CHAPTER 12.21

Magnesium Minerals and Metal

David C. Lynch

MAGNESIUM COMPOUNDS OF COMMERCIAL IMPORTANCE

The abundance of magnesium on land, in the seas, and in natural brines leads to its presence in plants and animals, but because of its reactivity, it is not found in elemental form in nature. Magnesium is the eighth most abundant element in the earth's crust and in seawater has a concentration of 1,300 ppmw (parts per million by weight) as Mg^{2+}. The concentration of magnesium in natural brines varies with climate. In the South Arm of the Great Salt Lake, near where US Magnesium processes lake water, the concentration of magnesium has ranged from a low of 0.18 wt % in 1986 when the lake volume was peaking, to approximately 1 wt % in 1963 when the lake was at its historic low (Tripp 2009), which is a water level the lake approached in 2017 (Larsen 2017). The nominal magnesium concentration in the Great Salt Lake is about 0.43 wt % (Tripp 2009), or 3.3 times that of seawater.

Magnesium is found in more than 60 minerals of which 6 are of commercial importance. Those minerals are identified in Table 1. These minerals are found worldwide in large deposits. Magnesium-bearing natural brines represent a resource in billions of metric tons, and there is a virtually unlimited source of magnesium in seawater (USGS 1995–2015).

Magnesite, Magnesia, and Periclase

Worldwide, magnesite is the primary magnesium compound mined, sold, and commercially processed (USGS 1992–2015). Magnesite is obtained from natural and synthetic sources (seawater, natural brines, or deep sea salt beds). In 1992, 75% of world magnesite production took place in six countries (in decreasing level of production): North Korea, China, Czechoslovakia, Turkey, Russia, and Austria. In 2015, more than 82% of production came from China, Turkey, and Russia. The growth of Chinese production of magnesite is presented in Figure 1, which shows that Chinese production grew from 15% of world output in 1992 to more than 69% in 2015. A similar dominance exists in magnesium metal production (covered later in the "Production and Commercial Uses of Magnesium Metal" section).

Table 1 Magnesium minerals of commercial importance

Name	Composition	Mg, wt %
Magnesite	$MgCO_3$	28.8
Brucite	$Mg(OH)_2$	41.7
Dolomite	$CaMg(CO_3)_2$	13.2
Carnallite	$KCl{\cdot}MgCl_2{\cdot}6H_2O$	8.7
Talc	$Mg_3Si_4O_{10}(OH)_2$	19.2
Olivine	$(Mg,Fe)_2SiO_4$	0–34.6

Magnesite is calcined:

$$MgCO_3 \rightarrow MgO + CO_2(g),\ \Delta H_{298K} = 100.9\ \text{kJ} \quad \textbf{(EQ 1)}$$

at temperatures between 700°–1,500°C (973 K and 1,773 K) in rotary kilns fired with oil or gas (Gill 1980), removing 96%–98% of the carbon as carbon dioxide (CO_2) and producing magnesium oxide (MgO). The oxide product is referred to as *calcined magnesia*, whereas naturally occurring MgO is called *periclase*, except as noted in the following discussion.

Calcined magnesia is classified by the calcine temperature, which impacts its density and reactivity. There are four general classes (Martin Marietta Magnesia Specialties 2018; Grecian Magnesite, n.d.):

1. **Light-burned.** A reactive magnesia is produced at calcine temperatures below 1,000°C (1,273 K) and is referred to as *caustic-calcined magnesia* or CCM. CCM is used in the chemical industry, agricultural supplements, environmental applications, and some cosmetics. The chemical purity of CCM varies from low (90%) MgO content for agricultural uses to the highest grades (~95%) used in the pharmaceutical and food industries.
2. **Hard-burned.** Hard-burned magnesia has low reactivity, having been calcined at temperatures between 1,000° and 1,500°C (1,273–1,773 K). Hard-burned magnesia is typically used in applications where slow degradation of chemical reactivity is required, such as refractories for the steel, cement, and glass industries.

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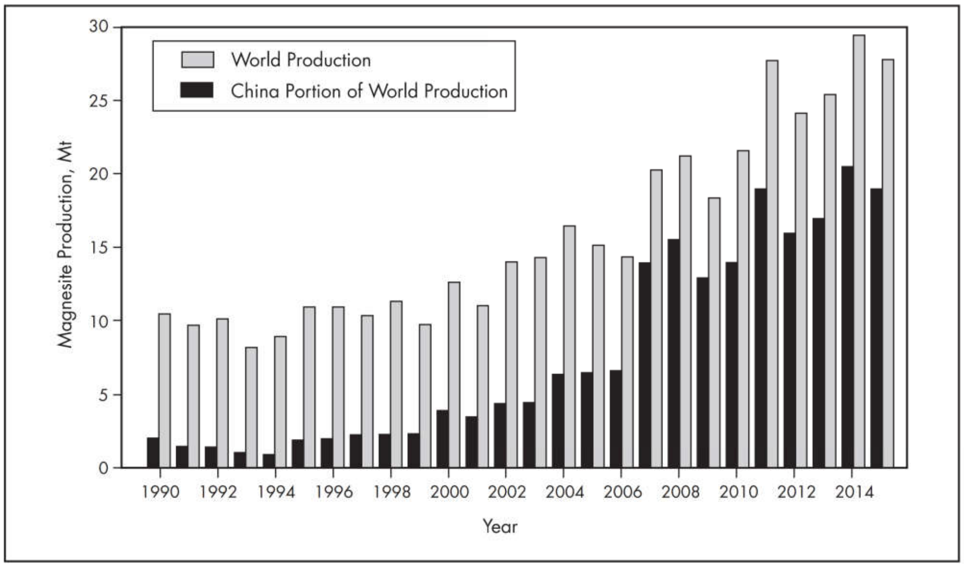


Source: USGS 1992–2015

Figure 1 Annual magnesite production

3. **Dead-burned.** Dead-burned magnesia is formed at calcine temperatures of 1,500°–2,000°C (1,773–2,273 K), resulting in a high-density and low-porosity inert magnesia with very little reactivity. The high temperatures employed produce a near-carbon-free product. Dead-burned magnesia's 50–100-µm crystals have exceptional dimensional stability and strength at high temperatures. These properties make dead-burned magnesia well suited in the manufacture of magnesia-carbon refractories, monolithic gunning refractories, and specialty precast and castable shaped ceramics. Dead-burned magnesia is also referred to as periclase.
4. **Fused magnesia.** High-grade magnesite or calcined magnesia is fused in an arc furnace at temperatures above 2,750°C (3,023 K) over a period of 12 hours with electricity consumption between 3,500 and 4,500 kW·h/t. Fused magnesia crystals greater than 1,000 µm are produced and have near theoretical density of 3.58 g/cm^3.

   Fused magnesia has superior strength, abrasion resistance, and chemical stability and as such finds uses in refractory and electrical insulating markets.

Brucite

Magnesium hydroxide is found in nature as the mineral brucite. It is also precipitated in large quantities from seawater by the addition of calcium hydroxide. Magnesium hydroxide is used as a fire retardant additive, antacid, and laxative. Prior to China's dominance in magnesium metal production (an issue discussed in the "Production of Magnesium Metal" section), magnesium hydroxide was the primary raw material used in the production of magnesium metal.

Dolomite and Dolostone

The term *dolomite* is used in this chapter to designate the near stoichiometric mineral $CaMg(CO_3)_2$, whereas dolostone (or dolomite rock) is a sedimentary rock containing a high concentration of the mineral, usually found with calcite ($CaCO_3$), also known as *limestone*. That association is a result of the process by which dolomite is formed. It is formed by the post-depositional alteration of lime mud and limestone by magnesium-rich groundwater, a process referred to as *dolomization*. Metamorphic transformation of dolostone produces dolomitic marble (King, n.d.).

