and brown. The hardness of carnallite is 1–2, and the specific gravity is 1.62 g × cm⁻³. The largest

carnallite deposits in the world are located in the Urals of the former Soviet Union and the Elbe area of eastern Germany. There is also a large amount of high quality carnallite in Qinghai Salt Lakes of China [16].

4. Serpentine

Serpentine, whose chemical formula is $Mg_3Si_2O_5(OH)_4$, is composed of silicon oxygen tetrahedra and magnesium hydroxide octahedra layer-by-layer at a ratio of 1:1. One layer of magnesium hydroxide octahedra and one layer of silicon oxygen tetrahedra form a crystal layer [17]. Theoretically, the contents of H_2O , SiO_2 , and MgO are 12.9%, 44.1%, and 43%, respectively. Because the serpentine ore usually contains a small amount of oxides of Al, Fe, Ni, and Ca, its chemical composition and the theoretical contents of chemicals in it vary from one deposit to another and even vary from one section to another section of the same deposit.

China has rich serpentine resources. With more than 1.5 billion tonnes of proven reserves distributed across the country, China has an obvious advantage in exploiting serpentine [18]. Among all serpentine resources, the reserves in the western region account for 98% of the country's total (only the reserves in the western and eastern Mangya mining areas in Qinghai Province claim a share of 48%), and the reserves in the remaining regions only account for 2% of the country's total. By provinces, Qinghai Province boasts the largest reserves, accounting for 63% of the country's total, followed by Sichuan Province (20%) and Shaanxi Province (12%). These three provinces combined account for 95% of China's serpentine reserves.

5. Liquid mineral resources (magnesium salt resources in salt lakes of China)

China's salt lakes containing magnesium salts are mainly distributed in the northern part of the Tibet Autonomous Region and Qaidam Basin of Qinghai Province. The reserves of magnesium salts in Qaidam Basin account for 99% of the total proven magnesium salt reserves in China. Magnesium salt resources in the Qaidam Basin are mainly distributed in Chaerhan Lake, Yiliping Lake, East Taijinar Lake, West Taijinar Lake, Dalangtan Lake, Kunteyi Lake, Mahai Lake, and other salt lakes. The salt lakes of Qarhan, Yiliping, East Taijinaer, and West Taijinaer have only magnesium chloride, whereas Dalangtan, Kunteyi, Mahai, Dachaidan, and other mining areas have basically equal amounts of magnesium chloride and magnesium sulfate. The total proven reserves of magnesium chloride are 4.281 billion tonnes (including 1.908 billion tonnes of basic reserves), and the retained reserves are 4.070 billion tonnes (including 1.798 billion tonnes of basic reserves). The total proven reserves of magnesium sulfate are 1.722 billion tonnes, including 1.229 billion tonnes of basic reserves.

Liquid mineral resources mainly exist in underground brine, salt lake water, and sea water. Containing 2×10^{15} tonnes of magnesium, sea water is the largest repository of magnesium mineral resources. Each year, large amounts of $MgCl_2$ and $MgSO_4$ are extracted from underground brine, salt lake brine, and seawater. Salt lakes usually refer to lakes that have a salt content higher than 35%. A salt lake is a place where various mineral resources concentrate. Most of China's salt lakes are distributed in

Qaidam Basin, Qinghai Province, the northern Tibet Autonomous Region, Shanxi Province, and Gansu Province. The salt lakes in these regions account for 99% of the identified magnesium salt resources in China. Among these salt lakes, Yuncheng Salt Lake in Shanxi Province contains 6.5×10^9 tonnes of magnesium salts, Qarhan salt lake of Qinghai Province contains more than 3.0×10^9 tonnes, and the salt lake deposits in Gansu Gaotai County contain 2.9×10^6 tonnes [19]. Magnesium salt resources in the Qaidam Basin are mainly distributed in Chaerhan Lake, Yiliping Lake, East Taijinar Lake, West Taijinar Lake, Dalangtan Lake, Kunteyi Lake, Mahai Lake, and other salt lakes. Among magnesium salts, magnesium chloride and magnesium sulfate are the two-dominant species. The salt lakes of Qarhan, Yiliping, East Taijinaer, and West Taijinaer have only magnesium chloride, whereas Dalangtan, Kunteyi, Mahai, Dachaidan, and other mining areas have basically equal amounts of magnesium chloride and magnesium sulfate. The total proven reserves of magnesium chloride are 4.281 billion tonnes (including 1.908 billion tonnes of basic reserves), and the retained reserves are 4.070 billion tonnes (including 1.798 billion tonnes of basic reserves). The total proven reserves of magnesium sulfate are 1.722 billion tonnes, including 1.229 billion tonnes of basic reserves [20].

The brine in Yuncheng Salt Lake belongs to the Na^+ , $\text{M}^{2+}/\text{Cl}^-$, and $\text{SO}_4^{2-}-\text{H}_2\text{O}$ quaternary system. The lake is a sulfate-type compound salt lake, containing 9.3 million tonnes of magnesium salts. For a long time, the main product of the mining activity at Yuncheng Salt Lake has been anhydrous sodium sulfate. At present, the annual output has reached 3.6 million tonnes, accounting for more than 30% of the country's total.

At present, all of the large amount of high-quality magnesia used in the production facilities in China is extracted from brine. For example, there are 31 salt lakes containing potassium and magnesium salts in Qinghai Province. Among them, the Chaerhan Salt Lake located in the middle and eastern Qaidam Basin is the largest and shows a trend of drying up. The lake hosts a modern sedimentary deposit mainly composed of liquid potassium and magnesium salts. The mining area is 5856 km^2 , and the altitude is 2677–2680 m. The reserve of intercrystalline brine is as large as 6.73 billion m^3 , belonging to the $\text{NaCl-KCl-MgCl}_2-\text{H}_2\text{O}$ quaternary system. It is now in the deposition period of potassium carnallite ($\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$) and bischofite ($\text{MgCl}_2\cdot 6\text{H}_2\text{O}$). Carnallite and bischofite can be obtained from brine through natural freezing and exposure to sunshine. They can be used as raw materials for magnesium smelting. At the end of 1992, an industrial test of the smelting magnesium process with potassium carnallite serving as the raw material started in Qinghai Minhe Magnesium Plant was conducted. After the test was successful, the process was applied in industrial production, using carnallite as the raw material. The carnallite is composed of KCl (17–20%), MgCl_2 (28–30%), NaCl (10–15%), and CaSO_4 (85%); 25 tonnes of carnallite is needed to produce 1 ton of metal magnesium.

Using magnesium salts from salt lakes to produce metal magnesium is also an important development direction, as exemplified by the metal magnesium smelting plant (under construction) of Qinghai Salt Lake Industrial Group whose production capacity will be 400,000 ton/year. The magnesium smelting processes include the Pidgeon process (silicothermic reduction method) and the electrolysis method. At

present, most magnesium smelting plants use the Pidgeon process. In 2010, the output of metal magnesium produced by the Pidgeon process in Shanxi Province reached 380,000 tonnes, accounting for 60% of the country's total.

At large salt lakes in the United States, bischofite is extracted to produce a series of magnesium salts, including powdery magnesium oxide, high-purity magnesium hydroxide, light burned magnesium oxide, and heavy burned magnesium oxide, forming an industrial chain of magnesium products. In the 1980s, Yamaguchi Company of Japan developed a technique for preparing magnesium sulfate whiskers. China has also done a lot of work in exploiting magnesium halide resources in salt lakes and developed processes to produce magnesium chloride hexahydrate, potassium magnesium sulfate fertilizer, ordinary magnesium sulfate, ordinary magnesium hydroxide, and flame retardant magnesium hydroxide. However, most of them are low value-added traditional products. There are few reports on the industrialization of high value-added products such as high-purity magnesium sulfate and flame-retardant magnesium hydroxide.

China is a top possessor of magnesium mineral resources in terms of both quantity and quality. This gives China a unique advantage in the exploitation and utilization of magnesium mineral resources [21], and thus, there are very favorable conditions for developing magnesium and magnesium alloy products in China. At the same time, there are still some problems in the exploitation and utilization of magnesium mineral resources in China, and these are mainly manifested in the following aspects [22].

First, although the total reserve of magnesium resources of China is enormous, the per capita resource is small, and the resources are unevenly distributed in different regions [23]. Among the magnesium resources, the proven reserves are less than the controllable reserves, and the consumption rate of magnesium resources will gradually exceed the growth rate of reserves, as indicated by the declining retained resources in most mining areas. However, the number of newly discovered magnesium mineral deposits is decreasing gradually, resulting in a shortage of backup reserves.

Second, most of the firms producing metal magnesium and magnesium alloys in China are small in scale; their production equipment is not sophisticated, and their technologies are not very advanced. Consequently, their production activities often cause serious water and air pollution. At present, firms producing metal magnesium and magnesium alloys in China mainly produce low value-added products, and low technology content is therefore still trapped in the development mode of "survival at the cost of environment and resources". China has yet to fully exploit its advantage of magnesium mineral resources.

Third, there is a serious problem of overmining magnesium resources, resulting in a low utilization level of magnesium resources. The problem is most pronounced in the production and utilization of magnesite and dolomite: there is a lack of classification systems for more efficient utilization of the ore resources of the same kind.

