MAGNESIUM AND MAGNESIUM ALLOYS

1. Introduction

Magnesium [7439-95-4], is the eighth most abundant element and constitues about 2% of the earth's crust. It is the third most plentiful element dissolved in seawater, with a concentration averaging 0.13%. Although magnesium is found in over 60 minerals, only dolomite [17069-72-6], magnesite [13717-00-5], brucite [1317-43-7], carnallite [1318-27-0], and olivine [1317-71-1] are of commercial importance. Magnesium and magnesium compounds are produced from seawater, well, and lake brines and bitterns, as well as from the minerals noted above.

In 1795, J. C. Delanethrie applied the term *magnesite* to a series of magnesium salts (carbonate, sulfate, nitrate, and chloride), and A. Brongmart applied the same term to a group of minerals including magnesium carbonates and silicates. Deposits of natural magnesium carbonate were discovered in Moravia, Czechoslovakia, and were described by C. F. Ludwig as talcum carbonatum in 1803. D. L. G. Karsten first restricted the term *magnesite* to the natural carbonate in 1808, and this term was gradually accepted.

Magnesite deposits were discovered in Austria and Greece during the latter half of the nineteenth century, and by 1890, magnesite was in general use in Europe for refractory linings in Bessemer and open-hearth furnaces. At the same time, magnesite mines were opened in Canada, and by 1909, substantial quantities of calcined magnesite were exported annually to the United States.

In 1886, deposits of magnesite were discovered in California, and by 1912, ground California magnesite was used in the western United States to replace specified grades of imported material. In 1913, production of magnesia (magnesium oxide) by precipitation using dolomite began in Pennsylvania. Deposits in Stevens Country, Washington, were recognized as magnesite in 1916, and mining started the next year. Mining of brucite began in 1929 from a deposit in Nye County, Nevada, and in 1937, magnesite mining started in a nearby deposit. Mining and processing domestic magnesium ores was expanded in the early 1940s to provide material for the production of chemicals and magnesium metal as well as refractories. Also in the early 1940s, magnesium chloride, recovered from seawater, was used in large quantities to produce magnesium metal in plants in Freeport and Velasco, Texas.

Magnesium metal was first reported to have been produced by Sir Humphry Davy in 1808 by reduction of magnesium oxide with potassium vapor. The first industrial production of magnesium was undertaken in France by Deville and Caron in 1863 and involved reduction of a mixture of anhydrous magnesium chloride and calcium fluoride by sodium. In 1833, Michael Faraday obtained magnesium by the electrolysis of fused anhydrous magnesium chloride, and in 1852, Robert Bunsen developed an electrolytic cell for this purpose. By the use of a modification of Bunsen's electrolytic cell, magnesium metal was produced on a pilot-plant scale in Germany in 1886, and by 1909, had advanced to limited industrial production. The first magnesium plant in the United States was constructed by the General Electric Co. at Schenectady, New York, in 1914. Magnesium production production in the United States increased steadily and

experienced a sharp increase during World War II because of the use of magnesium in incendiary bombs. The U.S. government constructed 13 magnesium metal plants between 1940 and 1943 to supply magnesium for the war. Shortly after the end of the war, these plants were either closed or sold to private industry (1).

2. Occurrence

World magnesite reserves are shown in Table 1. In addition to those estimates shown, magnesite deposits occur in Spain, Pakistan, and the Sudan. Deposits of less than 1×10^6 tons were reported in Mexico, Iran, the Philippines, Australia, Egypt, and the Republic of South Africa. Small deposits also have been noted in Cuba, Sweden, Norway, Poland, Scotland, France, Italy, Kenya, and Tanzania.

The reported estimate of 65×10^6 t of magnesite (15×10^6 t magnesium) reserve base in the United States is divided as follows: in Nevada, 88%, including 27×10^6 t of magnesite containing less than 5% CaO; in Washington, 11%; and in California, the remaining 1%. Magnesite also occurs in Texas, New Mexico, Idaho, Utah, Pennsylvania, Massachusetts, Maryland, New Jersey, and New York, but reserves have not been estimated in these States.

Brucite reserves are estimated to total 3×10^6 t in Nevada and 4×10^6 t in Russia. The mineral is also found in Arizona and in North Korea, the United Kingdom, Ireland, and Canada.

Reserves of olivine in North Carolina and Georgia are estimated at 230×10^6 t, averaging 48% MgO. Additionally, in Washington, the olivine reserve in the form of dunite is estimated at 50×10^6 t on Cypress Island and several million metric tons in the Twin Sisters region.

Reserves of magnesium salts obtained as brines from underground evaporate deposits are difficult to estimate. Available information on magnesium salts in surface evaporates is insufficient to estimate reserves. The Great Salt Lake contains an estimated 630×10^6 t of magnesium chloride.

Dolomite is a sedimentary rock commonly interbedded with limestone, which extends over large areas of the United States. Most dolomite occurrences are likely the result of replacement of calcium by magnesium in preexisting limestone beds. Magnesite is primarily found in four types of deposits: sedimentary beds, alterations of serpentine, vein fillings, and replacements of limestone and dolomite. Brucite is found in crystalline limestone and as a decomposition product of magnesium silicates associated with serpentine, dolomite, magnesite, and chromite. Olivine generally occurs as granular masses or disseminated grains and crystals, and is a common constituent of basic igneous rocks such as basalt and gabbro. Dunite is an olivine-rich rock (2).

Evaporites are deposits formed by precipitation of salts from saline solutions found both on the surface and underground. The geologic occurrence and chemical composition of inland brines cover a wide range, but little information has been published.

Magnesite, or magnesium carbonate ($MgCO_3$), has a theoretical magnesium content of 47.6%. Dolomite is a calcium carbonate–magnesium carbonate mineral ($CaCO_3 \cdot MgCO_3$) that has a theoretical magnesium content of 22%.

Brucite, magnesium hydroxide [$Mg(OH)_2$], contains up to 69% magnesium, and olivine ($Mg_2Fe_2SiO_4$) contains $\leq$10% magnesium. Of these minerals, magnesite and dolomite are the largest sources of magnesium and magnesium compounds.

Seawater, brines, and bitterns represent vast sources of magnesium and magnesium compounds. In the United States, about 75% of the magnesium compounds produced annually is recovered from seawater and brines, and almost 80% of the magnesium metal production capacity uses seawater or brines as a raw material.

Various magnesia products are made by calcining magnesium carbonate or magnesium hydroxide at different temperatures. Caustic-calcined magnesia, which is readily reactive with water, is calcined at temperatures up to 890°C. Dead-burned magnesia, also called-refractory or sintered magnesia, is calcined at temperatures up to 1450°C and is unreactive with water. Fused magnesia is produced at temperatures >3000°C. Magnesia produced from magnesite is generally called natural magnesia, and magnesia produced from seawater or brines is called synthetic magnesia.

3. Sources and Supplies

U.S. magnesium metal statistics are shown in Table 2. Historically, the United States has been able to meet its demand with domestic production and has been a net exporter of magnesium metal. As consumption has grown, U.S. production also has increased. There was significant growth in magnesium consumption in the 1970s with the introduction of the aluminum beverage can. As aluminum replaced steel as the material of choice for beverage cans, magnesium consumption grew steadily. This market, although still the largest for magnesium, has leveled off as the beverage can market has become saturated; currently this market grows relative to population.

In the 1990s, however, imports of magnesium have had an impact on the U.S. supply and demand of magnesium. When Norsk Hydro A/S opened its primary magnesium plant in Becancour, Canada, in 1990, production was targeted toward the U.S. market, and imports of primary magnesium from Canada increased significantly. With the dissolution of the former Soviet Union in 1991, imports of magnesium from Russia began entering the U.S. market. Antidumping and countervailing duties were assessed on imports of pure and alloy magnesium from Norsk Hydro in Canada in 1991, and imports from that country into the United States essentially ceased. By that time, the Russian material had begun entering the U.S. market, replacing some of the material from Canada. In 1994, the U.S. International Trade Commission began an investigation into antidumping of pure and alloy magnesium from Russia, China, and Ukraine. When the investigation began, imports from these countries also ceased.