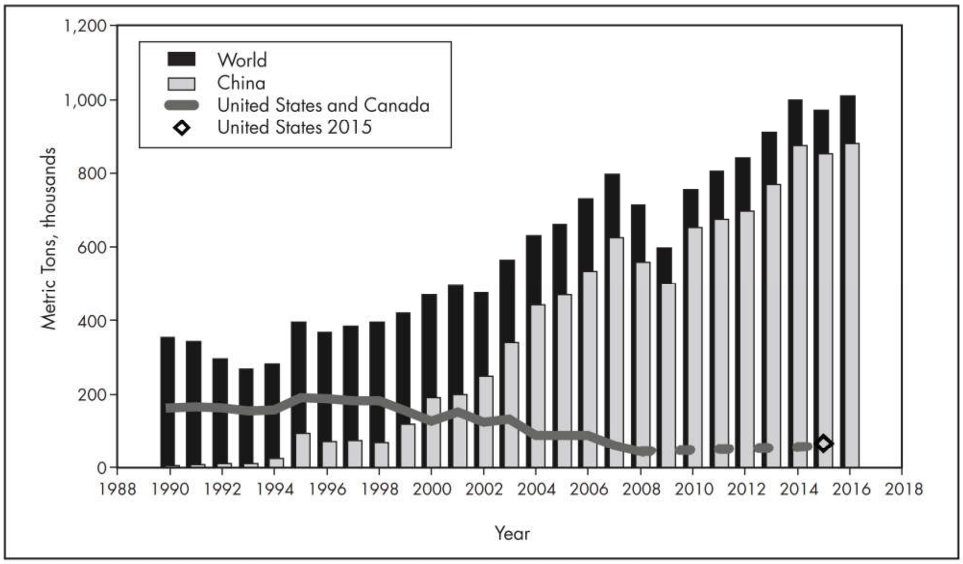
Dolostone is readily available and has many uses in construction. It is crushed, washed, and sized for use as a base material for roads and railroads, bearing the load and providing drainage that also suppresses vegetation growth. It is used as decorative stone and as aggregate in concrete and asphalt. The larger sized fraction of the crushed stone is used as riprap. Dolostone is also used as a cover barrier to protect underwater tunnels and other structures from accidental anchor strikes and sinking debris. Dolostone is quarried, cut, trimmed, ground, and drilled to desired size and shape for use in construction (King, n.d.; USGS 1995–2015).

Both dolomite and dolostone are used as acid buffers for soil, streams, chemical processes, and feed for livestock. They are used to form basic oxides that decrease the viscosity of slags used in iron and steel production. They are also used as an ingredient in the production of glass, bricks, and ceramics (King, n.d.; USGS 1995–2015).

Dolomite has had a checkered history as a raw material for production of magnesium metal, a subject covered in the "Production of Magnesium Metal" section. Currently, dolomite is the primary ore for production of magnesium metal.

Carnallite

Carnallite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$) is primarily used in producing fertilizers. It is an important source of potash. It is also a source of magnesium chloride and is used in Israel and Russia to produce magnesium metal (Neelameggham 2013). Solution mining is used in recovering carnallite. The process consists of drilling holes into an ore body and pumping heated water into the deposit. The heated water dissolves carnallite and other soluble salts, allowing the dissolved minerals to be pumped out. A portion of the water is removed from the solution through evaporation, leading to precipitation of potassium chloride and many of the other soluble salts. The one exception is magnesium chloride that remains in solution with



Data from USGS 1995–2015; Natural Resources Canada 2008; Roskill 2016

Figure 2 Primary production of magnesium

the remaining water and can be separated from the precipitates. Evaporation is used to further concentrate the magnesium chloride, leading to its precipitation (Padhy 2017).

Talc

Talc is a clay mineral composed of hydrated magnesium silicate, $Mg_3Si_4O_{10}(OH)_2$. It has a platelet structure with plates held together by weak van der Waals bonds. These two factors contribute to talc's use in plastics, paint, cosmetics, baby powder, and as a high-temtperature lubricant. It is used as filler in paper production and ceramics (whiteware, tile, pottery, and dinnerware). It is also used as a stiffening agent in plastics and rubber. Talc is added to asphaltic roofing material to improve resistance to the sun's ultraviolet radiation (King, n.d.).

Olivine

The International Mineralogical Association does not classify olivine as a mineral species, but as a mineral group with forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4) as end members. Fayalite and forsterite create a solid solution, with olivine generally identified as having more forsterite (>69 wt %) than fayalite. "Pure forsterite is uncommon, and pure fayalite is very rare" (King, n.d.).

Norway is the principal producer of olivine. It is mined as a gemstone, and non-gem-quality olivine is used as casting sand in aluminum foundries as it requires less water in holding the mold shape. Olivine is used as a tap plug in iron blast furnace operations, and it substitutes for dolomite in slags used in producing iron and steel.

More recently, olivine is being examined as a low-cost means for carbon dioxide sequestration (Ravilious 2016).

PRODUCTION AND COMMERCIAL USES OF MAGNESIUM METAL

Numbers for world production of primary magnesium are presented in Figure 2. The graph reveals that prior to 1999, the United States and Canada accounted for approximately 50% of world production. From 1999 to 2016, the Chinese share of the world's magnesium market has soared from 28% to 87%, while Canadian and U.S. production declined to 6% in 2008, which was the last year of Canadian production. There has been only one plant producing magnesium in the United States since 2003, operated by the Magnesium Corporation of America. The U.S. Geological Survey (USGS) stopped publishing U.S. production statistics in 1998 for proprietary reasons; however, the Canadians provided numbers for both countries from 2001 through 2007. Primary magnesium production in the United States for 2015 was reported to be 59,000 t (metric tons), which represents about 5.8% of world production (Roskill 2016).

Uses of magnesium metal vary depending on demand and cost. A valuable window on its uses, although limited to U.S. consumption, is provided by USGS for both primary and secondary magnesium. Consumption and use data over a period of 20 years at 5-year intervals is presented in Table 2. In the revised numbers for 2011, the USGS 2012 *Minerals Yearbook* offers the first report of the quantum increase in the use of magnesium as a reducing agent for titanium (USGS 1995–2015). Those who report numbers for magnesium production and use often do not include the magnesium used in the Kroll process for production of titanium, as it involves a production–recycle agreement (Evans 2007).

Table 2 U.S. consumption and uses of primary magnesium

Uses	1995	2000	2005	2010	2015*
Consumption, t	109,000	104,000	82,100	55,700	65,900 (42,900)
Structural products, %†	22	30	45	40	17 (25)
Aluminum alloys, %	55	53	37	43	33 (50)
Iron and steel desulfurization, %	12	12	9	11	11 (17)
Reducing agent, %‡	2	1	1	2	34

* Numbers in parentheses reflect values without the contribution from use as a reducing agent in titanium production.

† Casting and wrought products.

‡ Reducing agent for titanium (2015), zirconium, hafnium, uranium, and beryllium.

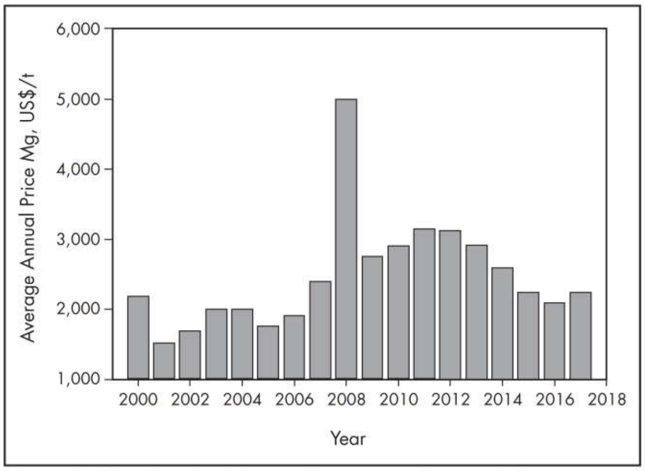


Figure 3 Yearly price history for magnesium metal

In the Kroll process, magnesium is used to reduce titanium tetrachloride, with the resulting magnesium chloride returned as raw material for production of magnesium metal by electrolysis. The numbers in parentheses in the last column of Table 2 are thus a better reflection of the trends observed in the rest of the table, while the other numbers in the last column reflect the magnitude of the effect of the Kroll process on the magnesium metal industry.

Secondary magnesium is recovered from both magnesium- and aluminum-base alloys and used to produce magnesium ingots, magnesium alloy castings, and aluminum alloys. In the United States, recycle and recovery of magnesium has grown and exceeded primary production in 1999. In the United States, secondary magnesium production was 39% of primary production in 1990, 46% in 1995, 198% in 2000, 182% in 2005, 144% (estimated) in 2010, and 136% in 2015. The remelting and casting of secondary magnesium requires between 3.6 and 6 MJ/kg (megajoules per kilogram), whereas production of primary magnesium with the Pidgeon process requires 144 MJ/kg (Johnson and Sullivan 2014).

Magnesium powders have been formed into structural near net shapes by thixocasting and variations of that technique, producing cast parts with 80%–120% greater strength than similar parts produced with conventional casting techniques. In thixocasting a precast billet with a non-dendritic microstructure, produced by intense stirring of the melt as the metal is being cast, is heated to a semisolid state and then injected into hardened steel molds (Neelameggham 2013).

The yearly average price for magnesium metal is presented in Figure 3. The climb in market price from 2005 to 2008 spawned new and revised interest in idled and mothballed plants, and new processes. Those interests faded with the decline in the world's economy at the end of 2008. Currently, there is optimism that the five-year slide in the market price from 2012 to 2016 found a floor at roughly $2,000 per metric ton. By December 2017, the market price had risen 12% over the previous year.

The price for magnesium metal has always been a double-edged sword: use and cost. The low density of magnesium (1.74 g/cm^3) is prized for use in the transportation industry, where energy efficiency is mandated by governments.