Fourth, mining activities inflict serious damage to the ecological environment in mining areas. When the stratum containing the dolomite is older, the content of MgO

in the ore is higher. Dolomite rocks that are hard can therefore withstand weathering better than many other rocks. So, they are usually found at high positions, and their mining process usually begins with large-scale blasting. Differing from dolomite, most magnesite and serpentine deposits are shallow, which is suitable for large-scale open-pit mining. Generally speaking, because of the lack of supervision and management of mining activities, mining of magnesium ores in a mining area is usually accompanied by damage to a large area of surface vegetation, inflicting serious damage to the ecological environment and affecting the ecological balance.

Fifth, there is a serious workplace safety problem in mining areas. In the process of ore mining, the operation is often carried out in a disordered manner as a result of the lack of planning, giving rise to safety accidents. Therefore, it is necessary to take measures to standardize the operation, strengthen supervision, and improve planning to achieve the best results in the exploitation and utilization of magnesium resources.

1.3 Development History of the Magnesium Industry

1.3.1 Development Course of the Magnesium Industry

From 1808 to the present, the development of the magnesium industry has continued for more than 200 years, and the industrial production era of magnesium has spanned more than 130 years since 1886. Before the 1950s, the development of the magnesium industry mainly relied on the military industry. Demand by the military industry, especially with the outbreak of two world wars, was a significant stimulus for the world's magnesium output. Magnesium output increased significantly during war and fell at the end of war. In 1910, the world's magnesium output was about 10 tonnes. In 1914, World War I broke out, and the world's output of primary magnesium increased to 350 tonnes the following year. By the end of the war in 1917, the world's output of primary magnesium had boomed to 3000 tonnes. With the end of the war, the world's annual output of primary magnesium fell to 330 tonnes in 1920. Similarly, under the stimulus caused by World War II, the world's magnesium output increased to 32,000 tonnes in 1939 and reached a peak of 235,000 tonnes in 1943. At the end of the 1940s, the world's annual magnesium output dropped again.

Roughly speaking, the development of the magnesium industry has gone through three stages. The first stage is the chemical method stage. British chemist Humphrey Davy electrolyzed a mixture of magnesium oxide and mercury and obtained magnesium amalgam as an electrolytic product. After removing mercury from the magnesium amalgam via distillation, silver-white metallic magnesium was obtained; this was the first appearance of magnesium in its elemental form, but the output was very small [24]. By 1831, French scientist Antoine Alexandre Brutus Bussy used molten anhydrous magnesium chloride (MgCl_2) and potassium vapor as raw materials to initiate a reduction reaction that produced a large amount of metallic magnesium in the laboratory for the first time [24]. Scientists in Britain, the United States, and other

countries did not begin to use chemical methods to prepare metallic magnesium until the 1860s, and a slight increase in the output of metallic magnesium was achieved. This stage is considered to be the first stage of the development of the magnesium industry, specifically, the chemical method stage. Magnesium production in this stage was generally limited to small-scale laboratory production and industrial production did not emerge. This stage lasted for 78 years until the world's first magnesium plant was completed in 1886.

In 1833, British scientist Michael Faraday achieved the first electrolytic reduction of molten MgCl_2 to produce metallic magnesium. In 1852, German chemist Robert Bunsen studied the use of electrolysis for producing metals. He was the first to successfully produce metallic magnesium via electrolysis of molten MgCl_2 , and he established the world's first electrolytic cell and used it for the electrolysis of anhydrous MgCl_2 . In 1886, Germany established the first industrial-scale electrolysis cell and implemented industrial production of magnesium. Griesheim-Elektron constructed the world's first facility for commercial production of magnesium in Stassfurt. In 1860, Johnson Matthey and CoinMna-Chester began to use similar processes to produce magnesium. In 1896, British Chemische-Fabrik Griesheim-Elektron and Aluminum Magnesium Fabrik jointly purchased the electrolytic magnesium process. Until 1914–1915, these companies remained the world's most important manufacturer of magnesium. In 1916, the US DOW Chemical Company established a magnesium smelting plant that was the world's largest magnesium company at that point, making DOW the world's leading manufacturer of magnesium. This time period is considered to be the second stage of the development of magnesium industry and is called the electrolytic smelting stage. As the demand for magnesium in market increased on a year by year basis along with continuous improvements to the electrolysis process and equipment, the electrolytic smelting method to produce magnesium has been one of the world's leading processes [3]. More than 80% of magnesium in developed countries is produced via electrolytic smelting.

The structure of electrolytic cell for magnesium has changed a lot since the magnesium electrolytic cell was used in industrial production at the end of the nineteenth century. The original electrolytic cell was a simple electrolytic cell without a diaphragm. Since the 1930s, this electrolytic cell has included a diaphragm. Since the 1960s, a new type of magnesium electrolytic cell without a diaphragm emerged and has been used, and this cell promoted the magnesium industry into a new stage of development. Until the mid-1990s, production of magnesium via electrolysis has always been dominant approach, and its output accounted for 70–75% of the total magnesium output.

As people's demand for magnesium and magnesium alloys continues to increase, the production of metallic magnesium via electrolysis alone cannot sufficiently meet people's needs any more. Several scientists have used chemical methods to study the smelting of magnesium-containing ore via thermal reduction. Therefore, the third stage in the development of the magnesium industry is called the thermal reduction stage. Because the application of magnesium and its alloys have gradually been extended, the demand for magnesium has increased accordingly. In 1913, the vacuum thermal reduction method was used for the process of reducing magnesium oxide

to make magnesium. The first method using silicon as a reducing agent to reduce magnesium oxide to produce metallic magnesium emerged in 1924. The use of silicon aluminum alloy as a reducing agent to reduce magnesium oxide to produce magnesium was achieved in 1932. In 1941, Professor L. M. Pidgeon of the University of Toronto in Canada successfully established a pilot plant in Ottawa where ferrosilicon was used as a reducing agent to extract magnesium in a vacuum reduction tank [25]. The silicothermic smelting process for magnesium is named after Professor L. M. Pidgeon and called the Pidgeon process. The Pidgeon process and the electrolysis process are still the two main magnesium smelting methods. In the early 1950s, a new thermal reduction smelting technology for magnesium was proposed by the French Pedmey Electric Metallurgical Company. This process uses ferrosilicon or aluminum as a reducing agent to reduce dolomite, and then magnesium is obtained in a large internally-heated furnace. This process is called the magnetherm method and is a semicontinuous method. The smelting method underwent rapid development in the middle of the twentieth century, and the amount of primary magnesium produced via this method accounts for one-half of the total output of primary magnesium in industrially developed countries. Since the early 1970s, the magnetherm method has been used and promoted in France, the United States, the former Yugoslavia, and Brazil. In China, magnesium is mainly produced through the Pidgeon process, and it has gradually become a advanced technological methods used in the production of magnesium industry today. In the late 1980s, with the further development of the Pidgeon method in China, the electrolytic smelting process was gradually replaced in the field of magnesium production. For instance, several magnesium plants that were planned by the U.S. Dow Chemical Company, Bosglon in Norway, Noranda Company in Canada, Puji Company in France, and Northwest Alloy Plant of the United States and Australia have stopped construction or have been postponed. Among the production enterprises currently operating abroad, the large-scale plants (with a capacity around 50,000 t/year) still use the electrolytic method. For example, the American Magnesium Company has a production capacity of 43,000 tonnes per year, and the Israeli Dead Sea magnesium plant has a production capacity of 55,000 tonnes per year. In addition to Commonwealth of Independent States (CIS) countries, the current foreign metal magnesium production capacity is 100,000–120,000 tonnes per year, and the products they produce still have a wide international market. The advantages and disadvantages of the two magnesium smelting methods are compared (Table 1.10).

1.3.2 Worldwide Distribution of Magnesium Industry (Outside of China)

Since 1960, various excellent properties of magnesium and its alloys have been gradually discovered, and the use of magnesium in the civilian market has greatly promoted the development of the magnesium industry. Magnesium has been widely used as an

Table 1.10 Comparison of two magnesium smelting method

Items	Electrolysis	Silicothermic (Pidgeon process)
Principle	The solution containing $MgCl_2$ is dehydrated to form anhydrous $MgCl_2$. The electrolysis of anhydrous or molten $MgCl_2$ produces metallic magnesium	Carbonate ore is calcined to produce magnesium oxide, and ferrosilicon is used for thermal reduction to produce metallic magnesium
Raw materials	Brine, magnesite, carnallite, etc	Dolomite
Advantages	Energy savings, good product uniformity, continuous production process	Low investment in equipment, low technical difficulty, high purity magnesium and abundant resources
Disadvantages	The preparation of anhydrous $MgCl_2$ is relatively difficult to control; dehydration requires higher temperature and an acidic atmosphere, has a higher energy consumption, causes prominent corrosion on equipment, and the treatment cost for "waste water, waste gas and waste residue." are large	Low heat utilization rate, short life of reduction furnace, discontinuous production process
Portion of production capacity	About 20%	About 80%

additive in materials such as aluminum-based alloys, architectural aluminum profiles, and beverage cans. Meanwhile, the continuous development and progress of magnesium production technology has expanded the production scale, increased output, and reduced energy consumption and costs.