At the same time that imports were dropping, demand in the United States began increasing, particularly for magnesium alloy die castings for automotive applications. U.S. producers were operating near their rated capacity, and supplies became very tight, which in 1995, caused a price escalation to a level that had not been experienced since magnesium was first produced commercially in the United States.

Resolution of the antidumping duties on magnesium from Russia whereby the large producing firms were allowed to import magnesium into the United States through specified importing companies without any penalty resulted in a resumption of imports of significant quantities of pure magnesium in 1996. Also in 1996, the antidumping duty on magnesium imports from Canada was eliminated, and the countervailing duties had been reduced to a level that would permit imports of magnesium alloy into the United States. As a result, by 1997, imports of magnesium in all forms had reached their highest level in decades and the United States became a net importer of magnesium. This situation is expected to continue because Dow Chemical Co. closed its plant in Freeport, Texas, in November 1998, and no new magnesium plants are planned in the United States. Current levels of U.S. trade in magnesium are shown in Table 3.

In addition to imports, magnesium recovered from old scrap has become an important factor in the total U.S. metal supply. In 1980, secondary magnesium from old scrap represented 14% of the total U.S. demand and increased to a level of 18% in 1995. Much of this increase resulted from increased recycling of used beverage cans, fabricated from aluminum–magnesium alloys. With the increased use of magnesium in automotive components (eg, wheels, brake and clutch pedal brackets, and engine and drivetrain components), secondary magnesium is expected to continue to supply an increasing portion of U.S. demand as cars are expected to be recycled for their metal content rather than junked.

4. Properties

Table 4 gives some of the physical properties of 99.9% pure magnesium. Magnesium is high in the electrochemical series, having a standard potential of -2.4 V. Like most metals, it is resistant to atmospheric and chemical attack because of a stable protective film, ie, oxide, carbonate, sulfate, fluoride, and others. The oxide film can be more protective if it is produced by an anodizing process. It is relatively easy to ignite fine powers or thin films of magnesium resulting in a strongly dazzling light. This property is exploited in the production of some fireworks and flares (see PYROTECHNICS). With pieces over 3-mm thick, combustion is difficult to sustain due to rapid heat transfer of the metal and the refractory nature of the magnesium oxide produced. Metal produced in casting processes must be protected from air at metal temperatures above 400°C, because the metal can sustain combustion above this temperature.
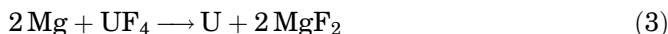
Metallic magnesium and water [7732-18-5] react. Under normal atmospheric conditions or in pure or chloride-free water of high pH, the reaction is suppressed by the formation of an insoluble magnesium hydroxide [1309-42-8] film.

$$Mg + 2\,H_2O \longrightarrow Mg(OH)_2 + H_2 \tag{1}$$
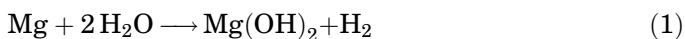
If conditions are such that the film does not form, such as in the case of acids, then the reaction proceeds until all the metal is consumed. The reaction

of magnesium with hydrofluoric acid [7664-39-3] is an exception to this rule, because a stable fluoride film forms.

The ability of magnesium metal to reduce oxides of other metals can be exploited to produce metals such as zirconium, titanium [7440-32-6], and uranium [7440-61-1] (see ZIRCONIUM AND ZIRCONIUM COMPOUNDS; TITANIUM AND TITANIUM ALLOYS; URANIUM AND URANIUM COMPOUNDS). These reactions are

$$2\,Mg + TiCl_4 \longrightarrow 2\,MgCl_2 + Ti \tag{2}$$

$$2\,Mg + UF_4 \longrightarrow U + 2\,MgF_2 \tag{3}$$

$$2\,Mg + ZrCl_4 \longrightarrow Zr + 2\,MgCl_2 \tag{4}$$
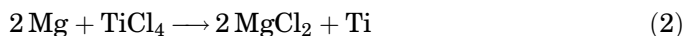
The most significant reactions of magnesium with air are

$$2\,Mg + O_2 \longrightarrow 2\,MgO \tag{5}$$

$$3\,Mg + N_2 \longrightarrow Mg_3N_2 \tag{6}$$

The magnesium nitride [12057-71-5] produced does not form a stable film. If sufficient nitrogen is present this reaction can be self-sustaining. The nitride produced can react with water to form ammonia [7664-41-7].
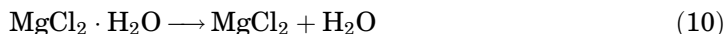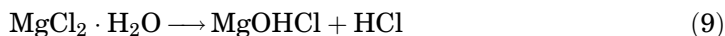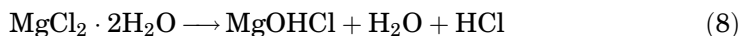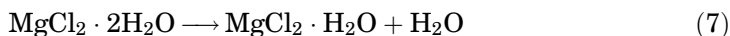
5. Manufacturing

Magnesium metal can be manufactured by electrolytic and metallothermic reduction. The method of choice depends on several variables including raw material availability, location, and integration into other chemical facilities. Producers and corresponding capacities are shown in Table 5 (see also ELECTRO-CHEMICAL PROCESSING, INORGANIC).

Because of the high projected growth rate in magnesium consumption for die castings in automotive applications, many firms have announced plans to construct new magnesium plants. Table 6 lists the potential new facilities scheduled to come onstream within the next few years.

5.1. Electrolytic Reduction. The largest manufacturers of magnesium use processes based on the electrolytic reduction of magnesium chloride [7786-30-3] to form magnesium and chlorine [7782-50-5]. Several variations exist in the raw materials, the method of preparing magnesium chloride, the design of the cells used for the electrolysis, and the utilization of the by-product chlorine.

Sources for magnesium ions include seawater, natural brines, magnesium-rich brines from potash production, magnesite [13717-00-5], $MgCO_3$, carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$, and dolomite [17069-72-6], $MgCO_3 \cdot CaCO_3$. Attempts have been made to recover magnesium ion from sulfate minerals (7), but none of this technology has been commercialized. Patents describe the recovery of magnesium ions from magnesium silicates (8,9). Magnesium chloride is formed from either an aqueous liquor that is then dehydrated, or by direct chlorination of

magnesium oxide formed by calcination of magnesium hydroxide, $Mg(OH)_2$, or oxide-based ores. The dehydration of magnesium chloride hexahydrate [7791-18-6], $MgCl_2 \cdot 6H_2O$, proceeds stepwise, first to the tetrahydrate, and then the dihydrate (10,11). Further dehydration produces some hydrolysis with concurrent formation of hydrogen chloride [7647-01-0].

$$MgCl_2 \cdot 2H_2O \longrightarrow MgCl_2 \cdot H_2O + H_2O \qquad (7)$$

$$MgCl_2 \cdot 2H_2O \longrightarrow MgOHCl + H_2O + HCl \qquad (8)$$

$$MgCl_2 \cdot H_2O \longrightarrow MgOHCl + HCl \qquad (9)$$

$$MgCl_2 \cdot H_2O \longrightarrow MgCl_2 + H_2O \qquad (10)$$

$$MgOHCl \longrightarrow MgO + HCl \qquad (11)$$

These reactions have been studied extensively, and many variations exist in the use of HCl atmospheres to maximize the desired reactions. The dehydration of carnallite occurs with minimum hydrolysis, but results in a mixed $MgCl_2$–KCl cell feed. The use of magnesium chloride hexammoniate [24349-22-2], $MgCl_2 \cdot 6NH_3$, has been proposed, but is not practiced commercially. This salt readily deammoniates to anhydrous $MgCl_2$.

Molten magnesium chloride can be formed by the direct carbochlorination of magnesium oxide obtained from the calcination of magnesium carbonate ores or magnesium hydroxide [1309-42-8].

$$MgO + C + Cl_2 \longrightarrow MgCl_2 + CO \qquad (12)$$
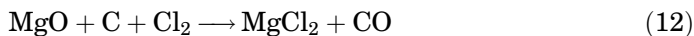
This reaction, carried out at high (700–800°C) temperatures, also converts several impurities in the ores to volatile chlorides, thus purifying the $MgCl_2$. A patent describes the carbothermal chlorination of magnesite directly (12).