Aluminum, with a density of 1.55 times that of magnesium, substitutes for that metal in castings and wrought products and has a price advantage (USGS 2017). In 2008, the prices of magnesium and aluminum peaked at more than $5,000 and $3,000/t, respectively. At the end of 2017, the difference in price between magnesium and aluminum was approximately $250/t.

Zinc also substitutes for magnesium in casings, but not on a weight-reduction basis with a density of 7.14 g/cm^3. Zinc usually has a price advantage, but at the end of 2017 was selling for about $1,000 more per metric ton.

Mineral Processing of Magnesium Ores

There are six commercial magnesium-containing minerals, some in multiple forms. These minerals have multiple uses, and thus the initial treatment of the ore may vary depending on final use. In general, and prior to any thermal processing, lump ore will be crushed, washed, and sized. Some ores will be cleaned using gravitational means, electrostatic separation, magnetic filters, and flotation. Wet or dry attrition scrubbing can be used to remove sharp edges and corners, as well as to remove additional surface material.

Magnesium-containing brines, seawater, and mined carnallite have their water content reduced by evaporation. Brines and seawater also undergo neutralization. Further processing prior to electrolysis is covered in the next section.

Production of Magnesium Metal

Neelameggham (2013) provides a summary of 19th-century efforts in producing magnesium metal. Those efforts involved different electrolytic processes. Late in that century, 1886, the Aluminium und Magnesium Fabrik of Germany electrolyzed molten dehydrated carnallite ($KCl{\cdot}MgCl_2$) in the production of magnesium. Chemische Fabrik Griesheim-Elektron (CFGE) further advanced this technology in 1896, and in the 20th century, CFGE became I.G. Farbenindustrie. Electrolysis of molten carnallite continues in this century (Neelameggham 2013). Prior to World War II, production of magnesium metal was by three primary means (Haughton and Prytherch 1938; Beck 1939; Schambra 1945; Ball 1956; Emeley 1966; Neelameggham 2013):

1. Electrolysis of fused chlorides
2. Electrolysis of magnesium oxide in solution with molten fluorides
3. Carbothermic production of magnesium vapor by direct reduction of magnesium oxide using carbon in an electric arc furnace with a hydrogen atmosphere and subsequent rapid cooling to reduce the extent of reoxidation by carbon monoxide

Silicothermic production of magnesium played an important role in producing magnesium for the Allies during World War II. Its use of thermal energy freed electrical energy for use in other war industries. Today we know this method of producing magnesium as the *Pidgeon process*, named after Lloyd Montgomery Pidgeon of the Canadian National Research Council. However, silicothermic production of magnesium was first developed by the researcher Amati at the University of Padua in Italy. Amati published in his thesis in 1938, a document archived at the university. Immediately afterward, industrial production was established in Bolzano, Italy. The process used externally heated retorts identical in concept to those used by Pidgeon two years later.

"Unlike aluminum, the demand for magnesium took a precipitous drop following World War II, causing" a decline in the variation of process production technology. "Carbothermic and fluoride–melt electrolytic processes exited commercial production. Silico-thermic processes took a backseat, until the mid-1990s, to the electrolytic conversion of magnesium chlorides" (Neelameggham 2013).

A review of magnesium metal production begins with electrolysis of fused chlorides, followed by discussion of the Pidgeon process; the discussion is concluded with review of the magnetherm process. The discussion begins with electrolytic-produced magnesium, not because of its current commercial importance, but as a result of its dominance in the second half of the last century, and because it is still practiced where natural brines are available. The magnetherm process also played a significant role in magnesium production in the second half of the last century, but like electrolytic production, it has precipitously declined with growth of magnesium production by the Pidgeon process in China. Discussion of the magnetherm process follows review of the Pidgeon process, as it is a variant of that process. Reasons for the dramatic growth of magnesium production in China are reviewed in the "Pidgeon Process" section.

Fused Salt Electrolysis

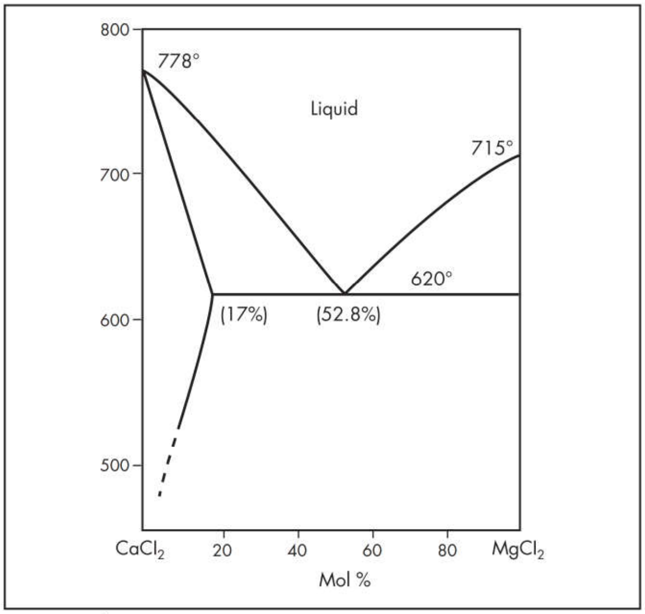
The thermodynamic stability of magnesium compounds precludes recovery of magnesium by aqueous electrolysis, except when the cathode is an amalgam consisting primarily of mercury. Recovery of magnesium in an amalgam leads to recovery of most other metal ions in the aqueous solution. Thus, this approach would require further distillation, which is complicated by a multitude of other metal atoms in the amalgam.

The answer to recovery of magnesium by electrolysis was, as in the case of aluminum production, to turn to halides. Identifying a suitable molten salt for production of molten magnesium by electrolysis begins with the normal melting and boiling point temperatures of the element, which are 649°C (922 K) and 1,090°C (1,363 K), respectively, and identifying a solvent compound of greater thermodynamic stability than the magnesium solute component. The solvents meeting the second restriction are alkali and alkaline earth halides.

The molten salt must exist at temperatures well below the normal boiling point of magnesium to avoid yield reduction through magnesium vapor loss. The operational temperature needs to be above the normal melting temperature of magnesium to prevent magnesium crystal growth on the cathode. The solubility of magnesium oxide in calcium chloride is insignificant, whereas it is highly soluble in calcium fluoride but at temperatures greater than 1,350°C (1,623 K). Magnesium chloride is both soluble in calcium chloride and at temperatures as low as 620°C (893 K), as shown in the phase diagram in Figure 4. The typical fused salt contains, in addition to both magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$), small concentrations of sodium chloride (NaCl), potassium chloride (KCl), and lithium chloride (LiCl).

A flow diagram for electrolytic production of magnesium metal is presented in Figure 5. The diagram includes two options depending on the degree to which water is removed from magnesium chloride. The anhydrous route using $MgCl_2$ is representative of the Norsk Hydro process, whereas use of $MgCl_2{\cdot}H_2O$ is typical of the Dow process.

Magnesium chloride is produced from seawater by producing concentrated brines through evaporation of water in holding ponds. Magnesium cations in the brine are converted to magnesium hydroxide, which has a solubility of only



Source: Smith 1983

Figure 4 $CaCl_2$–$MgCl_2$ phase

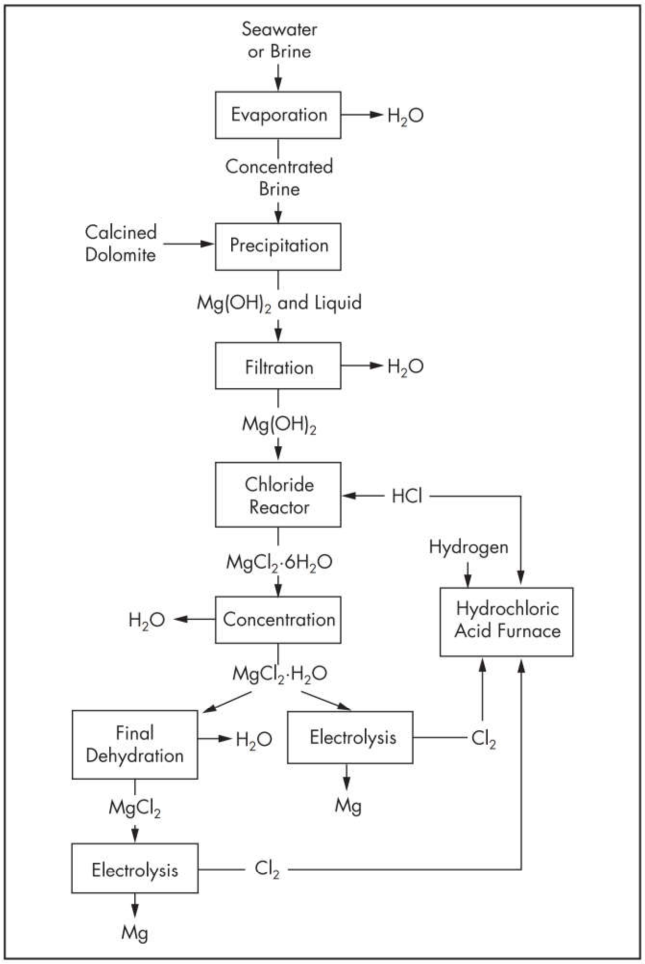


Figure 5 Flow diagram for electrolytic production of magnesium metal

0.00069 g per 100 g of water at 20°C (293 K), by the following reaction:

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \quad \textbf{(EQ 2)}$$

The hydroxide ions are supplied by calcium hydroxide, $Ca(OH)_2$, or sodium hydroxide (NaOH) as both are soluble. The magnesium hydroxide is filtered and converted to the chloride by reaction with hydrochloric acid:

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O \quad \textbf{(EQ 3)}$$

The resulting magnesium chloride solution is evaporated and partially dehydrated in the Dow process:

$$\begin{aligned} MgCl_2\ \text{(solution)} &\rightarrow MgCl_2{\cdot}6H_2O \\ &\rightarrow MgCl_2{\cdot}4H_2O \\ &\rightarrow MgCl_2{\cdot}2H_2O \\ &\rightarrow MgCl_2{\cdot}H_2O \end{aligned} \quad \textbf{(EQ 4)}$$

Or complete dehydration is used as in the Norsk Hydro process:

$$MgCl_2{\cdot}H_2O \rightarrow MgCl_2 \quad \textbf{(EQ 5)}$$

It is also possible with natural brines, where extensive solar evaporation ponds are available, to produce "magnesium chloride rich liquor through evaporative crystallization. This involves removal of large quantities of sodium chloride, potassium chloride/sulfate salts by the initial crystallization" (Neelameggham 2013). Near-complete dehydration (Reaction 5) is achieved by spray dryers as practiced by US Magnesium in Utah (United States). A similar process is under development in China at Qarham salt lakes and salt pans.

The resulting magnesium chloride must be purified. The magnesium chloride produced from seawater or natural brines requires removal of sulfates as they decompose in the molten salt, producing oxides that impact removal of other impurities and the electrolytic process.

Boron is a particularly troubling impurity, the source of which is usually seawater. Boron (as borates) in parts per million by weight concentration in the molten salt leads to deposits of borides on the magnesium produced at the cathode, which precludes coalescence of the magnesium droplets, preventing them from joining the pool of molten metal that forms on top of the fused salt (Neelameggham 2013).

Reactions occurring in the electrolytic cell are

$$\text{Cathode: } Mg^{2+}\text{(molten salt)} + 2e^- \rightarrow Mg\text{(liquid)} \quad \textbf{(EQ 6)}$$

$$\text{Anode: } 2Cl^-\text{(molten salt)} \rightarrow Cl_2\text{(gas)} + 2e^- \quad \textbf{(EQ 7)}$$

$$\text{Overall reaction: } MgCl_2 \rightarrow Mg + Cl_2 \quad \textbf{(EQ 8)}$$

The production of Cl_2 gas at the anode and molten Mg metal, which floats on top of the fused salt, at the cathode requires a physical separation between anode and cathode to prevent rechlorination of the magnesium. Considerable effort has been put into improving cell operation; for more in-depth reviews of cell design, readers are directed to Neelameggham (2013) and Evans (2007).

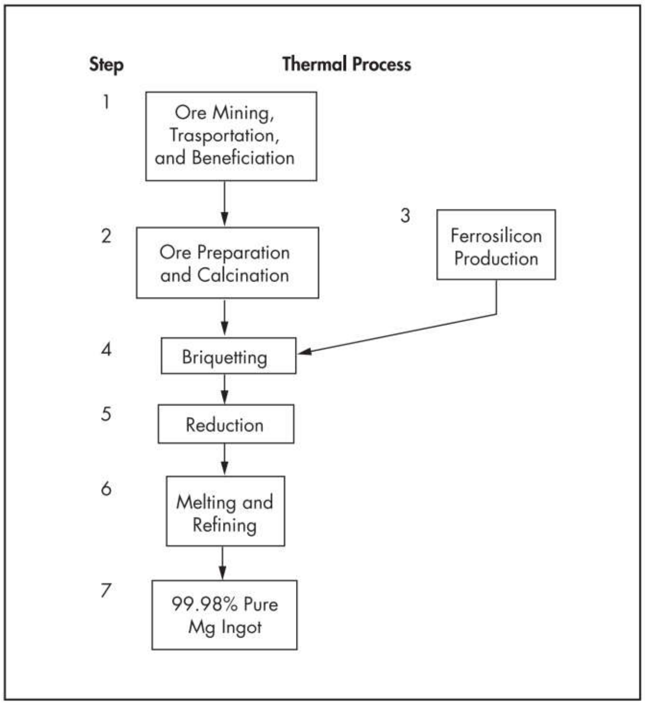
Pidgeon Process

World War II spawned the need for more magnesium production that led to widespread adoption of the Pidgeon process. After the war, economic conditions changed, and most plants using the Pidgeon process closed. Today, and for the first two decades of the 21st century, those conditions that produced a decline in magnesium production by the Pidgeon process have made the process dominant in China. That dominance began around 2000 with many small Chinese producers. Today the magnesium market is dominated by China (Figure 2). According to Abdellatif (2006):

> Chinese dominance may be attributed to several factors, four of which are:
>
> 1. The low cost of raw materials, particularly ferrosilicon
> 2. A cheap and abundant labour force
> 3. Inexpensive coal and energy
> 4. Safety, health, and environmental standards that are lower than those in Europe and the United States

These factors make it possible for the Pidgeon process to succeed in China, in spite of it being a batch and labour-intensive process.

A flow diagram for the Pidgeon process is presented in Figure 6. Dolomite, $CaMg(CO_3)_2$, or a combination of limestone ($CaCO_3$) and magnesite ($MgCO_3$) are mined, crushed, washed, and sized (Step 1 in Figure 6; note that the individual steps are numbered and used in subsequent tables to identify how specific operations contribute to overall energy requirements). The dolomite (or the limestone and magnesite) must be calcined in an operation separate from the reduction of magnesium oxide to remove carbon and oxygen (as CO_2) that otherwise would reoxidize Mg. During calcination, the following reaction occurs:



Source: Johnson and Sullivan 2014

Figure 6 Pidgeon process flow diagram

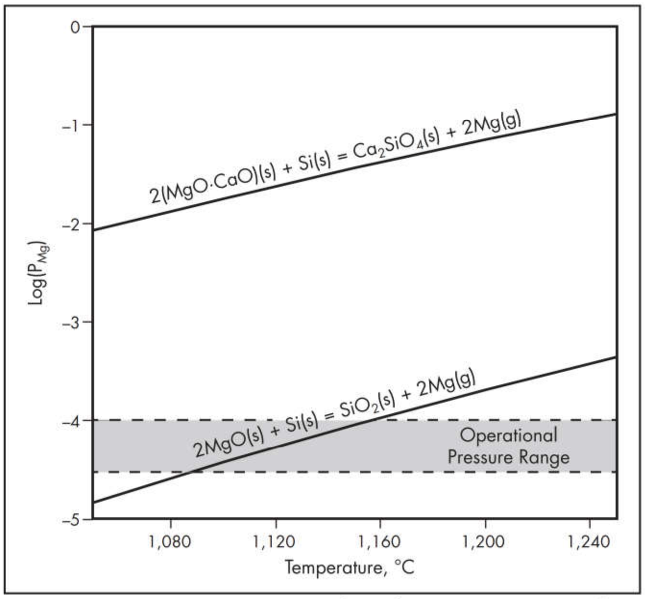


Figure 7 Magnesium pressure in bars for Reactions 10 and 11

$$MgCa(CO_3)_2 = MgO \cdot CaO + 2CO_2(g),\ \Delta H_{900C} = 290\ kJ \qquad \textbf{(EQ 9)}$$

The reaction, carried out at 900°C (1,173 K), is endothermic, and $MgO \cdot CaO$ is a eutectic-type mixture of the two separate oxide phases, often referred to as *dolime* (Step 2).

The Pidgeon process is based on the reduction of magnesium oxide by silicon (Toguri and Pidgeon 1961):

$$2MgO(s) + Si(s) \rightarrow SiO_2(s) + 2Mg(g),\ \Delta H_{1,150C} = 573\ kJ \qquad \textbf{(EQ 10)}$$

"The practical applications of this principal require the reduction of calcined dolomite ore [Step 5] with ferrosilicon at high temperatures. The overall reaction describing the process (Toguri and Pidgeon 1962) is as follows" (Ramakrishnan and Koltun 2004):

$$2(MgO \cdot CaO) + Si(ferrosilicon) = Ca_2SiO_4 + 2Mg(g),\ \Delta H_{1,150C} = 457\ kJ \qquad \textbf{(EQ 11)}$$

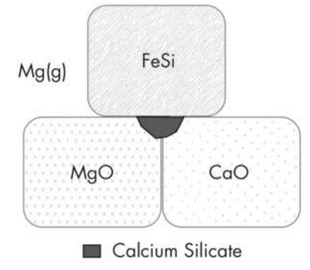
Silicon (with a high thermodynamic activity), in combination with calcium oxide (CaO) and in the production of a calcium silicate, serves as a superior reducing agent for MgO. The superiority is presented in Figure 7, where the equilibrium vapor pressure of magnesium by Reaction 11 is compared to that achieved by Reaction 10. The diagram reveals

- That formation of the calcium silicate increases the vapor pressure of the volatilized magnesium over just silica formation;
- It is important to keep a high activity of all the reactants;
- At the temperatures presented, the process must be operated under a vacuum to prevent establishing equilibrium and thus a stop to magnesium vapor production; and
- The vacuum required would need to be substantially greater for Reaction 10 versus Reaction 11.