After 1970, metallic magnesium began to be used for desulfurization in the steel-making process and became one of the main desulfurizers in the pre-treatment of hot metal. At the same time, for the reason of light weight, pressure castings made by magnesium and magnesium alloy have begun to be used in cars to reduce the weight and energy consumption of vehicles [26]. Since 1990, developments in magnesium-containing composite materials and ultralight magnesium-lithium alloys have further expanded the application scope of magnesium, spreading to include almost all industrial fields.

After entering the twenty-first century, the application and promotion of magnesium in various fields have gradually stabilized, and thus the world's primary magnesium output tended to increase steadily. China and Russia possess the largest magnesium processing equipment. These two countries produce two-thirds of the world's magnesium oxide. Japan, the Netherlands, and the United States mainly extract magnesium from seawater and brine. Their output of magnesium oxide accounts for about 52% of the total global magnesium output from seawater and brine. Australia,

Brazil, China, Iran, Israel, Japan, South Korea, Mexico, Norway, Russia, Turkey, the United Kingdom, and the United States also produce electrically-fused magnesia. In 2012, the global production capacity of fused magnesia increased by 175,000 tonnes, and the annual global production capacity of dead-burned magnesia was approximately 8.5 million tonnes.

According to data released by the US Geological Survey in 2015, the global output of primary magnesium in 2014 was 907,000 tonnes, year-on-year rises is 29,000 tonnes. China's output of primary magnesium is the highest in the world, accounting for 88.2% of the total world output. Besides China, the major producers of magnesium are Israel (30,000 tonnes), Russia (28,000 tonnes), and Kazakhstan (21,000 tonnes).

The main foreign magnesium manufacturers and their outputs are shown in Table 1.11. Table 1.12 shows the world's main magnesium-producing countries and their outputs.

Although the world's magnesium industry has developed rapidly, the production and development of primary magnesium has been unbalanced. After the 1990s, because of the impacts of the rapid increases in the output and export volumes of China's magnesium industry [27], some countries (such as France) have had to close a number of magnesium smelters, and in some countries such as Canada and Australia, it was difficult to construct new magnesium plants or to put them into normal production. The magnesium plant of Japan's Udu Kosan Co., Ltd. also withdrew from the world's magnesium smelting industry [28]. At present, apart from China, the main

Table 1.11 Major foreign magnesium manufacturers and productions

Nations	Company name	Annual production capacity (10,000 tonnes)
Israel	Dead Sea Magnesium Co., Ltd	3.3
Russia	Solsmck magnesium	2
Russia	Avisma magnesium	1.5
Brazil	Rima magnesium	2
Kazakhstan	Magnesium plant in Kamennogorsk	0.5
Norway	Magontec Xi'an Co., Ltd	0.5
Canada	Canada Magnesium Corporation	1.25
Egypt (Australia Magnesium)	Magnesium smelting plant in Sokhna	20
Congo	Kouilou magnesium smelting plant	6
USA	Rowley magnesium plant	5.9–7.3
Australia	Australia Magnesium International Ltd	7.1–20

Table 1.12 World's leading magnesium-producing nations and their outputs in 2013 and 2014 (10,000 tonnes)

Nations	2013	2014
Brazil	1.6	1.6
China	77	80
Israel	2.8	3.0
Kazakhstan	2.3	2.1
Korean	0.8	1.0
Malaysia	0.1	0
Russia	3.2	2.8
Global output	87.8	90.7

countries that producing magnesium metal are Israel, Russia, Kazakhstan, Brazil, etc.

1.3.3 Development of Magnesium Industry in China

Before 1995, China's primary magnesium output was very small, and the primary magnesium outputs of western countries accounted for about 80% of the world's total magnesium output. In the 1980s, there were only three magnesium smelters in China, Baotou Guanghua Magnesium Group Company, Qinghai Minhe Magnesium Plant, and the magnesium branch of Lushun Aluminum Plant. All three magnesium smelters use electrolytic methods, and thus, the investment cost of building a plant is relatively high and the preparation of anhydrous magnesium chloride is difficult to control. Also, the production is difficult, the equipment is easily corroded, and the output is low. Since 1987, the Pidgeon process has undergone rapid development in China, and many small magnesium smelters that use the Pidgeon process were built during this period [29]. The specific reasons for this include the following: the Pidgeon method is a relatively simple smelting process, and the equipment selection is simple; the investment in the construction of the plant is small; the purity of the magnesium produced is high; the production scale is flexible, and dolomite-rich mineral resources in China can be used directly as raw materials. In particular, the Pidgeon process was put forward in 1941, and after years of exploration and improvement, it is more in line with China's actual national conditions.

Since 1999, China has gradually become the world's largest producer of magnesium products. By 2007, China's output of primary magnesium reached 624,700 tonnes, of which the output of magnesium alloy reached 226,200 tonnes, as shown in Table 1.13. The magnesium industry has developed rapidly in China because of the advantages of resources, energy, labor and production methods. In 2007, China's output of primary magnesium accounted for more than 80% of the world's total output.

Table 1.13 Output of Mg and magnesium alloys in China from 2001 to 2007 (numbers are in 10,000 tonnes)

Year	2001	2002	2003	2004	2005	2006	2007
Global magnesium output	47.86	52.41	49.08	63.34	65.78	70.87	77.67
China's magnesium output	19.97	32.50	34.18	44.24	45.08	51.97	62.47
Global annual growth rate (%)	–	9.51	–6.35	29.05	3.85	7.74	9.60
China's annual growth rate %	–	62.74	5.17	29.43	1.90	15.28	20.20
Portion of China's output (%)	41.73	62.01	69.64	69.85	68.53	73.33	80.43
China's output of magnesium alloys	–	–	–	13.58	17.51	21.10	22.62
Portion of magnesium alloys in magnesium output (%)	–	–	–	30.70	38.84	40.60	36.21

Table 1.14 Mg output in China from 2004 to 2009 (numbers are in 10,000 tonnes)

	Production capacity of primary magnesium	Output of primary magnesium	Output of magnesium alloy	Output of magnesium powder
2004	76.0	45.0	13.5	9.1
2005	81.5	46.8	17.5	8.6
2006	90.2	52.6	21.2	10.0
2007	97.7	65.9	22.6	11.1
2008	116.2	63.1	21.1	13.9
2009	131.9	50.2	16.4	11.1

Based on statistics provided by the National Bureau of Statistics and the Magnesium Branch of China Nonferrous Metals Association, the year-on-year changes in production capacity and output of metallic magnesium in China from 2004 to 2009 are listed in Table 1.14. In 2009, 64 magnesium smelters were counted. The production capacity of primary magnesium was 1.319 million tonnes shows a year-on-year increase of 13.52%. The increase in 2009 was 5.34% lower than that in 2008. The output of primary magnesium was 502,000 tonnes and shows a year-on-year decrease of 20.44%. The output of magnesium alloys was 164,000 tonnes, showing a year-on-year decrease of 22.5%, and the output of magnesium powder was 111,000 tonnes, showing a year-on-year decrease of 19.8%. The decreases are a result of the financial depression that occurred from the end of 2008–2009; the magnesium industry market shrank, and the coal, steel, and alloy industries experienced downturns. These negative factors caused most of the magnesium producers to cut or suspend production, leading to a rapid decline in magnesium production and to greater gaps in magnesium production capacity and output.

After 2010, because of improvements in the world economic situation, the magnesium output in China showed a recovery. In the first half of the year, the output of primary magnesium was 324,500 tonnes, which was an 86.81% increase compared

to the same period in previous year. In 2010, data for newly-built magnesium smelting enterprises in China are shown in Table 1.15. Of the manufacturers listed in Table 1.15, all of them (except Qinghai Salt Lake Group Magnesium Industry Co., Ltd., which uses the Pidgeon process) use electrolysis to smelt magnesium.

According to statistics from the China Nonferrous Metals Industry Association, China's output of primary magnesium in 2014 was 873,900 tonnes, which is a 13.53% increase compared to the same period the previous year. China's primary magnesium production area has also spread from the original Hubei and Henan provinces to coal-rich provinces, such as Shaanxi, Shanxi, and Ningxia. Shaanxi is the province with largest magnesium output and produced a total of 404,600 tonnes in 2014, accounting for 46.30% of the national output. Of the areas in Shaanxi, the cumulative production of the Yulin area was 396,300 tonnes. Fugu county in the Yulin area has an output of 348,100 tonnes, which accounts for 39.83% of the country's total magnesium output and about 86% of the province's magnesium output. The year-on-year changes of my country's primary magnesium-producing areas in 2014 are shown in Table 1.16.

In 2014, the primary magnesium output of Shaanxi Province ranked first in China. Shaanxi Province's output reached 404,600 tonnes, which accounts for 46.30% of the total national output, and this province remained the largest primary magnesium-producing area in China for two consecutive years.

According to the latest statistics provided by the General Administration of Customs, China's total exported magnesium was 435,000 tonnes in 2014, showing a year-on-year increase of 5.80%. The export of magnesium ingots was 227,300 tonnes, showing a year-on-year increase of 7.18%. The export of magnesium alloy was 106,500 tonnes, showing a year-on-year increase of 4.42%. The export of magnesium powder was 88,000 tonnes, showing a year-on-year increase of 3.05%. The export of magnesium waste and scraps were 2900 tonnes, showing a year-on-year increase of 87.66%. The export of processed magnesium materials was 3700 tonnes, showing a year-on-year decrease of 16.83%. The export of magnesium products was 6600 tonnes, a year-on-year increase of 15.65%. In 2016, the primary magnesium output in China reached 910,300 tonnes; this was the maximum magnesium output in the past ten years [30]. In 2017, the global output of magnesium metal exceeded 1.2 million tonnes. China is one of the largest producers of magnesium in the world, with China's magnesium output accounting for more than 85% of the world's total output; the magnesium production and export volume rank first in the world. All exported magnesium is produced via the Pidgeon method [31]. In addition to being the leader of primary magnesium production, China has developed deep magnesium processing technology. Besides the leading position in the production of primary magnesium, deep processing technology of magnesium has been gradually transferred to China. Thus, it is anticipated that the magnesium industry in China has a bright future.