The magnesium chloride is then fed into electrolytic cells that use a molten chloride electrolyte. The standard reduction potential of magnesium ion (-2.4 V) precludes its being extracted by electrochemical processes (electrowon) from aqueous systems. Commercial cells operate at about 700°C. Chlorine [7782-50-5] is formed as a by-product. Manufacturers have developed their own cell designs optimized to their specific process. The magnesium product is recovered molten, and is forwarded to a casting plant where it is cast into ingots or alloyed and then cast. The by-product chlorine is either recycled back to the process, or forwarded to a chlorine user. The theoretical decomposition potential is 2.5 V, which requires a minimum electrical input of 5.5 kWh/kg metal. Actual decomposition potentials in the electrolytes used commercially are 2.6 to 2.8 V. Actual energy consumption is also considerably higher because of cell current efficiencies of 75–90% and the Joule heating of the electrolyte, electrodes, bus bar, and connectors. This energy must be added to the energy needed to produce the magnesium chloride cell feed to obtain the total energy needed for the process.

Dow Chemical Company Seawater Process. Seawater is the primary source for magnesium in The Dow Chemical Company process begun in 1941 in Freeport, Texas. A schematic is shown in Figure 1. Magnesium is present in seawater at a level of 1272 ppm. This is precipitated as magnesium hydroxide using either caustic soda or the calcined form of dolomite, dolime [50933-69-2], $MgO \cdot CaO$, as an alkaline source in large agitated flocculators. The magnesium hydroxide is then settled in Dorr thickeners, ie, tanks equipped with a slowly rotating rake at the bottom, which move settled solids to the center. The spent overflow enters the wastewater system where it is treated and returned to the ocean. The thickened underflow is pumped to rotary drum filters, where it is dewatered, washed, and reslurried with water. This slurry is then pumped to neutralizers, where it reacts with HCl to form a $MgCl_2$ liquor. Sulfuric acid [7664-93-9] is added to remove the excess calcium [7440-70-2], and the brine is filtered to remove calcium sulfate [7778-18-9] along with other solids such as clays and silica [7631-86-9]. This brine is purified to remove sulfate and boron and forwarded to the dryer. The purified brine is dried by direct contact with combustion gases in a fluid-bed dryer to produce granules of approximately 70% $MgCl_2$. Dow is the only magnesium manufacturer using water-based feed in electrolytic cells.

The Dow electrolytic cells (Fig. 2) are constructed of steel with cathodes welded to the tub-like container that holds the electrolyte. These are fitted with refractory covers through which cylindrical anodes pass. These anodes are independently suspended to allow them to be adjusted to maintain proper spacing and centering with respect to the cathode. Because the feed is aqueous, the graphite [7782-42-5] anodes and water or water decomposition products react to form carbon dioxide [124-38-9], and frequent adjustments of the anodes must be made while maintaining a tight seal on the cell system. The electrolyte is a mixture of molten chlorides at approximately 700°C. The bottom of the cell pot is surrounded by a gas-fired refractory chamber. This allows a great deal of flexibility in adjusting to various current loads, and the cells may even be restarted after a complete shutdown.

The cells are fed semicontinuously and produce both magnesium and chlorine (see ALKALI AND CHLORINE PRODUCTS). The magnesium collects in a chamber at the front of the cell, and is periodically pumped into a crucible car. The crucible is conveyed to the cast house, where the molten metal is transferred to holding furnaces from which it is cast into ingots, or sent to alloying pots and then cast. The ingot molds are on continuous conveyors.

Norsk Hydro Process. Norsk Hydro operates two magnesium plants, one at Porsgrunn, Norway, and one at Becancour, Province of Quebec, Canada, with capacities of 35,000 and 43,000 t/yr, respectively. The plant at Porsgrunn went on line in 1951 using the I.G. Farben process (13,14). Later, Norsk Hydro developed its own process for the preparation of $MgCl_2$ cell feed and electrolysis (15–21). The basic steps of the two processes are shown in Figure 3.

In the chlorination process, caustic magnesia is extracted from dolomite and seawater, then mixed with carbon and aqueous $MgCl_2$ on a rotating disk to form 5–10 mm diameter pellets. Hydrated oxide and oxychlorides act as binders. After a light drying, pellets containing approximately 50% MgO, 15–20% $MgCl_2$, 15–20% H_2O, 10% C, and a balance of alkali metal chlorides are conveyed

to the chlorinators. The lower one-third of the brick-lined cylindrical shaft furnaces are filled with carbon blocks acting as resistors heated by carbon electrodes. The charge resting on the resistor bed reacts at 1000–1200°C with recycled chlorine gas introduced into the resistor-filled zone. Molten magnesium chloride collects in the bottom of the furnace. The molten material is tapped and transported to the electrolytic cells in closed containers. By-product gases at 100–200°C, containing air, carbon monoxide [630-08-0], carbon dioxide, traces of HCl, Cl_2, sulfur dioxide [7446-09-5], hydrogen sulfide [7783-06-4], and chlorinated hydrocarbons, are scrubbed in several stages before release to a stack. The washwater is filtered and chlorinated hydrocarbons removed before release. At intervals, magnesium silicate-rich slag is removed from the chlorinators. The magnesium yield is approximately 90% and the carbon consumption is 0.45 t/t magnesium produced. The addition of magnesium chloride solution to the reactants compensates for chlorine loss. The magnesium chloride produced contains typically less than 0.1% MgO, 0.1% SiO_2, and 20 ppm boron. Each chlorinator has an equivalent annual production capacity of the order of 2000 t Mg.

The dehydration process in Norway has as its raw material basis brine from the potash industry of the following average composition: 33% $MgCl_2$; 1–2% magnesium sulfate [7487-88-9], $MgSO_4$; 0.5% sodium chloride [7647-14-5], and 0.2% potassium chloride [7447-40-7].

Feedstock for the plant in Canada is obtained by dissolving magnesite in hydrochloric acid. The brine is chemically treated with sodium sulfide [1313-82-2], calcium chloride [10043-52-4], and barium chloride [10361-37-2] to remove heavy metals and sulfates by precipitation and filtration. Purified brine is preheated by waste heat from the process and concentrated to 45–50% $MgCl_2$ in steam heated evaporators, before prilling in a prilling tower. Prilling is a process by which pellet-sized crystals or agglomerates of material are formed by the action of upward blowing air on a falling hot solution. The size of the prills is kept within close tolerances and controlled physical shape to optimize the subsequent dehydration. The prills are converted to anhydrous $MgCl_2$ in a two-stage fluidized-bed dehydration process. In the first stage, the prills are dried to approximately magnesium chloride dihydrate [19098-17-0], $MgCl_2 \cdot 2H_2O$, with hot air. In the second stage, the dihydrate prills are contacted with a hot, anhydrous HCl gas stream to form anhydrous $MgCl_2$. Water and $MgCl_2$ dust in the off-gases from the dehydration are absorbed in a concentrated $MgCl_2$ solution. The HCl gas is provided by an extractive distillation process, dried, preheated, and returned to the HCl dehydration step. $MgCl_2$ prills containing less than 0.1% MgO are transported pneumatically to the electrolytic cells. Magnesium and chlorine recoveries in this continuous closed process are 97% or better.

Originally, Norsk Hydro operated I.G. Farben electrolytic cells with current loads of 32–62 kA. Since 1988, Norsk Hydro has been operating its own internally developed electrolytic cell. This cell, in full-scale operation since 1978, is a sealed brick-lined unit with two separate chambers, one for electrolysis and one for metal collection (Fig. 4). Densely packed and cooled graphite anode plates enter through the top, and double acting steel [12597-69-2] plate cathodes enter through the back wall of the cell. Chlorine of 98 wt% concentration is collected from one central pipe in the anode compartment. The circulation of the electrolyte is parallel to the electrodes bringing the metal to the collection chamber,

from where it is extracted by vacuum and transported to the foundry. The cell is operated at $700-720°C$ with a current load of $350-400$ kA. The energy consumption is $12 - 14$ kWh/kg Mg. The cell life is on the order of five years. Most of the magnesium is cast into ingots or billets. The refining of the molten metal extracted from the electrolysis is performed continuously in large, stationary brick-lined furnaces of proprietary design (22). Such installations have a metal yield better than 99.5% and negligible flux consumption.