As a result of the last item, Reaction 10 is no longer considered for further discussion with respect to the Pidgeon process.

Reaction 11 is highly endothermic, requiring a constant heat source. Thus, the reaction rate is subject to heat transfer control. With adequate available heat, the reaction rate initially depends on the degree to which there is physical contact between reactants (Figure 8), and finally limited by solid-state diffusion of silicon as presented in Figure 9. The overall reaction rate is largely limited by solid-state diffusion. Briquetting of fine powders of the calcined dolomite and ferrosilicon is done to improve contact between reactants and to decrease the distance for Si solid-state diffusion.

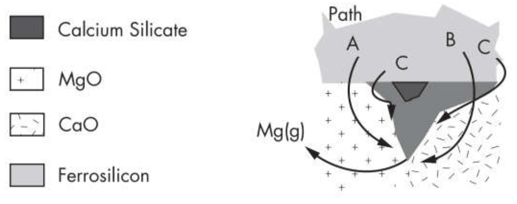
Retorts used in the Pidgeon process consist of a one-end-closed tube as presented in Figure 10. The open end of the tube has a collar and is sealed with an end plate during production of Mg. The end plate is removed to input the charge, which is pushed all the way to the closed end of the tube. The end plate is then used to seal the retort, and the pressure inside the retort is reduced to approximately 3–10 Pa during Mg production. At the end of production, the end plate is removed and the Mg recovered before the partially spent charge is removed. Retorts are mounted in banks as shown in Figure 11A, with the cooler end of the retort extending outside the furnace.



Where there is contact between MgO,CaO, and FeSi the following reaction occurs:

$2MgO + 2CaO + Si \rightarrow 2Mg(g) + Ca_2SiO_4$

Figure 8 The Pidgeon process requires contact between MgO, CaO, and ferrosilicon to initiate reaction



Chemical Reaction for Paths A, B, and C:
$2MgO + 2CaO + Si \rightarrow 2Mg(g) + Ca_2SiO_4$
Path A—Solid-State Diffusion of Si Through MgO
Path B—Solid-State Diffusion of Si Through CaO or Ca_2SiO_4 or Both
Path C—Solid-State Diffusion Along the Grain Boundary Between MgO and Ca_2SiO_4, and CaO and Ca_2SiO_4

Figure 9 Silicon must diffuse through reactants or Ca_2SiO_4 to the MgO–CaO interface for further Mg(g) production

The furnace temperature is between 1,300°C (1,573 K) and 1,400°C (1,673 K) to achieve the necessary heat transfer for the endothermic reaction, and a charge temperature of 1,150°C (1,423 K) to 1,200°C (1,473 K) inside the retort. The other end of the retort extends outside the furnace and has an internal temperature of 600°C (873 K) to 650°C (923 K). Mg vapor is drawn out of the hotter end of the retort where its equilibrium pressure with the charge exceeds the operational pressure of approximately 3–10 Pa created by condensation of Mg(s) in the cooler end of the retort. Production of Mg continues as long as the rate of production in the hot end of the retort is capable of producing a magnesium vapor pressure greater than that in the cooler end of the retort. The magnesium vapor condenses on an internal sleeve at the cooler end of the retort. The sleeve is attached to the end plate that is used to seal the retort, thus the deposited Mg can be easily removed from the retort without having to extract the retort from the furnace. In China, there have been attempts to create vertical retorts that offer some advantages over the horizontal retorts in automatic loading and unloading of charge and waste product (D. McCallum, personal communication).

Retorts in 1980 were made of nickel chrome steel, were typically 3-m long with inside diameters of 25 cm and 2.5-cm-thick walls (Gill 1980). Today 50-mm-thick boiler steel is used. The retorts lose structural strength after 6 to 9 months with eventual collapse inward under the vacuum (D. McCallum, personal communication). Figure 11B shows that today's retorts are longer and of greater diameter than those used in 1980.

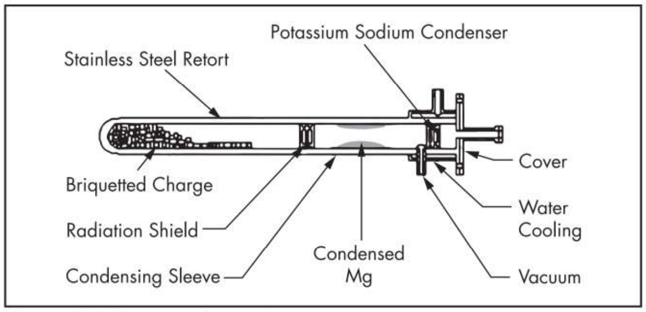


Figure 10 Retort schematic

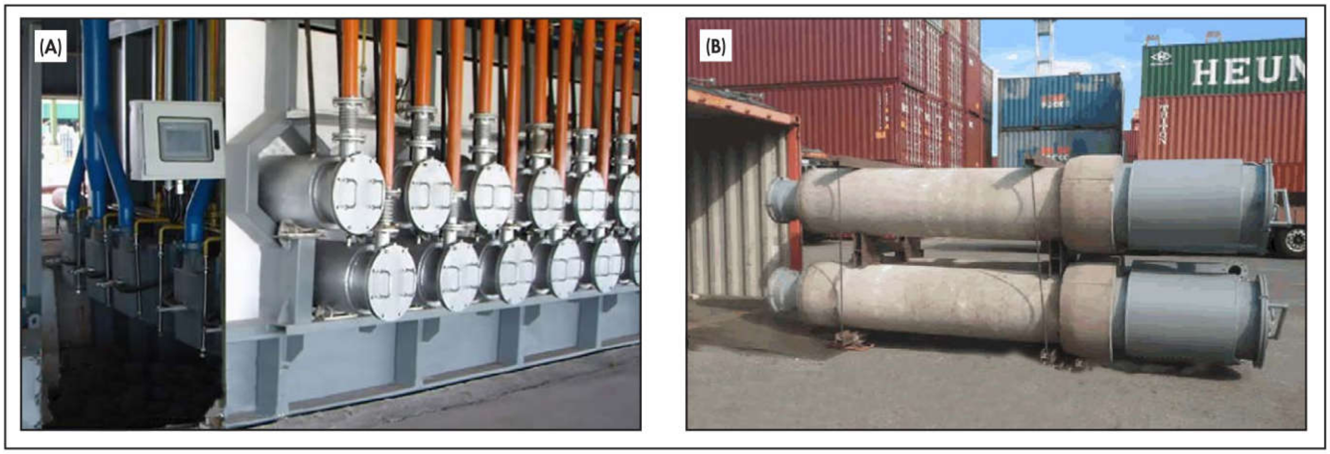
The Pidgeon process is a batch process and thus labor intensive. The increase in retort size does not impact the chemistry, but does reduce labor cost as more raw material can be charged to a retort.

In 1980, it was reported that each retort produced 14.5 kg of 99.98% pure magnesium from 109 kg of charge in 8 hours. The mass ratio of dolime to ferrosilicon was 5 to 1 (90.8 kg dolime to 18 kg ferrosilicon). The ferrosilicon is typically 75 wt % Si (6 moles Si to each mole of Fe). The dolime and ferrosilicon are ground, mixed, and briquetted. The briquettes are preheated to 700°C (973 K) before being charged to the retort. In 1980, the recovery of Mg in the product stream was about 63% (Gill 1980).

The Pidgeon process dominates commercial production of magnesium metal from ore. Argonne National Laboratory provides an excellent review of both energy requirements and the extent of greenhouse gas emissions from the process (Johnson and Sullivan 2014). Total energy requirements and how that energy is distributed between different energy sources are presented in Table 3, along with total greenhouse gas emissions in kilograms of CO_2 gas equivalent for producing 1 kg of primary Mg ingot for the process steps listed. The numbers in the table are per kilogram of virgin Mg for two different plants using the Pidgeon process. The cost figures in Table 4 have been computed using the unit costs listed in the table and numbers from Table 3. Table 5, from the Argonne National Laboratory report (Johnson and Sullivan 2014), shows how the sources of energy identified in Table 3 for Pidgeon B are distributed to the steps identified in Figure 6.