From January to June 2017, the export of China's magnesium and its products (including waste and scraps) was 245,083 tonnes, which is a 52.8% increase compared to the same period in the previous year. From January to June 2017, the value of China's exported magnesium and magnesium products (including waste and scraps) was 566,948 thousand USD, which is a 47.6% increase compared to the same period in the previous year. The export statistics of China's magnesium and

Table 1.15 Newly-built Mg manufacturers in 2010 (numbers are in 10,000 tonnes)

Area	Name	Location	Scale under construction	Scale planned	Owner	Time to start production
Ningxia	Ningxia Sun Magnesium Industry Co., Ltd	Sun Mountain Development Zone, Wuzhong, Ningxia	3.5	10.0	DunAn Holding Group Co., Ltd	2010
	Ningxia Huaying Mining Co., Ltd	Sun Mountain Development Zone, Wuzhong	1.0	5.0	Ningxia Huaying Mining	2010
	Ningxia Kaitai Magnesium Industry Co., Ltd	Huianbao town, Yanchi county	1.5	5.0	Shanghai Zhonghe	2011
Inner Mongolia	Baotou Dongfang Ecological Magnesium Industry Co., Ltd	Guyang county, Baotou	1.0	5.0	China Direct Investment Corporation	2011
Shanxi	Shengying He Light Metal (Shanxi) Company	Panlong Town Economic Park, Wuxiang	1.0	5.0	China Minmetals Corporation	2010
Shaanxi	Fugu County magnesium industry group	Fugu County	1.5	5.0	Fugu Magnesium Group	2010
	Fugu County magnesium industry group	Fugu County	1.5	5.0	Fugu Coal Chemical Group	2010
Qinghai	Qinghai Salt Lake Group Magnesium Industry Co., Ltd	Chaerhan Salt Lake	5.0	40.0	Qinghai Salt Lake Industry Group	2011
Total			16.0	80.0		

Table 1.16 Output variations of main primary magnesium-producing areas in 2014

Areas	Output in 2013 (10 k tonnes)	Output in 2014 (10 k tonnes)	Cumulative year-on-year change (%)
Shaanxi	34.33	40.46	17.86
Shanxi	23.67	24.97	5.49
Ningxia	10.81	9.3	-13.97
Xinjiang	2.29	4.45	94.32
Henan	4.01	4.14	3.24
National	76.97	87.39	13.53

Table 1.17 Statistics for China's volume of exported magnesium and magnesium products (including waste and scraps) from January to June 2017

Month	Weight (ton)	Value (k USD)	Year-on-year ratio in weight	Year-on-year ratio in value
Jan	40,937	100.136	45	49.5
Feb	41,459	94.131	98.7	88.7
Mar	44,407	102.342	46.6	45.6
Apr	41,105	95.610	44.6	38.2
May	36,831	84.195	81.9	70
Jun	40,723	91.563	26	17.1

magnesium products (including waste and scraps) from January to June 2017 are shown in Table 1.17.

From January to July 2019, the volume of China's exported magnesium and magnesium products (including waste and scraps) was 245,083 tonnes, which is a 17.9% increase compared to the same period in the previous year. From January to July 2019, the value of China's exported magnesium and magnesium products (including waste and scraps) was 698,470 thousand USD, which is a 47.6% increase compared to the same period in the previous year. Statistics of China's exported magnesium and magnesium products (including waste and scraps) from January to July 2019 are shown in Table 1.18.

1.4 Production Process of Metallic Mg

At present, more mature methods of producing metallic magnesium in the industrial productions used by various countries are generally divided into two categories according to differences in magnesium ore resources [32–35]. The first category is electrolysis of molten magnesium chloride, in which $MgCl_2$ is used as a molten electrolyte to obtain metallic magnesium via electrolysis with the use of direct current.

Table 1.18 Statistics of China's volume of exported magnesium and magnesium products (including waste and scraps) from 2013 to July 2019

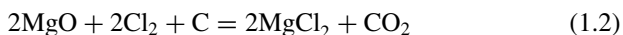
Year	Volume of exported magnesium and magnesium products (including waste and scraps) (ton)	Year-on-year increase in export volume (%)	Value of exported magnesium and magnesium products (including waste and scraps) (k USD)	Year-on-year increase in export value (%)
2013	411,123	10.8	1,187,366	2.6
2014	434,996	5.8	1,171,995	-1.3
2015	405,551	-6.8	1,006,936	-14.1
2016	356,537	-12.1	852,234	-15.3
2017	451,939	26.8	1,052,556	23.5
2018	409,788	-9.8	1,031,498	-2.5
2019 1-7	268,476	17.9	698,470	24.4

Generally, anhydrous $MgCl_2$ or anhydrous carnallite is prepared by chlorinating or dehydrating magnesite, carnallite, brine, or sea water as raw materials, and then magnesium is obtained via electrolysis. The second category is thermal reduction, which is also called the silicothermic method. In recent decades, great breakthroughs have been made in the use of smelting technology for magnesium. Because of the developments in smelting technology, the price of magnesium has dropped significantly, and the magnesium-to-aluminum price ratio has decreased from 1.8 to 1.4 or lower [36].

1.4.1 Magnesium Smelting via Electrolysis

In terms of electrolysis, the technology used for dehydrating magnesium chloride solution to obtain anhydrous magnesium chloride has achieved breakthroughs and has become increasingly mature. Additionally, the structure and capacity of the electrolytic cell have also been undergone great development and improvement, which have reduced the energy consumption of the electrolysis process. Electrolysis of molten magnesium chloride includes two major production processes: production of magnesium chloride and electrolysis of magnesium chloride to obtain magnesium. Electrolytic smelting of magnesium involves electrolyzing anhydrous magnesium chloride in the molten state to generate magnesium and chlorine gas via electrolysis. Depending on the raw materials and processing methods used, electrolysis methods can be mainly divided into the following specific methods [37]: the Dow process [38], Norsk Hydro process, chlorination process of magnesium oxide (IG Farbenindustrie Process) [39], Magnola process [40], carnallite method (Russian Process), and electrolysis of magnesite.

- (1) DOW method. In 1916, the American Dow Chemical Company used seawater containing MgCl_2 and lime milk as raw materials to extract and prepare $\text{Mg}(\text{OH})_2$. $\text{Mg}(\text{OH})_2$ is then chemically reacted with hydrochloric acid to form a solution of magnesium chloride. The solution is purified and concentrated to obtain $[\text{MgCl}_2 \cdot \frac{3}{2}\text{H}_2\text{O}]$. $[\text{MgCl}_2 \cdot \frac{3}{2}\text{H}_2\text{O}]$ is used as the raw material for electrolysis and is sent into the electrolytic cell to obtain crude magnesium directly via electrolysis; the chlorine by-product can then be recycled. The temperature for preparing magnesium metal via the Dow Process is generally around 750°C .
- (2) Norsk method. Norway's Norsk company is the main magnesium producer in Europe. It uses brine waste that contains MgCl_2 provided by the German potassium industry. Crystal water in MgCl_2 crystals is removed via high-pressure dried HCl gas to produce anhydrous MgCl_2 powder. Molten MgCl_2 is then electrolyzed to prepare metallic magnesium. The Norsk Hydro process is the only method that does not use a chlorination reactor to prepare anhydrous MgCl_2 .
- (3) Chlorination method of MgO (I. G. Farben process). The German IG Farben Industrial Company used natural magnesite and coke as raw materials and calcined them at $700\text{--}800^\circ\text{C}$ to obtain calcined dolomite (MgO) with better activity. MgO powder with a size that must be less than 0.144 mm is mixed with carbon, in what is called a briquetting process. The briquettes are calcined and chlorinated in a vertical electric furnace to obtain anhydrous MgCl_2 , and then MgCl_2 is electrolyzed to obtain metallic magnesium. The following chemical reaction occurs during the preparation of MgCl_2 (Scheme 1.2)



- (4) Magnolia smelting process. The characteristic of this process is that magnesium chloride is used in a serpentine as the raw material for electrolytic smelting. In this process, the tailings of asbestos minerals were immersed in concentrated hydrochloric acid to prepare MgCl_2 solution. The pH and ion exchange technology are adjusted to prepare an ultrahigh pure MgCl_2 solution, and then the solution is dehydrated and electrolyzed to obtain crude magnesium.
- (5) Carnallite method. The chemical formula of carnallite is $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. In this process, carnallite is purified, crystallized, and dehydrated to obtain anhydrous carnallite, which is then directly electrolyzed to produce metallic magnesium. Because of chlorination during anhydrous treatment, dehydration and hydrolysis reaction of carnallite are weaker than those of MgCl_2 , showing slight hydrolysis only. At the same time, the electrolytic cell must be cleaned frequently. This is mainly because of the presence of KCl in the carnallite method [41].
- (6) Electrolytic magnesium smelting using magnesite as raw material. This method uses magnesite as a raw material to carry out electrolytic magnesium smelting. In this process, magnesite is used as a raw material, and the mineral powders

are chlorinated. The obtained magnesium chloride melt is then electrolyzed to prepare metallic magnesium [42].