Magnesium Corporation of America (Magcorp) Process. The magnesium facility in Rowley, Utah, originally built by NL Industries in 1972, was purchased by AMAX, Inc., in 1980, sold in 1989 to a private investment group, and was named Magcorp.

This magnesium plant (Fig. 5) utilizes brine from the Great Salt Lake as feed for solar evaporation ponds. The Great Salt Lake magnesium concentration is about 0.4%, about four times that of the world's oceans. The evaporated brine contains 7.5% magnesium, 4% sulfate, 0.5% sodium [7440-23-5], 0.7% potassium [7440-09-7], 0.1% lithium [7439-93-2], and 20% chloride [16887-00-6] (23). The brine-holding ponds contain enough brine to supply two years of raw material ready for processing. This brine is further concentrated and treated with $CaCl_2$ to remove sulfate. Solids such as calcium sulfate, potassium chloride, and sodium chloride are removed in thickeners and settling ponds. Boron is removed by solvent extraction. Cogeneration is used to provide heat for further concentration of the brines and for drying the brine into powder. Spray dryers flash dry the solution into powder. The dry magnesium chloride powder contains mainly $MgCl_2$ along with about 4% MgO, 4% H_2O, and other salts which comprise the cell electrolyte. The dryers are heated with exhaust gases from gas-fired turbines that generate some of the power used to operate the electrolytic cells.

The spray dried $MgCl_2$ powder is melted in large reactors and further purified with chlorine and other reactants to remove magnesium oxide, water, bromine [7726-95-6], residual sulfate, and heavy metals (24,25). The molten $MgCl_2$ is then fed to the electrolytic cells which are essentially a modification of the I.G. Farben cell. Only a part of the chlorine produced is required for chlorination, leaving up to 1 kg of chlorine per kg of magnesium produced. This by-product chlorine is available for sale.

Liquid magnesium is removed from the electrolytic cells under vacuum and transferred to the cast house where it is refined, purified, and cast into a wide variety of shapes, sizes, and alloys.

Russian Process Technology. Magnesium production in the former Soviet Union is apparently done via molten chloride electrolysis (5,26). The basic process uses carnallite [1318-27-0], $MgCl_2KCl6H_2O$, either from natural deposits or as a by-product of processing natural salt deposits, as its raw material. Recrystallized carnallite has an average value of 32% $MgCl_2$. This material is dried in a two-step process (27–29). The first stage consists of a fluid-bed/moving-bed furnace with three distinct temperature zones. The temperature increases in each zone, going from 130 to 200°C, which results in a product containing $1-2\%$ MgO and $3-6$ H_2O. This product is then sent to a chlorinator, which operates at $700-750°C$. The chlorinator is designed to remove most of the remaining impurities and settle out any solids. Considerable research effort is

being done to improve the efficiency of the chlorination step. The molten $MgCl_2$/ KCl is tapped and either sent directly to the cells while still molten, or cooled to a solid and then fed to the cells.

Up until the late 1960s, the cells used in Russia were basically I.G. Farben diaphragm cells. In the period of 1972–1977, production was converted to diaphragmless cells (30). These cells operate in the temperature range of 680–720°C and at currents of 150–200 kA. The electrolyte used depends on the feed. Using carnallite feed the electrolyte is 5–15% $MgCl_2$, 60–80% KCl, 8–20% NaCl, and < 1% CaCl; using anhydrous $MgCl_2$ feed from titanium production, the electrolyte contains 8–18% $MgCl_2$, 30–55% KCl, 30–60% NaCl, and 0–10% $CaCl_2$. A small amount of calcium fluoride [7789-75-5], CaF_2, is maintained in the electrolyte in either case. Cell temperatures are somewhat higher and current efficiencies are somewhat lower in carnallite fed cells.

Russian production may be going to a flow line cell concept (31). In this process, dehydrated carnallite is fed to a chamber where it is mixed with spent electrolyte coming from the electrolytic cells. The spent electrolyte first enters a metal collection chamber, where the molten magnesium is separated. The electrolyte is then enriched with carnallite and any insoluble impurities are allowed to settle. The enriched electrolyte is then returned to the electrolytic cells. The result is that most of the remaining impurities are removed in the first electrolytic cell.

Titanium—Magnesium Chloride Recycle Processes.   Titanium [7440-32-6] is manufactured by the Kroll process, where magnesium is used as a reducing agent for titanium tetrachloride [7550-45-0] (see TITANIUM AND TITANIUM ALLOYS) (see eq. 2). This reaction produces a pure anhydrous magnesium chloride that can then be used in an electrolytic cell to convert it back to magnesium metal. Electrolytic cells have been developed to take advantage of this type of feed. Alcan has developed both monopolar and multipolar cells for the production of magnesium (32,33). Alcan monopolar cells are used by Oremet Titanium (Albany, Oregon) and by Timet (Henderson, Nevada). The first Alcan multipolar cell was perfected at Osaka Titanium Co. (now Sumitomo Sitex) in Osaka, Japan. This cell operates between 80 and 140 kA and has an energy consumption of $9.5 - 10$ kWh/kg of magnesium. The cell consists of a chamber for electrolysis and a chamber for metal collection. The electrolytic chamber has a central anode and a terminal cathode with several intermediate bipolar electrode assemblies. These bipolar electrodes are disposed in series in the path of the electrolytic current between the anode and the cathode. A bipolar electrode is an electrically conductive plate inserted between the anode and the cathode of a conventional electrolytic cell. The side of the plate facing the anode becomes cathodic and the opposite side becomes anodic. The bipoles are tapered to almost surround the anode, including the edges and bottom. A curtain wall partially submerged in the electrolyte separates the two collection chambers. The metal produced is swept by the anodically evolved chlorine to metal collection ducts that carry it to the metal collection chamber (34). All the Alcan cells show excellent operation characteristics with $MgCl_2$ from titanium manufacture, but none is in use with brine or ore-based feed processes.

The Ishizuka cell (35–37), another multipolar cell that has been in use by Showa Titanium (Toyama, Japan), is a cylindrical cell divided in half by a

refractory wall. Each half is further divided into an electrolysis chamber and a metal collection chamber. The electrolysis chamber contains terminal and center cathodes, with an anode placed between each cathode pair. Several bipolar electrodes are placed between each anode–cathode pair. The cell operates at $670°C$ and a current of 50 kA, which is equivalent to a 300 kA monopolar cell.

Magcan Process. The Magcan process is based on a technology developed by MPLC of Great Britain and Alberta Natural Gas for the preparation of anhydrous $MgCl_2$ directly from magnesite ore (11). The Magcan plant (Aldersyde, Alberta, Canada) underwent start-up in 1990 but was shut down in 1991. In this process, magnesite ore is crushed, screened, and placed in the top of a vertical reactor. Carbon monoxide [630-08-0] and chlorine gas are injected into the bottom of the chlorinator. The magnesite passes down the reactor where it is chlorinated by the following reaction:

$$MgCO_3 + Cl_2 + CO \longrightarrow MgCl_2 + 2\,CO_2 \tag{13}$$
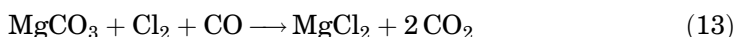
Molten anhydrous magnesium chloride is tapped from the bottom of the reactor. Iron, aluminum, and silicon-based impurities are also converted to their chlorides, which volatilize out of the reactor. Carbon monoxide is generated from coke, carbon dioxide, and oxygen. The magnesium chloride is sent to electrolytic cells. Russian diaphragmless cells purchased from the defunct American Magnesium Co. are used.

Dead Sea Works Process. The Dead Sea Works, a subsidiary of Israel Chemicals Ltd., announced plans in 1992 to construct a $25,000$ t/yr magnesium plant at Beer-Sheva, Israel. The plant, to be based on Russian carnallite technology, is designed to use an existing potash plant as the source of carnallite. The chlorine by-product can be either liquefied and sold, or used in an existing bromine plant. Waste streams from the carnallite process, as well as spent electrolyte from the electrolytic cells, can be returned to the potash plant.

Queensland Metals Process. The Queensland Metals Corp. is developing a large magnesite deposit in Kunwarara, Queensland, Australia (38,39). The first phase of development of this ore is a plant to produce magnesia, MgO. Feasibility studies relating to producing magnesium metal from this deposit have also begun. Research efforts aimed at producing a high quality magnesium chloride are underway. An option to license the Alcan electrolytic cell has also been taken.