Using data in Table 5 and the listed heating values, the cumulative energy demand for Pidgeon B in Table 3 exceeds the energy computed by 51 MJ. It is assumed that the difference is associated with the heating value used for the coke oven gas, and that a better value is 27.5 MJ/m^3 rather than 20 MJ/m^3, as the heating value of the gas will depend on the hydrogen content in the coal used to produce the gas.

Using the new value for the coke oven gas, the energy consumption for the reduction step in Figure 6 is computed to be 100.2 MJ/kg of magnesium produced in the Pidgeon process. The theoretical value, assuming the briquettes are charged to retorts at 700°C (973 K), is 13.7 MJ/kg of Mg. The energy efficiency is computed to be 13.7%, a value that compares favorably to the 12% reported in the literature for



Courtesy of Federal Pipe Centrifugal Casting Machine Company

Figure 11 (A) Retorts in operation and (B) new retorts

Table 3 Energy units, cumulative energy demand, and greenhouse gas values

Process, 1 kg Mg	Electricity, kW·h	Gas, m^3	Coal, kg	Diesel, L	Cumulative Energy Demand, MJ/kg	Greenhouse Gas, kg/kg	Included Steps (from Figure 6)
Pidgeon A	12.9	—	10.4*	0.111†	393	37.5	1–7
Pidgeon B	10.16	6.8‡	1.05§	—	256	30.3	1–7

Adapted from Johnson and Sullivan 2014
* Anthracite coal, heating value ~28 MJ/kg.
† Diesel, heating value ~43 MJ/L.
‡ Coke oven gas, heating value ~20 MJ/m^3.
§ Coke, heating value ~31 MJ/kg.

Table 4 Energy cost as a function of energy source

	Unit Price						
Process, 1 kg Mg	Electricity, \$0.10/kW·h	Natural Gas, \$0.106/m^3	Coke Oven Gas*, \$0.053/m^3	Coke, \$0.224/kg	Coal, \$0.108/kg	Diesel, \$0.156/L	Total Energy Cost
Pidgeon A	\$1.29	—	—	—	\$1.123	\$0.017	\$2.43
Pidgeon B	\$1.016	—	\$0.360	\$0.235	—	—	\$1.61

Source: Johnson and Sullivan 2014
* The cost of coke oven gas is assumed to be half that of natural gas, as the heating value is one-half that of natural gas.

Table 5 Inputs to Pidgeon B process, 1 kg of magnesium ingot

Step	Operation	Output	Coke Oven Gas, m^3	Electricity, kW·h	Coke, kg	Other Inputs
1	Mining	10.5 kg dolomite	—	—	—	—
2	Ore preparation and calcining	—	2.6	0.192	—	—
3	Ferrosilicon preparation	1.05 kg $FeSi_6$	—	8.92	1.05	1.19 kg quartz, 0.24 kg iron
4	Briquetting	—	—	0.672	—	0.13 kg CaF_2, 0.1 kg fluxes
5	Reduction	—	3.6	0.320	—	—
6 and 7	Refining and ingot production	1 kg Mg	0.6	0.049	—	—
Total			**6.9**	**10.16**	**1.05**	

Source: Johnson and Sullivan 2014

Chinese production (Ramakrishnan and Koltun 2004). The Pidgeon process is the simplest process, but it is both labor intensive and the least energy efficient process for producing magnesium (Simandl et al. 2007).

In China, the economics of the Pidgeon process has been improved by tailoring the waste from the retorts, which amounts to approximately 80% of the initial charge, to match both the chemistry and mineralogy of portland cement (D. McCallum, personal communication). Composition requirements for both portland cement and waste from the Pidgeon process are presented in Table 6. Numbers for the latter are computed from typical operations data (Gill 1980), assuming the waste from the retort is allowed to be fully oxidized. Portland cement can be produced by increasing the magnesium yield or reducing the amount of MgO charged to a retort, and adding additional CaO, either to the retort or to the oxidized waste. Currently, the prices of portland cement and magnesium metal in the United States are nearly identical on a mass basis. Given that the waste amounts to four times the mass of magnesium metal produced, a magnesium producer may more accurately be viewed as a cement company producing a bit of magnesium (D. McCallum, personal communication). China is the world's leader in production of portland cement.

Table 6 Comparison of portland cement composition to typical waste from Pidgeon process

Composition	Portland Cement, wt %	Pidgeon Process, wt %
CaO	60–66	51
SiO_2	19–23	29
Al_2O_3	2–6	—
Fe_2O_3	1–6	6
MgO	<5	14
CaO:SiO_2 mass ratio	>2	1.8

Magnetherm

Although there are no currently operating magnetherm plants in North America, the process did play an important role in magnesium metal production during the second half of the 20th century. With the uptick in the price of magnesium during the period from 2006 to 2008 (Figure 3), there was optimism that idled magnetherm plants would reopen. That optimism was dashed with the Great Recession in 2009. Plans for a similar process under development by Mintek (Abdellatif and Freeman 2008) failed to gain momentum as well. Magnetherm is a variant of the Pidgeon process, and given its earlier historical importance, its chemistry is worth reviewing.

Christini wrote a Minerals, Metals & Materials Society–award winning paper on the magnetherm process as practiced by Alcoa in Addy, Washington, United States (Christini 1980). The process was originally developed by the French company Pechiney in the 1950s and further adapted by Alcoa in the 1960s. A flow diagram for the process is presented in Figure 12. The magnetherm process, like the Pidgeon process, uses ferrosilicon to reduce magnesia in the production

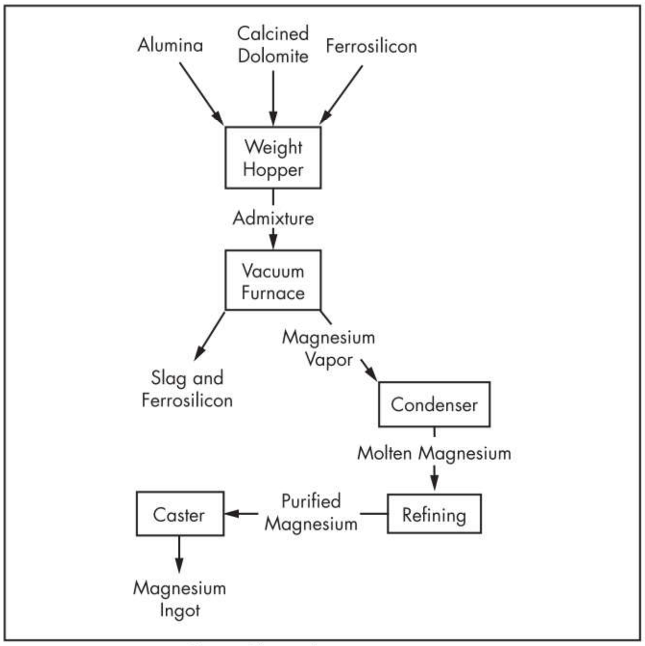


Figure 12 Magnetherm flow diagram

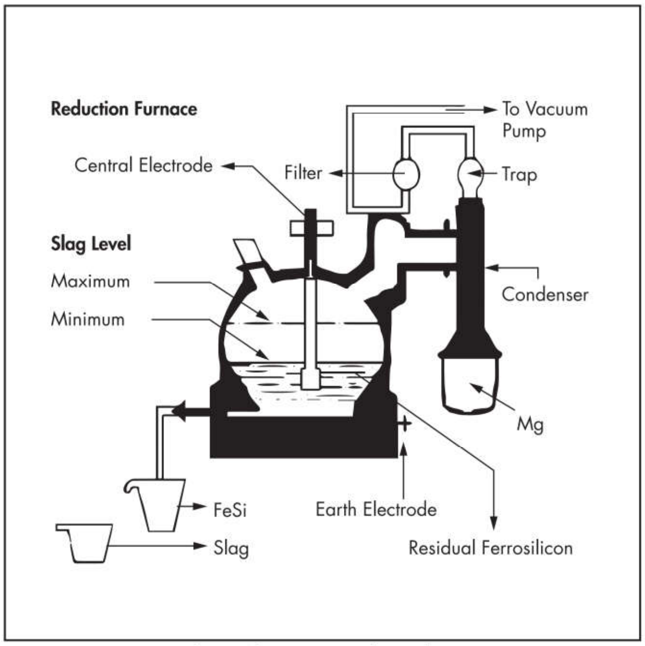


Figure 13 Magnatherm furnace and condenser

of magnesium vapor. However, the operational temperature is 1,550°C (1,823 K) and the magnesia is dissolved in a CaO-SiO_2-Al_2O_3 slag. The magnetherm process was developed to overcome the undesirable aspects of the Pidgeon process. The magnatherm process is less labor intensive, operates semi-continuously at reduced vacuum, and produces magnesium vapor at both higher reaction rate and yield—all aspects that improved the economics of production in the West. The magnetherm process does require a significant initial investment in comparison to the Pidgeon process. That disadvantage and the low labor cost in China are largely responsible for the rapid growth and use of the Pidgeon process in the East and demise of the magnetherm process in the West.