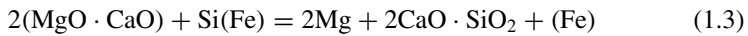
In summary, electrolytic smelting processes have advanced production technology and lowered energy consumption, preparing magnesium via electrolysis has two shortcomings. First, the purity of the prepared magnesium is relatively low. Crude magnesium produced via electrolysis reduces the corrosion resistances of magnesium and magnesium alloys because crude magnesium contains chlorides as an electrolyte and some impurities such as Cr, Mn, Fe, Si, Ni, K, and Na. Thus, corresponding measures must be taken to enhance the purity of the prepared metallic magnesium. The second shortcoming is that it is relatively difficult to prepare anhydrous MgCl_2 . During dehydration of MgCl_2 crystals to prepare anhydrous MgCl_2 , anhydrous MgCl_2 is extremely easy to hydrolyze, and it generates basic magnesium chloride, $\text{Mg}(\text{OH})\text{Cl}$. As a result, the production process of preparing dehydration process is relatively difficult to control. Even under an atmosphere of HCl , the dehydration of hydrated MgCl_2 needs to be performed at a high temperature of 450°C . The difficulty causes a series of problems; specifically, a large investment of production enterprises is required, power consumption is large (production of 1 t of magnesium consumes 12,680–13,250 kWh), resulting environmental pollution is serious, equipment corrodes, and the construction period of plants is long. According to statistics, the cost of dehydrating MgCl_2 accounts for more than half of the production cost of magnesium

1.4.2 Magnesium Smelting via Thermal Reduction

Smelting magnesium via thermal reduction uses some reducing agent to reduce magnesium-containing ore under high temperature and vacuum conditions. The formed magnesium vapor is then cooled and crystallized by a condenser to obtain crude magnesium. According to different reducing agents, magnesium smelting via thermal reduction is divided into the silicothermic method, carbon thermal method, and thermal reduction method with carbide. The carbon thermal method and thermal reduction with carbide are rarely used in industry, but the silicothermic method is often used in industry and is divided into an internal heating method and external heating method. The Pidgeon process and Magnétherm process [43] are common methods used to reduce magnesium oxide with ferrosilicon as a reducing agent. The former is an external heating method, and the latter is an internal heating method. According to the continuity of production, the silicon thermal method can be divided into a batch type and semi-continuous type. At present, the Pidgeon process has been widely used to smelt magnesium in China.

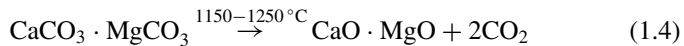
In the thermal reduction method, large-scale semi-continuous vacuum reduction furnaces are increasingly being put into production, and computer control has been adopted. Magnesium smelting via thermal reduction is also called as thermal smelting. The principle is that magnesium ore undergoes a reduction reaction in a

reduction tank under high temperature and vacuum conditions to form magnesium vapor. The vapor is cooled in a condenser and crystallized to obtain crude magnesium. The reducing agent is generally ferrosilicon. Thermal smelting of magnesium mainly takes place in a reduction tank at 1100–1250 °C and under a vacuum of 1.3–13.3 Pa. 75% Si (Fe) alloy and calcined dolomite are used to carry out reduction reaction to prepare metallic magnesium. The reduction reaction equation is shown as Scheme 1.3:

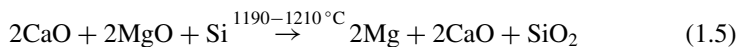


Depending on the different equipment that is used, traditional silicothermic reduction can be divided into four methods: Canada's Pidgeon process, Italy's Balzano process, France's Magnetherm method, and South Africa's Mintek thermal magnesium process (MTMP method).

- (1) Pidgeon method. In 1941, L. M. Pidgeon invented the Pidgeon process, using the silicothermic process to smelt magnesium. In this process, ferrosilicon and dolomite (briquettes composed of crushed and calcined dolomite and fluorite) are added in an externally-heated vacuum distillation tank to smelt magnesium. This is an externally-heated intermittent silicothermic-reduction process [44]. Over time, the Pidgeon process has been continuously developed and improved, forming a relatively complete theoretical system. Thus far, the Pidgeon Process has remained the most representative and most widely used magnesium smelting process in China. The Pidgeon process can be divided into five stages: ore crushing, calcination, briquetting, reduction, and refining. During high-temperature calcination of dolomite at 1423–1473 K and 10^{-2} – 10^{-1} Torr (1 Torr=133.322 Pa), the following chemical reaction occurs (Scheme 1.4):



The calcined white powder is crushed, ground, and mixed with fluorite powder (containing 95% CaF_2 , mainly acting as a catalyst and without chemical reaction [45] and ferrosilicon powder (75% silicon content) to make briquettes. (The making pressure is 9.8–29.14 MPa). The briquettes are placed in a reduction tank. The reduction reaction takes place in the reduction tank at a temperature of 1190–1250 °C and under a vacuum of 1.3–13.3 Pa to obtain magnesium vapor. The vapor is then condensed and crystallized into crude magnesium in the condenser [46]. The chemical reaction is expressed in Scheme 1.5.



After undergoing flux refining, ingot casting, and surface treatment, crude magnesium is finally converted to high-purity metallic magnesium ingots. The flow chart for magnesium smelting using the Pidgeon process is shown in Fig. 1.3.

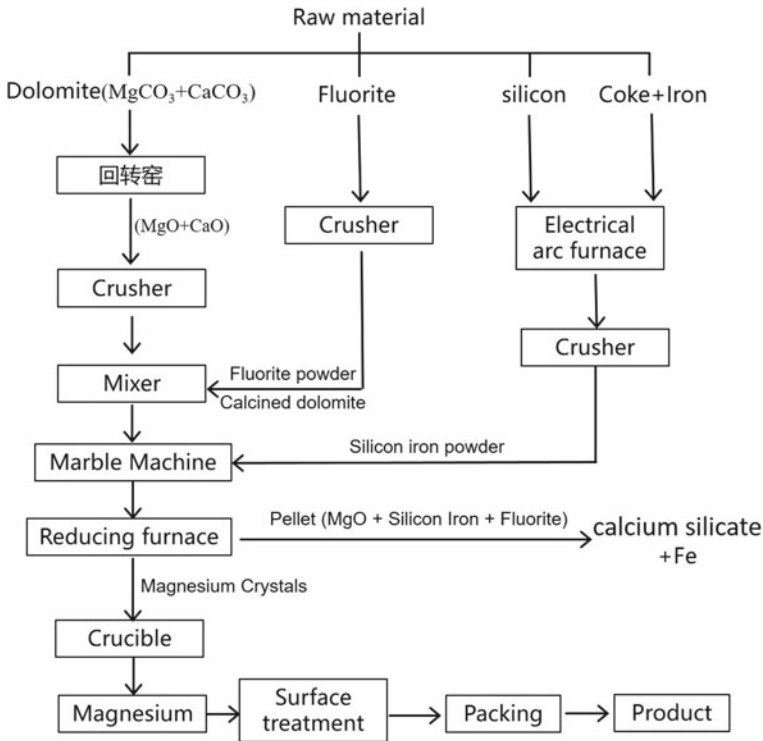


Fig. 1.3 Flow chart of magnesium smelting via the Pidgeon process

The advantages of the Pidgeon process include a low investment, simple production process, short construction period, and high product quality. However, the Pidgeon process cannot proceed continuously. It is an intermittent production method, and each production cycle of the Pidgeon process lasts about 10 h. The entire production cycle can be divided into three stages. The first is the preheating stage. In this stage, dolomite is crushed, placed in a furnace, and preheated to remove CO_2 and moisture in the crushed material. The second stage is a low-vacuum heating stage. In this stage, the reduction tank is sealed and heated under a low vacuum. The third stage is a high-vacuum heating stage. The temperature in the reduction tank is controlled to be about $1200\text{ }^\circ\text{C}$, the degree of vacuum is maintained between 1.3 and 13.3 Pa, and the constant-temperature calcination time is about 9 h. The magnesium vapor generated in the reduction tank condenses and crystallizes on the crystallizer because of the action of the water cooling jacket that surrounds the reduction tank. Finally, the vacuum is terminated, and the reduction tank is opened to remove the crystallized magnesium ring and residue on the condenser.

When applying the Pidgeon smelting process, the preparation of calcined dolomite and briquettes is an important link [47]. First, the Pidgeon process requires calcined

dolomite that has higher activity because better quality calcined dolomite is beneficial for the reduction reaction. If the calcination temperature is too high, it will cause the calcined dolomite surface to be over-sintered, and the activity of the calcined dolomite decreases. At the same time, the calcined dolomite produced by the reaction is highly hydrophilic, and therefore, it needs to be sealed in storage and the sealed-storage time should not be too long. To obtain an economical and effective formulation of raw materials, the ratio of ferrosilicon and fluorite powder used in the preparation of briquettes must be dynamically adjusted according to the composition and morphology of the calcined dolomite. Also, the density and looseness of the prepared pellets must be determined according to the chemical compositions of the dolomite that is extracted from different areas.