Noranda Process. Noranda, Inc. (Toronto, Canada) has developed technology to recover magnesium chloride from asbestos [1332-21-4] tailings (40,41). Several patents have been issued covering this process technology, which involves using HCl to leach magnesium from silicate materials at elevated temperatures followed by purification steps. This $MgCl_2$ solution can then be fed to a dryer. The chlorine from the electrolytic cell is used to make HCl and recycled to the leaching step.

5.2. Thermal Reduction. Magnesium metal can also be formed by the thermal reduction of magnesium oxide with a reactive metal, such as silicon [7440-21-3], which forms a stable oxide.

$$2\,MgO + Si \longrightarrow 2\,Mg + SiO_2 \tag{14}$$
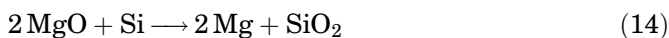
Silicon is normally used in the form of a high grade ferrosilicon alloy, and the MgO is normally supplied in the form of dolime. Ferrosilicon is prepared by the carbothermal reduction of silica in the presence of iron:

$$SiO_2 + 2\,C + Fe \longrightarrow Si(Fe) + 2\,CO \tag{15}$$
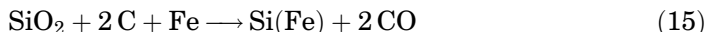
Additional components such as alumina [1344-28-1] are also added to obtain more favorable thermodynamics, and to obtain a slag having favorable properties. Many different feed and slag compositions exist, as do alternative reductants for ferrosilicon. It is also theoretically possible to manufacture magnesium metal by the reduction of MgO with carbon.

$$MgO + C \longrightarrow Mg + CO \tag{16}$$

Three basic processes exist for the thermal reduction of magnesium oxide: the Pidgeon process, the Magnetherm process, and the Bolzano process.

Pidgeon Process.   The Pidgeon (42−45) process (Fig. 6) was the first commercial thermal reduction process using silicon, and was developed in the 1940s. This process is used by Timminco (Haley, Ontario, Canada). The overall reaction for this process is

$$2\,MgO + 2\,CaO + Si \longrightarrow 2\,Mg + Ca_2SiO_4 \tag{17}$$
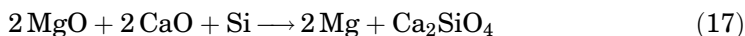
The raw materials for the process are dolomitic limestone that has been calcined to form the oxide, and ferrosilicon (65−85% Si). The dolime and ferrosilicon are finely ground, mixed, and compacted into briquettes. These briquettes are inserted into seamless stainless steel tubes 3 m long having a bore diameter of 28 cm and a capacity of 350 kg. The charge is distributed through the length of the reaction section of the horizontal retort and placed into a gas-fired or electrically heated furnace. The operating cycle consists of three phases. Initially, the retort is heated to drive off any CO_2 and water remaining in the charge. The retort is then sealed and operated at low vacuum to complete this burnoff. The retorts are then evacuated to 13 Pa (0.1 mm Hg) and brought to a temperature of 1200°C. The magnesium vapors condense to form a solid metal crown at the water-cooled collection end of the tube. The size of the retort tubes is limited by the heat transfer to the reactants from the furnace.

The retorts must be opened, the reaction products removed, and the retorts filled with raw materials and resealed. The typical cycle is 8−10 hours. Capacity is controlled by the number of retorts used and the number of furnaces available. The metal crowns are removed, remelted, and cast into ingots, or alloyed and then cast.

Magnetherm Process.   The Magnetherm process (Fig. 7) was developed over a period from 1950 to 1963 by Group Pechiney. Ugine Kuhlmann of France (14,46−49). This technology is practiced by Société Francaise d'Electrometallurgie (SOFREM) (Marignac, France), Northwest Alloys (Addy, Washington), and Magnrohm Co. (Bela Sterna, Yugoslavia). In this process, alumina is added to the reactor to maintain a liquid slag, allowing the reactor to be heated by the

electrical resistance of the slag.

$$2\,CaO \cdot MgO + Al_2O_3 + (Fe)Si \longrightarrow Ca_2SiO_4 \cdot Al_2O_3 + Fe + 2Mg \qquad (18)$$

The magnesium ion source is normally a calcined dolomite or a mixture of calcined dolomite and calcined magnesite. Alumina, usually in the form of bauxite [1318-16-7], is added to control the properties of the slag. The reducing agent is mainly ferrosilicon, but some aluminum is also used, particularly by Northwest Alloys. The resulting calcium aluminosilicate [1327-39-5] slag remains liquid and the magnesium vapor is condensed.

The Magnetherm reactor used by Northwest Alloys is shown in Figure 8. The reactants are fed into a carbon-lined vessel, where the reaction is carried out in a range of 1300−1700°C and at a pressure of at least 2.7 kPa (20 mm Hg). Under these conditions, the metallic reducing agent reacts with the magnesium oxide in the calcium−silicon−aluminum−magnesium oxide slag to produce magnesium vapor. The composition of the slag is controlled to maintain a minimum calcium oxide [1305-78-8], CaO, to SiO_2 weight ratio of 1.68 and minimum Al_2O_3 to SiO_2 ratio of 0.44. The vapor is condensed as either a liquid or a solid.

The driving force for moving the magnesium vapor to the condenser is the volume change of the magnesium vapor going from a vapor to a liquid or solid state. A small amount of argon [7440-37-1] is purged to the reaction vessel through the feed system to minimize the condensation of magnesium metal on the colder parts of the feed system. The process operates on a 16−24 hour cycle, with the cycle split in two halves. The end of the first half is used to tap slag and refill the feed system with dolime. The end of the second half is used to replenish all feed materials, tap slag, and remove the filled magnesium crucible. Thus in every cycle, the condenser assembly shown in Figure 8 is removed and a clean, empty unit is attached to the reduction vessel for continued operation on the next cycle. The slag is removed from the furnace using an oxygen [7782-44-7] lance to penetrate a clay plug or a carbonaceous plug. The calcium aluminosilicate slag is a cementaceous product and can be used as a cement or liming agent.

The quantity of feed materials required are 1−1.05 kg of metallic reductant, 5.4 kg of dolime, and 0.35 kg of calcined bauxite or alumina to produce 1 kg of magnesium. The quantity of slag produced depends on the feed material composition and may vary from 5.2 to 5.9 kg/kg of magnesium.

Bolzano Process.   The Bolzano process was developed by Societa Italiana per Magnesio e Lehge do Magnesio of Bolzano, Italy (50,51). In this process, the reactants are calcined dolomite and ferrosilicon that are compressed into solid blocks and stacked with electrical heating conductors between the blocks. The block assembly is placed in a refractory-lined furnace so that heat applied to the system goes only to the compressed reactants and not to the chamber. The furnace is the lower portion of the assembly, which also has an upper bell-shaped section joined to the lower portion by a flange. The top portion is cooled and acts as a condenser for the magnesium vapors formed in the furnace.

The process operates at 1200°C and <400 Pa (3 torr) and has a cycle time of 20−24 hours. The reactor is opened at the flange and the metal removed. Energy

usage in the furnace is $7-7.3$ kWh/kg magnesium. A similar process is used by Brasmag (Minas Givras, Brazil) (52).

Carbothermal Reduction.   At temperatures above $1850°C$, carbon monoxide is more stable than magnesium oxide. This allows the formation of magnesium vapor from the reaction of magnesium oxide and carbon [7440-44-0] at these temperatures. However, the reaction is reversible, and the product gas must be rapidly quenched to prevent the reforming of MgO. Shock cooling has been used, which produces a finely divided magnesium dust that is pyrophoric. A plant was operated by Kaiser (Permanente, California), during World War II, but it had difficulty separating this dust from the quenching medium and was shut down (53).

5.3. Refining and Casting of Magnesium.   Most magnesium extraction processing is followed by a refining operation to remove impurities and to manufacture clean alloy compositions. The metal is then converted to ingots, slabs, or billets, which are short, thick, cylindrical bars. Magnesium is also converted directly into granules for subsequent use in steelmaking. Some magnesium process slags are beneficiated to recover magnesium granules without a remelting operation. Typical impurities are nonmetallic inclusions, metallic impurities, and hydrogen.