The magnetherm furnace with condenser is represented schematically in Figure 13. Calcined dolomite (dolime), alumina, and ferrosilicon are mixed, weighed, and charged to the furnace intermittently. The addition of alumina to the admix lowers the fusion temperature of the slag that consists of approximately 55 wt % CaO, 25 wt % silicon dioxide (SiO_2), 14 wt % aluminum oxide (Al_2O_3), and 6 wt % MgO. Some of the silica in the slag is produced as a result of the reduction of magnesia with silicon. The operational pressure for the magnetherm process in producing magnesium vapor is approximately 5,000 Pa as compared to the 3–10 Pa for the Pidgeon process. The higher pressure is achieved with the higher operational temperature, producing both molten slag and molten ferrosilicon. With the molten phases and the gaseous product, the process can be run in a quasi-continuous manner with the vacuum in the furnace being broken only twice during a typical 20–24-hour cycle resulting in the production of 3–8 metric tons of Mg. Furnace operation is interrupted when the slag and ferrosilicon rise to the maximum level indicated in the drawing. Tapping of the molten phases produces a minor downtime. A longer downtime occurs when the magnesium crucible is removed, replaced, and slag and molten ferrosilicon tapped. The molten magnesium is taken to the foundry, where the metal is fluxed with a chloride salt (KCl and $MgCl_2$), and the purified metal is poured into ingot molds (Christini 1980).

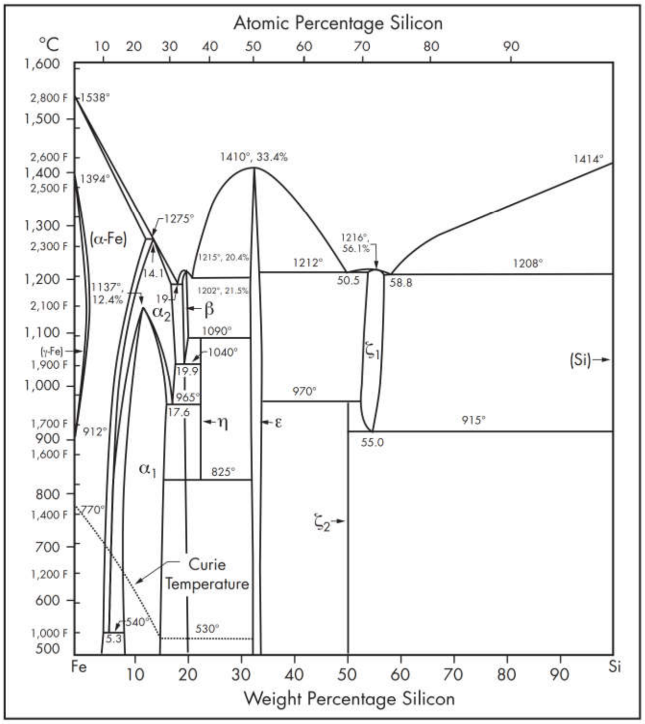
The reaction occurring in the furnace

$$2MgO(slag) + Si(l\text{-ferrosilicon}) \rightarrow SiO_2(slag) + 2Mg(g),\ \Delta H_{1{,}550C} = 514\ \text{kJ} \quad \textbf{(EQ 12)}$$

requires high activities for MgO and Si and a low activity for SiO_2 to reduce the level of vacuum required to produce Mg vapor. The data in Figure 7 suggests that raising temperature increases the vapor pressure of Mg, and thus reduces the degree to which a vacuum must be applied. From the Fe–Si phase diagram in Figure 14, and at a temperature of 1,550°C (1,823 K), it is possible to deduce that the activity of Si in the molten FeSi (75%) will be high but have a value something less than the ideal value. An activity approaching 0.8 for the silicon is not unexpected.

To achieve the maximum activity for MgO in the slag, the slag composition must be saturated with MgO. That occurs when the slag composition is in contact with the primary phase field for MgO. The phase diagram for the liquidus surface for the CaO-MgO-SiO_2 system presented in Figure 15 reveals that the minimum temperature for the maximum activity of MgO ($a_{MgO} = 1$) in the slag occurs at a temperature of approximately 1,600°C (1,873 K). That occurs where the primary phase fields for dicalciumsilicate (Ca_2SiO_4), periclase (MgO), and merwinite ($3CaO{\cdot}MgO{\cdot}2SiO_2$) coexist, a point marked by the black diamond on the phase diagram. The high temperature associated with that point would reduce the extent of vacuum required to draw off the magnesium vapor. Higher temperatures pose a serious problem for the long-term structural integrity of the furnace. The exterior of the furnace is "water cooled by a combination of sprays, over flow weirs, and water cooled flanges to maintain a freeze zone of slag within the furnace." The freeze zone is critical to prevent the outer steel shell from being penetrated by the ferrosilicon (Sever and Ballain 2013).

Alumina is added to the admix charged to the furnace to reduce the fusion temperature of the slag. The phase diagram in Figure 16 incorporates the impact of alumina on the liquidus surface presented in Figure 15, but at a constant alumina content of 15 wt %. The temperature at the point in Figure 16 where the primary phase fields for dicalciumsilicate (Ca_2SiO_4), periclase (MgO), and merwinite ($3CaO{\cdot}MgO{\cdot}2SiO_2$) meet is now reduced from 1,600° to 1,485°C (1,873 to 1,758 K).



Source: Lyman 1973

Figure 14 Iron–silicon phase diagram

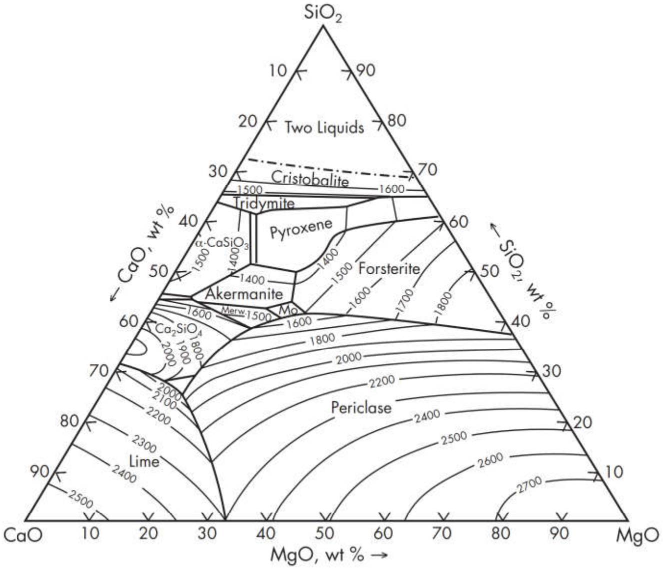
It is important to remember that the admix charged to the furnace will be rich in MgO and poor in SiO_2, as the former is the source for Mg vapor, and SiO_2 is the product of the reduction Reaction 12. The final desired composition of the slag will be near the boundary separating primary phase MgO (periclase) and Ca_2SiO_4, producing a lower fusion temperature of the slag and maximum thermodynamic activity of MgO in the slag while limiting MgO loss. If a higher temperature was employed in the furnace, an example being 1,900°C (2,173 K), loss of magnesium to the slag would double at MgO saturation.

Although it is essential to have a high value for the activity of MgO in the slag, Reaction 12 indicates that it is also essential to have a low value of the activity of SiO_2 in the same phase. Figure 17 contains the isoactivity curves for SiO_2 in the slag phase at 1,550°C (1,823 K) for the Al_2O_3-CaO-SiO_2 slag. Although MgO is not included in that graph, it has long been established that MgO and CaO behave similarly in slags and, as such, small additions of MgO to a slag with a significant concentration of CaO does not impact the activity of the other components in the slag. Point b in the ternary system presented in Figure 17 has been identified by Christini as being equivalent to the slag composition in the quaternary system (Al_2O_3-CaO-MgO-SiO_2). At that point, the activity of SiO_2 in the slag is 0.001.