The key step in the Pidgeon process is the reduction. The reduction directly affects the length of the production cycle and the quality of the final product. The activity of the calcined dolomite, briquette-making pressure, and formulation of components in the early stage all affect the reduction [45].

To make the reduction proceed more thoroughly and economically, the amount of ferrosilicon and fluorite powder used in the preparation of the briquettes must be dynamically adjusted according to the characteristics of the calcined dolomite, and the briquetting pressure for preparing the briquettes must be reasonably determined according to the chemical composition of the dolomite ores. Through such adjusting and determination, the optimal formulation of raw materials and the parameters can be determined.

The Pidgeon process makes full use of resources such as dolomite, coal, and ferrosilicon in the central and western regions of China. Because of low labor costs, reduction furnaces in foreign countries that use heavy oil and electricity as fuels can be converted to those that use coal as fuel, and this greatly reduces the production costs. Thus, this process has gradually replaced the electrolytic reduction process. To produce 1 t of metallic magnesium, the consumption ratio of dolomite, ferrosilicon, and fluorite as the main raw materials is about 15:1.3:0.21. The consumption of the main primary energy is about 4 t of standard coal when an advanced regenerative reduction furnace is used, and 7–10 t of standard coal is consumed when an old-style reduction furnace directly fired by coal is used. Therefore, this is a high energy consumption industry for primary energy, and the energy consumption per 10,000 yuan of output value is more than 2 t of standard coal. Jiang Hanxiang et al. [48] studied the main factors that affect the recovery rate of magnesium metal during the preparation of magnesium via the Pidgeon process. The results indicate that when the calcination temperature is 1230 °C and the ratio of raw materials is 1:1.15, the formation rate of magnesium reached maximum value after a reduction cycle of 10 h, and the average magnesium recovery rate exceeded 75%.

The advantages of the Pidgeon process include the following: short process, fewer equipment requirements, simple operation, low investment, short plant construction period, and suitable for primary energies such as coal, natural gas, heavy oil, and gas. In the production process, no harmful gases are generated or discharged. By-product slag can also be used as a raw material in the production of cement and fertilizer. Thus, many small and medium-sized enterprises in China use the Pidgeon process

to produce magnesium [49]. In addition, dolomite minerals are widely distributed in China; the reserves are rich with remarkable quality, and this provides unique conditions for developing magnesium smelting using the Pidgeon process.

However, in recent years, with the requirements of the national energy-savings and emission-reduction policies and with the awareness of the need for environmental protection, the adverse effects that result from the Pidgeon process have become distinctively obvious [50]. The more severe problems are the huge energy consumption and the generation of serious environmental pollution. To solve both problems, more in-depth research is necessary regarding the thermal decomposition of dolomite and the thermal reduction process of MgO. Combined with the life cycle theory, the current technological level can be modified and improved. The economic and environmental benefits of magnesium production can be comprehensively evaluated, and novel magnesium smelting processes that are green and energy-saving can be developed. A novel green and energy-saving magnesium smelting process can provide technical support for China's magnesium smelting industry using the Pidgeon process to improve the production standard, reduce and save energy consumption, and carry out the automation and mechanization of the magnesium alloy industry.

- (2) Balzano method. The Balzano Process evolved from the Pidgeon process and originated in a small magnesium smelting plant in Balzano, which is a town in Italy. At present, the Balzano process is used by Brasmag, Brazil. The Balzano process uses a larger vacuum reduction tank and adopts internal electric heating during vacuum reduction; thus, the energy consumption of this method is much lower than that of other reduction methods. The production raw material is still dolomite. Different from other thermal reduction methods, in the Balzano Process, after the calcined dolomite and ferrosilicon are pressed into briquettes and placed in the reduction tank, an electric heater is used directly to heat the briquettes instead of heating the entire reduction tank. The pressure inside the tank is 3 Pa, and the reaction temperature is 1200 °C. The heating furnace consumes only 7–7.3 kWh to produce 1 kg of magnesium, and other production process parameters are similar to those of the Pidgeon Process [51]. This indicates that the energy consumption of the Balzano Process is significantly lower than that of other thermal reduction methods.
- (3) Magnetherm method, also known as the semicontinuous thermal reduction method [52]. This method originated in France and was proposed by Pechiney Aluminum Company around 1960. The Magnetherm process soon became the main method for producing magnesium in the northwestern United States. Different from the Pidgeon process, the steel shell of the sealed reduction furnace that is used in the process is lined with insulation materials and carbon materials so that it has a high reaction temperature (1300–1700 °C) when it is heated internally by electric resistors [53]. The raw materials in the reduction furnace include calcined dolomite, ferrosilicon, and calcined bauxite, which can decrease the melting point of slag. The heat generated by the current passing slag can keep the temperature of the furnace at 1723–1773 K; liquid slag can be

directly extracted, which does not destroy the vacuum in the furnace. Semicontinuous thermal reduction uses continuous feeding and intermittent slagging. It does not generate harmful gases and has a larger production capacity, although the cost is higher [54]. The reduction reaction in an electric furnace is carried out under vacuum conditions. This method uses dolomite and bauxite as raw materials and Si (Fe) as a reducing agent. The main features of the Magnetherm process are similar to those of the Balzano method. They all use electric heating in a reactor. Generally, the temperature in the reactor is in the range of 1300–1700 °C, and all of the materials are liquid in the magnesium smelting furnace that is used in the Magnetherm Process. There are two main reasons why the Magnetherm process requires such a high-temperature calcination: First, when a large amount of raw materials are fed into the reactor, the reactor still needs to maintain a degree of vacuum (0.266–13.3 kPa). Second, the reduction reaction requires high temperature conditions. In the Magnetherm process, magnesium vapor is concentrated on the condenser in a gaseous or liquid state, and the entire production cycle is 16–24 h. The daily magnesium output of the Magnetherm process is generally 3–8 t, and every 7 tonnes of raw materials consumed can produce 1 ton of metal magnesium.

- (4) MTMP method. In 2004, Mintek and Eskom in South Africa jointly published the Mintek thermal magnesium process (MTMP), which is also called the South African thermal method because this method was jointly developed by two companies that are in South Africa. MTMP uses ferrosilicon as a reducing agent to extract Mg from dolomite or MgO with an electric arc furnace at a reaction temperature that is controlled to be between 1700 and 1750 °C. Finally, magnesium vapor is enriched in a condensing chamber and takes a liquid form [51]. MTMP allows instantaneous discharge of waste slag, and the reduction process is carried out under atmospheric pressure. When discharging waste slag and extracting magnesium, the vacuum environment does not need to be cut off, and so continuous production can be achieved.

With the continuous development of magnesium smelting technology, MTMP has been constantly optimized. In 2002, the quality of metallic magnesium produced via MTMP can reach more than 80%, but there is still the problem of not taking magnesium in time, which means that the production process cannot work continuously. In October 2004, a new type of condenser was used in MTMP, and the entire production cycle was 8 days. The condensing device in MTMP magnesium smelting includes: a melting furnace, industrial elbow, electric arc furnace, second condensing chamber, stirrer, over-pressure protection device, and piston for cleaning particles.

In MTMP, the temperature of the electric arc furnace is in the range of 1000–1100 °C, the average feed rate of raw materials is 525 kg/h, and the ratios of the feed materials are about 5.5% Al, 10.7% Fe, and 83.8% dolomite; the ratios of the feed materials can be controlled using a valve. The mixed raw materials undergo reduction reactions in the reaction furnace to generate magnesium vapor. The magnesium vapor is condensed into liquid magnesium as it passes through the industrial elbow. The liquid magnesium is enriched in the furnace (the upper end of the furnace is equipped

with a secondary enrichment device to enhance the purity of the magnesium), and magnesium can be regularly extracted as the final product through the lower end of the furnace [55].

1.5 Industrial Policy of China's Magnesium Industry

Since 2001, the National Development and Reform Commission and the Ministry of Science and Technology have listed magnesium alloy as a priority industry for development; the Ministry of Science and Technology has listed *Development and Industrialization of Magnesium Alloy Applications* as a major scientific and technological research project during the 10th Five-Year Plan. In the *Interim Provisions on Promoting Industrial Structure Adjustment* and *Industrial Structure Adjustment Guidance Catalog* promulgated by the National Development and Reform Commission on December 21, 2005, the casting of high-quality magnesium alloy and the processing technologies for plates, pipes, and profiles were included in the encouraged development projects. In 2006, the Ministry of Science and Technology promulgated the *Key Technology Development and Application for Magnesium and Magnesium Alloy* as a major support project in "11th Five-Year Plan". The nation invested another 50 million yuan as a guide for funding the development of key technologies and applications of magnesium. The explicit orientation of the national policy is conducive to the transformation of China's magnesium industry from primary magnesium production to the production of high-tech and high-value-added deep-processed products. These can accelerate the transformation of mainland China's magnesium industry from resource advantages to economic advantages, and they can convert China from being the major magnesium producer to being a powerful country in the magnesium alloy industry [56].