Nonmetallic Inclusions.   Inclusions in the form of magnesium oxide, magnesium nitride, and magnesium chloride impair the appearance and corrosion resistance of magnesium alloys. Impurities can have a detrimental effect on the performance of aluminum alloys that are made with magnesium. Alkali metal chlorides wet the surface of magnesium and the inclusion. Because of the higher density of the alkali metal chlorides relative to magnesium, the chlorides sink to the bottom of melts as a slag. Intermetallic compounds formed in the production of magnesium alloys as a rule have higher densities than the melt and also report to a slag layer. Fluxes added to magnesium melts have densities similar to the melt and are used to coat the surface of the melt to prevent oxidation (54).

Metallic Impurities.   Iron [7439-89-6], nickel [7440-02-0], and copper [7440-50-8] reduce the corrosion resistance of magnesium and magnesium alloys significantly. These metals form very small galvanic islands which act as cathodes. These impurities are controlled by the choice of raw materials used to make up the feed to the electrolytic or metallothermic processes. Other common impurities found in magnesium are aluminum, manganese, zinc, silicon, and sodium. Aluminum is sometimes introduced by the reduction of alumina brick or tile used in the construction of magnesium cells and furnaces as well as alumina in the raw materials (55). Iron is soluble in molten magnesium in the range of $250-400$ ppm at normal processing temperatures. Most electrolytically derived magnesium contains iron in this range. Intermetallic compounds of these impurities have also been found.

The iron concentration can be kept low by operating at low temperatures. Iron can be removed by addition of manganese [7439-96-5] or manganese chloride [7773-01-5] because it forms an intermetallic complex which is denser than the metal and becomes part of the slag (56). Addition of titanium tetrachloride gas to the metal reduces iron levels as well, but has a disadvantage of the possible discharge of titanium tetrachloride to the atmosphere above the furnace and

subsequent conversion to titania and HCl (54). An alternative method is the addition of zirconium metal, which forms an intermetallic compound and settles. Excess zirconium is removed by additions of silicon (57). Sodium, calcium, and strontium can be removed by the addition of magnesium chloride which is reduced producing the respective metal chloride.

Metallic impurities are also detrimental in applications where magnesium is used as a reductant such as in the Kroll process. The produced metal can be contaminated with boron rendering it useless in some nuclear applications.

Hydrogen. Hydrogen [1333-74-0] is formed when magnesium reacts with moist air (58–60). The normal level of hydrogen in magnesium is 1–7 ppm, which is acceptable for most purposes. Higher levels (~ 24 ppm) cause macroporosity in metal castings and there is some evidence that the intermediate levels can produce some microporosity in castings. Hydrogen can be completely removed by forcing an inert gas such as argon or chlorine into the melt. Nitrogen [7727-37-9] has also been used in this application although the formation of magnesium nitride may be of concern.

Equipment. The standard equipment in magnesium foundries consists of large stationary brick-lined reverbatory furnaces which can hold up to 10–15 t of molten magnesium. Reverbatory furnaces are furnaces in which heat is supplied by burning a fuel in a space between the reactants and the low roof. The stationary furnaces can be heated electrically or with gas or oil burners. Some furnaces heat the melt by submerged electrical heating systems. Magnesium is usually alloyed in steel pots which are used to formulate an alloy composition, remove hydrogen, and remove iron. The magnesium can then be transferred to a reverbatory furnace for settling of intermetallics (55).

Metallothermic magnesium is recovered in the solid state. Magnesium produced in this manner is then remelted and refined for subsequent casting.

Casting. The casting of magnesium can be highly automated. It normally involves the transfer of molten magnesium, introduction into a mold, protection of the cast surface, and handling of the solidified product. Molten metal transfer is accomplished by mechanical or electromagnetic pumping or by static displacement. Magnesium contracts about 4.2% in the liquid/solid-phase transformation and can lose up to 5% of its volume in cooling to room temperature (5). The surface can reveal shrink holes and surface cracks. These can be the result of change of volume in the process and the size and shape of the ingot mold used. Turbulent casting of the ingot can produce a sponge-like dross that detracts from the surface appearance of the ingot. This dross may be removed by skimming before solidification is complete. It is necessary to prevent oxidation of the metal during casting because magnesium spontaneously ignites in air in the molten state. To suppress oxidation, a number of techniques are employed. Casting of magnesium under a sulfur dioxide [7446-09-5] air mixture is one method used to suppress oxidation of the metal (61). Sulfur [7704-34-9] powder can also be used to provide the sulfur dioxide through application to the metal surface (62). A newer method is to use a mixture of sulfur hexafluoride [2551-62-4], carbon dioxide [124-38-9], and air to suppress oxidation (63–66). This method can be used to replace molten fluxes in casting pots. The necessity of a protective atmosphere increases the cost of magnesium casting practice over that of aluminum.

Billets, which are cylindrical bars, are cast in multistrand continuous or semicontinuous direct-chill casting (67) machines. These machines use water to cool the bar as it is produced. The water is then removed from the metal with rubber wipers. This process has the advantage of water removal from the surface without the use of a large pit to contain the water. Large pits containing water can be dangerous in continuous casting since metal run-outs from partially solidified metal bars can cause explosions due to the reaction of the molten magnesium or aluminum with water. Sulfur hexafluoride gas protection systems are used in this application since they eliminate the need for fluxes to prevent oxidation. The size of continuous casters for magnesium is limited compared to aluminum because of the low heat content of magnesium and its tendency to oxidize. Very large machines with 50 or more strands are used for aluminum casting. To avoid discoloration and surface corrosion during transport and handling, the metal is protected by plastic or treated paper wrappings.

6. Economic Aspects

Although world demand for magnesium is growing, it is not growing at a fast enough rate to support the additional production from all the plants in the Table 6. Many of the companies that proposed the new magnesium plants are looking for a long-term purchase agreement or some type of financial commitment from a large end user of magnesium (primarily the automobile manufacturers) before the company will begin plant construction.

In addition to the companies listed in Table 6, several other firms, particularly in Australia and Canada, have begun preliminary investigations into producing magnesium. In Canada, several firms are looking at asbestos tailings as a potential source of magnesium; development of these plants could hinge on the commercial success of Magnola's operation. Magnesite is the feed material that is begin investigated in Australia. In addition to having significant undeveloped magnesite resources, energy costs in Australia are low, which make this location attractive for energy-intensive operations, such as magnesium metal production.

Traditionally, magnesium metal and alloy prices had been set by the producer, and quantity discounts were given to large customers. Beginning in the 1990s, however, magnesium prices became more market-driven.

In early 1990, North American production increased with the opening of a new 40,000 t/yr plant in Canada. Much of the Canadian production was imported into the United States, alleviating a supply shortage. As a result, producers' quoted prices dropped in 1990, and by the end of 1991, primary magnesium reportedly was selling at about $1.10–1.20 lb. These low prices prompted one of the U.S. producers to request countervailing and antidumping duty investigations into imports of magnesium from Canada in September 1991; as a result of this action, magnesium imports from Canada essentially ceased.

With the dissolution of the former Soviet Union at the end of 1991, however, new suppliers entered the world market. Because of stockpiles that had been built up over many years, Russia and Ukraine had significant quantities of magnesium available to exchange for hard currency in the world market. In spite of the cessation of magnesium imports from Canada, magnesium imports

were strong because of the increased supply of metal, particularly from Russia. As a result, U.S. prices dropped significantly in 1992, and a two-tier price system was established: a U.S. import price, and a U.S. transaction price, which reflected the prices charged by the U.S. producers.

By mid-1992, the U.S. International Trade Commission (ITC) had established both antidumping and countervailing duties on magnesium imported from Canada, so this material essentially was eliminated from the U.S. market (68). Imports of magnesium from Canada were approximately replaced by imports from Russia, so there was no significant change in U.S. magnesium supplies, and as a result, the U.S. price moderated during 1992–1993.

Low unit values for magnesium imported from Russia and Ukraine prompted one of the U.S. producers to request an antidumping duty investigation of magnesium imports from these two countries as well as from China in mid-1994. This resulted in a cessation of magnesium imports from these countries as well. As domestic demand countinued to increase, mostly for magnesium components for automotive applications, the elimination of imported magnesium from Canada, China, Russia, and Ukraine led to tight U.S. supplies. As a result, the price began to increase.