With this last missing number, it is possible to compute the equilibrium vapor pressure of Mg in Reaction 12. The standard states for the reactants and products in the reaction are for the pure compound or element in its stable form at 1,550°C (1,823 K) and for magnesium vapor at a pressure of 1 bar. At that temperature and at equilibrium, ΔG° for the

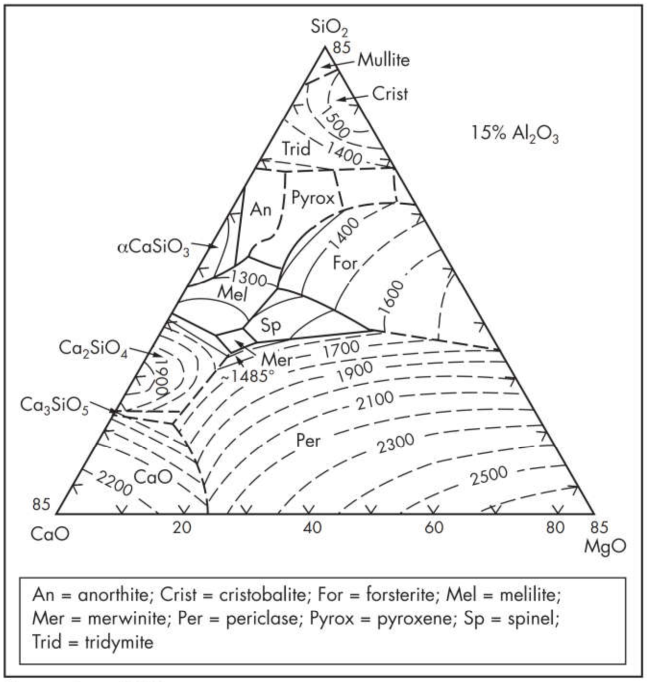
Compounds

Name	Composition
Periclase	MgO
Cristobalite Tridymite	SiO_2
Lime	CaO
Diopside	CaO : MgO : $2SiO_2$
Pyroxene	Solid solution along section $MgO{\cdot}SiO_2$–diopside
Akermanite	$2CaO{\cdot}MgO{\cdot}2SiO_2$
Monticellite (Mo)	$CaO{\cdot}MgO{\cdot}SiO_2$
Merwinite (Merw)	$3CaO{\cdot}MgO{\cdot}2SiO_2$
Forsterite	$2MgO{\cdot}SiO_2$



Source: Roth and Vanderah 2005

Figure 15 Liquidus surface of the CaO-MgO-SiO_2 phase diagram



An = anorthite; Crist = cristobalite; For = forsterite; Mel = melilite; Mer = merwinite; Per = periclase; Pyrox = pyroxene; Sp = spinel; Trid = tridymite

Source: Levin 1969

Figure 16 Iso-section for 15 wt % Al_2O_3 liquidus surface for the Al_2O_3-CaO-MgO-SiO_2 system

reaction is 126.93 kJ and the equilibrium constant, K, has a value of $2.31 \cdot 10^{-4}$. Using the activities just discussed

$$K = 2.31 \cdot 10^{-4} = \frac{a_{\mathrm{SiO_2}} \cdot P_{\mathrm{Mg}}^2}{a_{\mathrm{MgO}}^2 \cdot a_{\mathrm{Si}}} = \frac{0.001 \cdot P_{\mathrm{Mg}}^2}{1^2 \cdot 0.8} \quad \textbf{(EQ 13)}$$

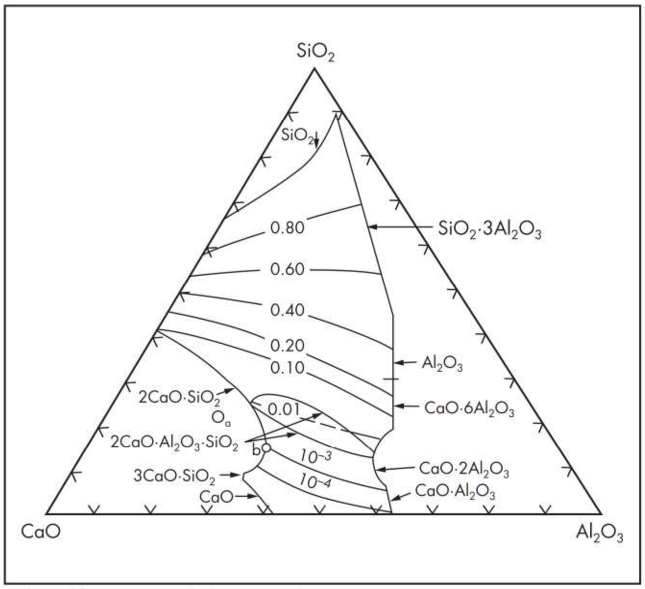
$$P_{\mathrm{Mg}} = 0.43 \text{ bar} \quad \textbf{(EQ 14)}$$

By operating the magnetherm furnace at 0.05 bar, Reaction 12 can never achieve equilibrium. The reaction proceeds as written, and Mg vapor is transformed to liquid in the condenser.

The electrode shown in Figure 13 is submerged in the slag. An AC current passes through the molten slag, providing resistance heating below the upper surface of the slag. That arrangement ensures that the natural convective flow pattern of hot slag rises in the center of the furnace and sweeps vertically away toward the cooler walls of the furnace before sinking and then is drawn back toward the electrode to be heated and rise again.

Christini (1980) has pointed out that the flow pattern is essential to achieve maximum magnesium yield. He has demonstrated that Reaction 12 is thermodynamically favored at the upper surface of the molten slag and that hydrostatic head significantly precludes the reaction from occurring in the bottom of the melt where excess ferrosilicon forms a pool in contact with the molten slag. The flow pattern of the slag helps keep the small particles of ferrosilicon to stay suspended in the slag before sinking to the bottom of the furnace, thereby providing greater time for reaction between MgO in the slag and Si.

Approximately 7 metric tons of material are charged to the magnetherm furnace for every metric ton of Mg metal produced (Yudiarto 2013).



Adapted from Rein and Chipman 1965

Figure 17 Isothermal section of Al_2O_3-CaO-SiO_2 with isoactivity line for SiO_2 in slag phase at 1,550°C (1,823 K)

REFINING OF MAGNESIUM METAL

Magnesium from the Pidgeon process comes in a solid form called *crown*. The crown is fused in a steel crucible along with mixed chloride salt solution containing both $MgCl_2$ and KCl. The flux acts as a heat transfer medium and as a protective layer over the top of the magnesium, preventing oxidation of the metal by isolating it from air. The $MgCl_2$ in the salt also reacts with Ca and K dissolved in the molten magnesium, exchanging the impurities with Mg. In the electrolytic process, this step is excluded as the molten magnesium is removed from the cell along with some of the electrolyte. Fluorspar (CaF_2) and magnesium oxide (a thickening agent) are added to the molten salt to help in the settling of oxide impurities in the molten metal (Neelameggham 2013).

Casting

The "surface of molten magnesium is sensitive to inclusions from oxidation, [therefore] an inert blanket gas is generally used to protect the metal. Alternatively, sulfur powder is spread across the surface of molten magnesium for protection …" (Johnson and Sullivan 2014). Beginning in 1980, sulfur hexafluoride (SF_6), a nontoxic gas, was first used as a preferred blanket gas. By the early 1990s, the gas was determined to be "an extremely potent greenhouse gas, with a global warming potential (GWP) of 23,900·$[CO_2]_{eq}$ per [kilogram] of gas" (Johnson and Sullivan 2014). Alternative blanket gases under consideration are sulfur dioxide (SO_2) with no GWP, but it is corrosive and a known pollutant, and hydrofluorocarbon (HFC)-134a with a GWP of 1,300. Consumption of blanket gases per kilogram of Mg ingot are estimated to be 1.1 g for HFC-134a, 0.58 g for SF_6, and 0.05 kg for S (Johnson and Sullivan 2014).

ADVANCES IN MAGNESIUM METAL PRODUCTION TECHNOLOGY

During the first half of the last century, as previously noted, there was considerable effort in carbothermic production of magnesium vapor by reacting magnesium oxide with carbon. That process produced both magnesium vapor and carbon monoxide. The primary problems were high operational temperatures, T >1,700°C (1,973 K); reoxidation of the magnesium vapor by the CO(g) prior to production of magnesium liquid droplets; and ultimately on further cooling, production of a pyrophoric and explosive powder. Australia's CSIRO (Commonwealth Scientific and Industrial Research Organization) claims to have solved the reversion problem with their MagSonic technology. The new approach still relies on reacting magnesium oxide with carbon to produce Mg(g) and CO(g), but the gases undergo supersonic quenching at four to five times the speed of sound with only about 10% reversion and produce magnesium powder that is 99.9% pure (Prentice et al. 2012).

SAFETY CONSIDERATIONS

Caution is required when producing molten magnesium and magnesium powder. The U.S. Bureau of Mines has listed magnesium powder's relative explosion hazard index as severe. Only metal powders of aluminum-magnesium alloy and atomized aluminum were found to be more dangerous (Jacobson et al. 1964). Molten magnesium when exposed to air can create a dangerous situation. The author of this chapter visited Alcoa's Addy, Washington, facility for the production of magnesium metal by the magnetherm process. During that visit, and shortly after touring the magnesium refining facility, where molten magnesium is covered by a protective molten salt consisting of $MgCl_2$ and KCl, there was a temporary disruption to the process; a loud bang and a half dozen or more small balls of white-hot magnesium rising about 15 m above the refining facility and fanning out a similar distance. The magnesium balls burned in air leaving a trail of white smoke consisting of MgO. The tour guide commented that the incident was not the norm, but not unusual.

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