In 2009, China carried out industry integration regarding the policies issued by relevant departments. In *Promoting the Adjustment and Optimization and Upgrading Plan of the Raw Material Industry in the Central Region* ([2009] No. 664 of the original Ministry of Industry and Information Technology), the Ministry of Industry and Information Technology required the elimination of "small nonferrous" enterprises that had a magnesium output lower than 10,000 tonnes per year. The *Shanxi Province Metallurgical Industry Adjustment and Revitalization Plan*, which was issued in 2009, clearly requires that the comprehensive energy consumption of magnesium smelting enterprises should be less than 5.6 t of standard coal/t. At the end of 2011, all magnesium producers with an annual output that was lower than 10,000 tonnes would be eliminated. By the end of 2015, all magnesium producers that had an annual output of lower than 20,000 tonnes would be eliminated.

Originally organized by the former National Development and Reform Commission and now drafted by the Department of Raw Material Industry of the Ministry of Industry and Information Technology, the "*Magnesium Industry Access Conditions*" clarifies strict access requirements in seven aspects: the company's layout and scale,

process equipment, product quality, resource and energy source consumption, environmental protection, safe production and occupational hazards, and supervision and management. Among these aspects, there is a requirement for the scale of an enterprise, which states, "The annual production capacity of existing enterprises should be greater than 15,000 tonnes; the annual production capacity of renovated and expanded enterprises should be greater than 20,000 tonnes, and the annual production capacity of new magnesium enterprises should be greater than 50,000 tonnes". According to the requirement, the annual energy output of the eliminated enterprises will reach 783,000 tonnes, and the annual production capacity of the remaining enterprises will be only 536,000 tonnes.

At present, a number of magnesium industry producing groups and industrialization bases have begun to take shape in China. They are mainly distributed in eastern areas such as Jiaodong Peninsula and the Yangtze River Delta, in western areas such as Qinghai, Ningxia and Chongqing, in southern areas such as the Pearl River Delta, and in northern areas such as Liaoning, Jilin, Heilongjiang; Also, they are in Henan, Beijing, and other areas. Thus, it is seen that an industrial chain related to innovative technology of magnesium and magnesium alloys has initially formed. The industrial chain runs through China's east, west, north, and south, showing a high-tech pattern that ranges from raw material production, manufacturing of production equipment, and development of magnesium alloy products to the formation of demonstrated industrialization bases, thereby promoting changes in the structure of China's magnesium industry and driving the magnesium industry toward deep processing. Before 2015, there were no large-scale magnesium projects that were put into production abroad, and they will still rely on China's supply. At the same time, a series of factors (such as new materials, a low-carbon economy, and policy guidance) have made domestic companies optimistic about the magnesium industry and driven a large amount of social investment, laying the foundation for China to make the leap from being a country with abundant magnesium resources to being a powerful country in applications of magnesium and magnesium alloys [55].

At present, the magnesium output of Shaanxi, Shanxi, and Ningxia provinces are 355,000 tonnes, 79,000 tonnes, and 60,000 tonnes respectively. Collectively, this accounts for 86.7% of the national output. The magnesium smelting industry has achieved a profit of -40 million yuan, showing a year-on-year decrease of 40 million yuan.

From January to October 2018, China's magnesium output was 570,000 tonnes, which was a decrease of 22.4% compared to the same time period in the previous year. The export volume of various magnesium products was 324,000 tonnes, which was a decrease of 15.4%. The export value was 810 million USD, which was a decrease of 9.3%. Among the magnesium products, the total export volume of magnesium ingots was 163,000 tonnes, which was a decrease of 20.2%. The export volume of magnesium alloys was 89,000 tonnes, which was a decrease of 10.9%, and the export volume of magnesium powder was 63,000 tonnes, which was a decrease of 11%.

In November 2018, the average domestic price of magnesium spot was 18,206 yuan/ton, which was a 27% increase compared to the previous November. From January to November, the average domestic spot price of magnesium was 16,359

yuan/ton, which was a 10.2% increase compared to the same time period in the previous year. Since 2018, the price of magnesium maintained an upward trend with some fluctuations, and it increased to 18,500 yuan/ton in early November, which was close to the highest point in recent years [57].

In 2018, the overall operation of the magnesium industry was steady, domestic consumption increased, and the price of magnesium continued to increase. However, the stress that resulted from environmentally friendly renovation of the smelting process, which was more intense, and the application of deep-processed products needed to be accelerated. Thus, the transformation and upgrading of the magnesium industry remained arduous.

First, the output of primary magnesium decreased year-on-year, and the price went up with fluctuations. According to 2018 statistics from the Nonferrous Metals Association, magnesium output was affected by environmental protection and production restrictions. Specifically, China's output of primary magnesium was 860,000 tonnes with a year-on-year decrease of 5.4%. Contraction on the supply size supported an upward trend in the price of magnesium. The annual average spot price of magnesium was 16,488 yuan/ton, with a year-on-year increase of 10.5%. According to a survey organized by an industry association, the actual profitability of magnesium smelting companies has increased year-on-year, and industry benefits have continued to improve.

Second, the domestic consumption of magnesium continued to grow while the volume of exported magnesium fell. In 2018, China's magnesium consumption was 450,000 tonnes with a year-on-year increase of 7%, and there was a 2% increase in the magnitude. However, because of the decrease in the consumption of 3C products, growth in the consumption of processed magnesium material decelerated. The demand for magnesium from abroad has fallen, and the total volume of various exported magnesium products in the entire year was 410,000 tonnes with a year-on-year decrease of 11%. The volume of exported magnesium products accounted for 48% of the magnesium output.

Third, industrial structures were adjusted, and there were breakthroughs in high-end applications. In 2018, Baowu Iron and Steel Group invested in Yunhai Metal to jointly expand the applications of magnesium, and they achieved a strong collaboration between state-owned and private enterprises. Henan Hebi Magnesium Trading Center was established to promote the circulation of magnesium products and to promote healthy operation of the domestic magnesium market via innovative trading modes. New progress has also been made in the production and application of high-end magnesium materials. For instance, automobile wheels that consist of forged magnesium alloys have been industrialized and exported to European and American markets. Large-scale and stable preparation of new controllable and degradable magnesium alloy materials have been achieved for bone repair and have been supplied to domestic medical device companies.

Fourth, environmentally friendly renovation is under heavy stress, and the task of green development is arduous. In recent years, domestic magnesium smelting technology has undergone continuous modification while the levels of mechanization and automation have remained relatively low. Working conditions need to be

improved, and the level of energy savings, emission reductions, and waste slag recycling urgently need improvements. In 2018, with in-depth advances in pollution prevention and control, some magnesium smelting enterprises terminated production because of the renovation requirements that are based on environmental protections. The difficulty of employment of enterprises became prominent, and the task of achieving green development of the magnesium industry has been arduous.

In 2019, the development of lightweight transportation at home and abroad provided more opportunities for expanding magnesium applications. Meanwhile, stricter requirements were put forward for improving the level of green development for the entire magnesium industry chain. Modifying smelting technology and expanding magnesium applications will be important for promoting high-quality development of the magnesium industry. The Ministry of Industry and Information Technology will continue to promote relevant local governments and enterprises to establish platforms for research and development of magnesium smelting technology. They also support the magnesium industry in implementing technological transformations for green production, encourage wider application of key products such as magnesium wheels, and accelerate large-scale application of the magnesium industry [58]

1.6 Problems with Magnesium Slag After Smelting

1.6.1 *Properties and Damage of Magnesium Slag*

Two major issues that China faces are energy and the environment. In 2014, the annual magnesium output of China reached 873,800 tonnes [59]. However, for every tonne of metallic magnesium that was produced via smelting, approximately 6.5–7 tonnes of magnesium slag were produced. Therefore, based on the current output, more than 6 million tonnes of magnesium slag was produced in China last year. Considering the cumulative effect of the past two decades, the total amount of magnesium slag is huge.

Magnesium slag is an industrial solid waste that is produced in the process of preparing magnesium metal via electrolysis or thermal reduction with magnesium-rich minerals, such as dolomite, serpentine, and magnesite [60]. Magnesium slag is a gray alkaline block or powder. After slag absorbs moisture, a suspension that is very alkaline (pH around 12) and has stable properties forms. As a result, the soil ever stacked with magnesium slag is easy to harden and salinize; this endangers the growth of crops and affects the future normal use of land. The disordered and random accumulation of a large amount of magnesium slag enters rivers and groundwater systems with rainwater leaching and infiltration; this can change the pH of a water body and seriously affect the ecological security of water resources.

From the perspective of chemical composition, magnesium slag is mainly composed of CaO, SiO₂, Al₂O₃, MgO, and Fe₂O₃. Because of different sources

of magnesium ores and different production processes of smelted magnesium, the content of each component is not constant and exhibits a certain amount of fluctuation.

Magnesium slag is a by-product of magnesium smelting. With the rapid growth of magnesium production, the harm of magnesium slag has been obvious. Thus far, magnesium slag cannot be effectively used and the only treatment is dumping and filling. Furthermore, magnesium slag is easily weathered into powder-like matters in the wind; it does not easily settle out of the wind, and the polluted surfaces are difficult to control.

The harm of magnesium slag to the human body is manifested in various ways. Long-term inhalation of concentrated dust can cause diffuse and progressive fibrosis-based systemic diseases (pneumoconiosis). Magnesium dust can be dissolved on the bronchial wall, where it can be absorbed and then carried by the blood to the whole body, resulting in systemic poisoning. Contact or inhalation of dust can cause local irritation to the skin, cornea, and mucosa, producing a series of pathological changes.