Supplies remained tight through most of 1995, and by midyear, the price escalated to its highest level since magnesium was first produced in 1915.

The ITC established final antidumping determinations in April 1995 for magnesium imports from China, Russia, and the Ukraine (69–71). Because the antidumping duty on Russian magnesium was established at 0% for all the large producers (as long as they imported the magnesium through specified importing companies), it was again possible to import magnesium from Russia, which had been the United States' largest magnesium supplier.

By 1996, the price began to drop as Russian magnesium returned to the U.S. market. At the same time, the countervailing duties on magnesium imports from Canada dropped enough so that Canada began to export significant quantities of magnesium alloy into the United States. With these sources of imported material, the United States experienced an oversupply of magnesium, and prices dropped dramatically by year end 1996. Also in 1996, the United States imported more magnesium that it exported for the first time in more than 20 years.

The United States continued to rely on imports of magnesium to meet its increasing demand, so U.S. prices continued to weaken slightly through 1998, although they were returning to more normal levels from the 1995 price spike. World supply also increased as a new 27,500 t/yr primary magnesium plant was commissioned at the end of 1996 in Israel. Primary magnesium prices for 1992–1998 are shown in Figure 9.

Magnesium alloys, unlike other metals, have been traditionally priced lower than the primary metal price. The published prices are generally about 10 cents per pound less than those for primary metal and respond to the same market influences as primary metal prices, although the fluctuations have been less dramatic.

Costs to produce magnesium metal vary greatly, depending on the feed material and the process used. Operating costs for magnesium production range from $309 to $2283/ton, with energy costs as the largest component of the total operating cost. A weighted-average operating cost was estimated to

be $1122/ton. Total production costs from seawater sources were lower than from brines or dolomite sources. Magnesium compound operating costs also vary depending on source material and processing techniques. Operating costs range from $24 to $425/ton for magnesium compound production, with seawater as the most costly source. The weighted-average operating cost for magnesium compounds production from all sources was $288/ton. Energy costs also represent the largest component of total operating costs (72).

Analysts at Commodities Research Unit (CRU) evaluated the direct operating costs of magnesium plants that operated during 1991. The operating cost curve showed that about one-half of the producers had direct operating costs less than $1.00 per pound of magnesium, and about 20% of the production was at direct operating costs above $1.25 per pound. In their cost estimates, CRU evaluated capital and operating costs for a 60,000-ton/year greenfield magnesium plant constructed in Australia. Capital costs were estimated at $470 million, with a 20% rate of return on investment over a 10-year life of the loan. In addition, operating costs were estimated to be $1.76 per pound in constant 1990 dollars, with most of the costs being capital charges resulting from the rate of return on investment and loan life. If the rate of return was lowered to 10% and the life of the loan was extended to 20 years, capital charge would drop by one-half (73).

6.1. Tariffs and Depletion Provisions. The tariffs on magnesium metal for countries with which the United States has normal trade relations are shown in Table 7. In addition, because of trade agreements, some countries have special, tariff rates; these are also shown in the table. Tariff rates have been established for countries with nonnormal trade relations (NTR) with the United States; these countries are Afghanistan, Cuba, Laos, North Korea, and Vietnam. Because there is no appreciable trade between the United States and these countries, the non-NTR tariff rates are not shown.

Depletion allowances have been established for some domestic and foreign ores of magnesium and its compounds. Magnesium chloride from brines, wells, or saline perennial lakes within the United States has a depletion allowance of 5%. The depletion allowance for both domestic and foreign ores of dolomite and magnesium carbonate is 14%. Depletion allowances for other ores are as follows: brucite, 10% (domestic and foreign), and olivine, 22% (domestic) and 14% (foreign).

7. Grades, Specifications, and Quality Control

Primary magnesium metal contains a minimum of 99.8% magnesium, which is of sufficient purity for most applications. Higher purity can be obtained by distillation. Magnesium alloys are most commonly designated by a system established by the American Society of Testing and Materials (ASTM) that covers both chemical compositions and tempers (74,75). Tempers are treatments which usually improve toughness. The designations are based on the chemical composition, and consist of two letters representing the two alloying elements specified in the greatest amount, arranged in decreasing percentages, or alphabetically if of equal percentage. The letters are followed by the respective percentages rounded off to whole numbers, with a serial letter at the end. The serial letter indicates

some variation in composition. The following letters designate various alloying elements: A, aluminum; C, copper; D, cadmium; E, rare earths; H, thorium; K, zirconium; L, lithium; M, manganese; Q, silver; S, silicon; T, tin; W, yttrium; and Z, zinc. For example, AZ91 contains about 9% aluminum (A) and 1% zinc (Z), and HK31 contains about 3% thorium (H) and 1% zirconium (K).

8. Analytical Methods

Because the production of magnesium is a large-scale industrial process, fast and reliable methods for magnesium analysis have been developed for the quick turnaround times necessary in a production foundry. Referee methods, which are more time consuming but have larger ranges and greater accuracy compared to the production methods, have also been developed.

8.1. Production Methods.   Analyses of magnesium or magnesium alloy batches are typically performed by atomic absorption (AA) spectroscopy, by emission spectroscopy employing an inductively coupled plasma (ICP) source, or direct spark emission spectroscopy. The atomic absorption method requires the dissolution of the sample in a standard solution followed by introduction into the flame of the AA unit. The absorption of light by the flame at specific wavelengths defines the concentration of the species. These methods require careful dilution of the sample and standard solutions since the response of the instruments are only linear over a small concentration range. The ICP emission instruments also require careful dilution but are linear over a wider range. Direct spark emission spectroscopy is a quick method of analysis, but is also subject to many sources of error. Sample preparation is important in this analytic method. The most severe limitation of this method is the absorption of light energy by atoms not completely excited. This is especially true in the case of aluminum, where the response is linear over a small range and the response curve is not very steep.

8.2. Referee Methods.   ASTM has collected a series of standard referee methods for the analysis of magnesium and its alloys (76). These methods are accurate over a larger range of concentration than the production methods, but are time-consuming in their application. The methods are based on potentiometric titration, photometric methods, or gravimetric methods. The photometric methods are most common and are relatively straightforward.

9. Environmental Concerns

Certain forms of magnesium metal, such as turnings, dusts, and scrap, react with water to generate hydrogen. This reaction may lead to spontaneous explosion; hence, these forms of magnesium must be stored and shipped in containers to insure a moisture-free environment.

The cover gas, sulfur hexafluoride, that is used to protect molten magnesium from oxidation, has been implicated as a potential factor in global warming. Although studies on its effect continue to be done, its long atmospheric life (~3000 years) and high potential as a greenhouse gas (24,900 times the global

warming potential of carbon dioxide) has resulted in a call for voluntary reductions in its emissions (77).

10. Recycling and Disposal

Recycled magnesium is derived from two sources: aluminum- and magnesium-base scrap. Aluminum-base scrap consists of both new and old scrap of aluminum–magnesium alloys. The primary component of aluminum-base scrap, from which magnesium is recovered, is aluminum beverage cans. Although only about 75% of the magnesium originally present in these types of alloys is recovered, it represents a substantial source of secondary magnesium. Magnesium in these aluminum alloys is not separated from the aluminum; rather, most of it remains as an alloying constituent when the beverage can scrap is recycled.

Magnesium-base scrap generally is in forms similar to those of other nonferrous metals. Castings, gates, runners, drippings, turnings, and drosses from processing operations are the principal sources of new scrap. Old scrap comes from a variety of sources, including aircraft parts, military applications, and discarded power tools.

Melting is the most common process used to recycle magnesium, because it allows almost all types of scrap to be processed into various secondary end products. Because magnesium resembles aluminum closely, there is usually a certain percentage of aluminum scrap mixed in with the magnesium scrap. The aluminum scrap is hand-sorted from the magnesium scrap, and the magnesium scrap then is sorted by alloy. Sorting is a critical step in producing a product of desired specifications.