The harm that magnesium slag has on the environment is mainly manifested in the following two ways:

- (1) Magnesium slag easily causes dust pollution. After reduction, magnesium-containing slag is dust that has a high content of fine powder, and 60–70% of the particles are less than 160 μm in diameter. After reduction, the completely pulverized magnesium slag can basically pass through a 200-mesh sieve, and its fineness is similar to that of cement. These magnesium slag particles are finer than common coal ash dust. They can be suspended in the air and do not settle easily; thus, they easily form dust pollution in the natural environment. Furthermore, they are easily inhaled into the respiratory tract and can cause respiratory diseases. In addition, the dry and windy climate of the northern region exacerbates the severity of damage.
- (2) Magnesium slag easily causes soil compaction. After reduction, magnesium slag has a strong ability to absorb moisture, and this can easily cause soil salinization and compaction of soil. The land and surrounding areas on which magnesium slag has accumulated basically cannot be used for agricultural cultivation any more, and this results in the reduction of a large amount of farmland resources. With a reduction in China's arable land and an increase in global food prices in recent years, the harm of magnesium slag on cropland has gradually become severe [61].

1.6.2 Treatment and Efficient Utilization of Magnesium Slag

Magnesium smelting industry is an industry that consumes a high amount of energy and materials; meanwhile the pollution that it generates in production is severe. Although cleaner coke oven gas has been used to replace coal, the by-product of magnesium smelting (reducing slag) has not been well treated. With a continuous increase in magnesium output, the environmental pollution caused by magnesium slag is attracting increasing attention. How to combine our own characteristics and

local conditions to reasonably and effectively utilize magnesium slag is a difficult problem that we face.

Although China has many favorable conditions for developing the magnesium industry, in the increasingly intense market competition, the magnesium industry still faces several problems: relatively old technical equipment, low thermal efficiency, high labor intensity, and serious pollution, especially the large amount of waste slag that is produced in the production process. In the 2010 edition of “*Industrial Structure Adjustment Guidance Catalog*” promulgated by the National Development and Reform Commission, magnesium smelting projects are still listed in the restricted category. This categorization is conducive to curbing the low-level construction and disorderly development of the magnesium industry; it can also promote the optimization of each step in the Pidgeon process and the comprehensive use of waste residue from magnesium smelting as a resource.

According to the “*State of the Environment Bulletin of China*” [62], which was published by the Ministry of Environmental Protection of the People’s Republic of China, the national discharge of industrial solid waste gradually increased during the period of 2000–2014. In the past five years, the annual growth rate of industrial solid waste reached 10%. The solid waste that is generated by industries such as electric power, heat production and supply, metal smelting and processing, and mining of nonferrous metals accounted for about 80% of all solid wastes [63]. On the whole, China’s industrial solid waste is still in a stage where there is large production and a low utilization rate.

At present, there is no effective treatment method for magnesium slag; thus, it is mainly treated via stacking and burying methods like landfill in mountain depressions and dumping in wasteland, and this results in a very low utilization rate. The massive discharge and accumulation of magnesium slag requires a lot of land resources [64], causes dust pollution, and has direct impacts on crops and the surrounding environment. Magnesium slag hardens the land so that arable land that is polluted with magnesium slag loses its fertility. This leads to decreased crop yields and reduced area of arable land. Magnesium slag flows into rivers with rainwater, has a great impact on bodies of water, and seriously endangers human health and the growth of crops. Therefore, magnesium slag has become a major hazard that results from the magnesium industry. With the rapid development of the magnesium industry, the amount of magnesium slag is increasing, and the harm it causes to the environment is attracting more attention. Thus, it is clear that the harm caused by magnesium slag is urgently needed to deal with. It is particularly crucial to find a scientific and reasonable way to solve the pollution of magnesium slag, and the approach should bring huge social and ecological benefits [61].

China is a major magnesium-producing country and has relatively less applications of magnesium slag than developed countries. China has abundant magnesium resource storage and a large export volume, and there are fewer magnesium producers abroad. There are very few studies on applications of magnesium slag that have ever considered it as an industrial waste. Thankfully, in response to the problem of using magnesium slag as a resource, domestic researchers have carried out a lot of research and made certain achievements. Some magnesium plants in China have

applied magnesium slag in road paving, brick production, and cement production for use in construction. However, most magnesium slag is still disposed on in landfills. In view of the potential value of magnesium slag, domestic researchers have carried out research work in related applications and have obtained some research results; the results have mainly focused on the use of magnesium slag in preparing cement clinker or admixtures, building bricks, wall materials, cementitious materials, etc.

Magnesium slag is rich in CaO, SiO₂, MgO, and other components that have higher alkaline oxide contents [65]. In the production of cement, magnesium slag can be used as alkaline substances that can be added to raw materials, thereby improving the quality of cement and enhancing its stability [66]. In the production of wall materials, introducing finely-ground magnesium slag powder can promote various chemical reactions between components in the raw materials and can stimulate the activity of magnesium slag; thus, low-cost, high-strength, and low-density wall materials can be produced through a simple and easy process [67]. Magnesium slag can also be used as a desulfurizer because the amount of calcium oxide in magnesium slag is relatively high. Substituting magnesium slag for some of the calcium oxide in a circulating fluidized bed boiler can achieve the desulfurization effect [68].

Results of heavy metal leaching toxicity for magnesium slag are shown in Table 1.19 [57]. Regardless of whether the HJ method with water leaching or TCLP was leaching with a buffer solution (pH = 2.88) was used, the leaching results were

Table 1.19 Heavy metal leaching toxicity results for magnesium slag

Heavy metal	HJ557-2010 leaching test			TCLP leaching test			NEN7341
	Detected value (mg/L)	Limit(mg/L)	mg/kg	Detected (mg/L)	Limit (mg/L)	mg/kg	mg/kg
Cr	0.012 ± 0.002	10	0.12 ± 0.02	0.034 ± 0.003	5	0.68 ± 0.06	0.75 ± 0.11
Cu	0.043 ± 0.004	50	0.43 ± 0.04	0.021 ± 0.005	15	0.42 ± 0.10	2.34 ± 0.021
Zn	<0.001	50	<0.01	<0.001	25	<0.02	4.52 ± 0.83
Ni	<0.01	10	<0.01	0.008 ± 0.002	20	0.16 ± 0.04	3.20 ± 0.55
Pb	Not detected	3	<0.1	<0.01	5	<0.2	<0.50
Cr ⁶⁺	Not detected	1.5	Not detected	Not detected	–	Not detected	Not detected
Cd	Not detected	0.3	Not detected	Not detected	1	Not detected	Not detected
As	Not detected	1.5	Not detected	Not detected	5	Not detected	Not detected
Hg	Not detected	0.05	Not detected	Not detected	0.2	Not detected	Not detected

far below the standard limit, and this indicates that magnesium slag is not a hazardous waste containing heavy metals and can be used in agricultural resource utilization.

Scientific and technological researchers have conducted a lot of research on the resource utilization and harmless use of magnesium slag. Zhu Guangdong et al. [65] added reducing slag into a three-wire electric furnace, heated the reducing slag to a molten state, then turned water-quenched slag into cement raw material after a series of operations, such as water quenching. This approach is an effective and feasible method for solving the problem solid waste discharge in the magnesium industry. Han Tao et al. [69] invented a method for preparing high-performance magnesium slag. By spraying a dilute acid solution on high-temperature magnesium slag when it is just removed from the tank, the expansion rate of the magnesium slag was reduced while the content of active ingredients in the mineral increased. In recent years, environmental pollution problems such as stacking of magnesium slag have gradually become burning question. Li Dongxu et al. [70] invented a method for making magnesium slag bricks without using sintering process. By adding 50–70% magnesium, slag bricks made using this method have a compressive strength that reaches 35.6 Mpa in 38 days. The nonsintered bricks have a series of characteristics, such as high strength grade, early strength, low shrinkage, and good frost resistance. Han Tao et al. [71] aimed at the slow hydration speed and slow strength growth of C_2S (dicalcium silicate) in magnesium slag raw materials and provided a method for preparing nonsintered bricks using magnesium slag. The added amount of reduced magnesium slag was 30–50%, and the 28-day strength was 19.7–36.8 Mpa. Wu Laner et al. [72] invented a phosphorus compound that can stabilize β -dicalcium orthosilicate in reduction slag generated from magnesium smelting via the Pidgeon process. The modified magnesium slag can be used as a concrete admixture or cement admixture. Wu Laner et al. [73] also invented a magnesium slag modifier and a modification method for magnesium slag. In this method, β -dicalcium orthosilicate can be converted to γ -dicalcium silicate during the Pidgeon process. With the addition of a small amount of boric acid and the use of a high-temperature roasting process, the problem of pulverizing magnesium slag is solved. Wu Yong [74] crushed magnesium smelting slag into powder and then dissolved it with acid and a precipitation agent to make $CaSO_4 \cdot 2H_2O$ precipitate from $CaCl_2$ solution. The filtered $CaSO_4 \cdot 2H_2O$ precipitate can be produced into gypsum powder, and the filtrate can be used as liquid nitrogen fertilizer. Therefore, the comprehensive treatment of magnesium slag is the main subject of the sustainable development of the magnesium industry.

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