In melting, sorted scrap is charged to a steel crucible, heated to 675°C. As the scrap at the bottom begins to melt, more scrap is added. The liquid magnesium at the bottom is covered with a flux or inhibitive gas to control surface burning. After any alloying elements are added, such as aluminum, manganese, or zinc, and melting is complete, molten magnesium is transferred to ingot molds by either hand ladling, pumping, or tilt pouring.

In addition to melting, magnesium scrap may be recycled by direct grinding of the scrap into powder for iron and steel desulfurization applications. This method is limited to using only specific types of clean scrap. Dosses and other contaminated scrap are not used because they can introduce impurities into the finished product, and these types of scrap can increase the danger of fire in the direct grinding (78).

11. Health and Safety Factors

Magnesium articles or parts are difficult to ignite because of good thermal conductivity and high (>450°C) ignition temperatures. However, magnesium can be a fire hazard in the form of dust, flakes, or ribbon when exposed to flame or oxidizing agents. A magnesium powder or dust ignites readily, if

suspended in air in concentrations above the lower explosive limit (0.04 g/L). Such ignition can result in a violent explosion (79).

Magnesium fires are readily extinguished with the appropriate metal-extinguishing powder. Magnesium fires do not flare up violently unless there is moisture present. Therefore, water is not recommended for extinguishing magnesium fires and must be avoided with molten magnesium or magnesium powders. Proper storage of magnesium products greatly reduces the risk of accidental ignition (80).

Because magnesium is essential to most plant and animal life, dietary deficiency, rather than toxicity, is the more significant problem.

12. Uses

12.1. Magnesium Metal. The largest use of magnesium metal is as an alloying addition to aluminum to increase the hardness and corrosion resistance of the pure metal. The 5000 and 7000 series alloys of aluminum contain up to 5.5 and 3.5% magnesium, respectively. The single largest application for magnesium-containing alloys of aluminum is the aluminum beverage can, which has a magnesium content of about 4.5% in the lid (alloy 5181 or 5182, UNS A95181 and A95182, respectively) and about 1.1% in the can body (alloy 3004, UNS A93004). Since the early 1980's, magnesium consumption in this market has grown at an average compound annual rate of 3.2%. Except for the significant increases in aluminum recycling, this rate might have been greater. More than 60% of aluminum beverage cans are recycled annually conserving both the aluminum and magnesium content of the alloys as well as the energy required to produce them (81).

Magnesium and its alloys have structural uses in the forms of die castings, gravity (sand and permanent mold) castings, and wrought products. Die castings are the largest structural application for magnesium. U.S. automakers have recently introduced magnesium components such as instrument panels, seat components, clutch housings, headlamp assemblies, and grille covers to reduce vehicular weight. The power tool market includes magnesium castings in chain-saws and lawnmower housings. Die-cast magnesium also is used in videocamera, cellular phone, and computer components.

The low density of magnesium is especially important for gravity-cast military and aerospace applications. Gravity castings are essentially all produced as sand castings, with permanent mold and plaster casting representing a small segment of the alloy market. Typical applications include helicopter gear housings, aircraft canopy frames, air intakes, engine frames, speed brakes, and auxiliary component housings.

Magnesium is also used in wrought from in products such as extrusions, forgings, sheet, and plate. Applications for these products range from bakery racks, loading ramps, tennis rackets, and hand trucks to concrete finishing tools, computer printer platens, and nuclear fuel element containers and aerospace assemblies.

In the iron–steel industry, magnesium is used as an external hot-metal desulfurization agent, and it is used in the production of nodular iron.

Magnesium's unique affinity for sulfur allows it to be injected into molten iron, where it vaporizes and reacts to form magnesium sulfide, which floats to the surface as a readily separated phase. This allows the steel producer the flexibility to use lower cost raw materials, while maintaining the ability to produce the high quality, low sulfur product required for high-strength, low alloy steels. The magnesium used is often derived from low quality streams or alloy scrap, which is then ground to a coarse powder and combined with lime prior to injection in the hot metal. Lime blends have been found to provide significantly improved efficiencies based on the magnesium required.

Magnesium, in combination with ferrosilicon, is used in the production of-ductile (nodular) iron because of the ability of magnesium to promote the formation of spheriodized (globular) graphite particles in place of the normal flake structure. This results in an iron product having improved toughness and ductility. Two principal applications for ductile iron are in the production of pipe and of automotive engine and drive train components.

Magnesium is used as a catalyst for producing certain organic chemicals and petrochemicals. Magnesium is used as a reducing agent for producing other nonferrous metals such as titanium, zirconium, hafnium, beryllium, and uranium. Anodes of magnesium are frequently used for the cathodic protection of iron and steel, particularly in underground pipe and water tanks, as well as water heaters and marine applications. Magnesium also has smaller applications in graphic arts, pyrotechnics, and in alloys other than aluminum. Data on world shipments of primary magnesium, by application is shown in Table 8.

The two end uses with the largest growth since 1983 or 1984 have been die casting and desulfurization. Growth in die casting has been largely a result of increased use of magnesium components in automobiles. Table 9 shows the growth in magnesium die castings content of the average North-American-produced family vehicle.

In the 1990s the use of magnesium in automobiles has increased dramatically; between 1990 and 1997 the total magnesium die castings content doubled. Some of the components in which magnesium alloy has replaced steel or aluminum are brake and clutch pedal brackets, instrument panels, cylindrical head covers, transfer case housings, intake manifolds, and seat components.

Most of the original reason to use magnesium was because of its light weight. Auto manufacturers wanted to reduce overall vehicle fleet weight to meet Corporate Average Fuel Economy Standards mandated by the U.S. government, and many of these components were considered after the original car model was well into the design process. This proved to be a costly way to incorporate magnesium. Once the companies started to use magnesium alloy, magnesium was shown to have advantages other than its light weight. In many cases, parts that were made of several steel pieces that had to be separately stamped then welded together, could be made as a one- or two-piece magnesium casting, reducing the cost of the finished part. As a result, magnesium components are now being designed into cars rather than being retrofitted after the design is completed. Including the material in the design process allows more opportunities to incorporate magnesium parts in a new or redesigned model.

These changes in the automotive industry have led to a significant increase in the demand for magnesium die castings. Magnesium industry growth projec-

tions for this applications are 15% per year; statistics from the IMA indicate that from 1991 to 1997, global demand for magnesium die castings increased from 24,000 to 64,000 tons, with a projected increase to 110,000 metric tons by 2001 (82).

The use of magnesium for desulfurization has grown significantly in North America and Europe since 1983 or 1984. However, it has increased to the point where it has almost 100% of the market in these geographic areas; therefore the growth rate is expected to slow. Because magnesium desulfurization reagents can be manufactured from either primary or recycled magnesium, there may be a switch from primary magnesium to lower cost alloy scrap and low-grade materials.

12.2. Magnesium Alloys. Primary magnesium metal and alloys have also been assigned unified numbering system (UNS) designations according to the Standard Recommended Practice for Numbering Metals and Alloys (83). The UNS designation for a metal or alloy consists of a letter followed by five numbers. The UNS system is intended to provide a nationally accepted means of correlating the many alloy designation numbers used by various organizations and an improved system for indexing, record keeping, data storage and retrieval, and cross referencing. The numbers M10001 through M19999 have been reserved for magnesium and magnesium alloys. The letter M denotes a class of miscellaneous nonferrous metals and alloys. The magnesium primary grades and alloys registered with ASTM have been assigned UNS numbers and are listed in ASTM B275.

ASTM B296 defines the temper designations used and ASTM B661 defines the heat treatment schedules required to achieve the desired tempers for magnesium alloys. The temper designation is separated from alloy designation by a dash. The following describes the ASTM tempers commonly used for magnesium cast and wrought products (84):

-F	as fabricated
-O	annealed recrystallized (wrought products only)
-H	strain hardened
-H1	strain hardened only
-H2	strain hardened and then partially annealed
-H3	strain hardened and then stabilized
-T	thermally treated to produce stable tempers other than -F, -O, or -H
-T2	annealed (cast products only)
-T4	solution heat treated and naturally aged to a substantially stable condition
-T5	cooled and artificially aged only
-T6	solution heat treated and then artificially aged
-T7	solution heat treated and then stabilized
-T8	solution heat treated, cold worked, and then artificially aged

12.3. Composition and Properties of Selected Alloys. Table 10 shows the chemical compositions and physical properties of the magnesium alloys used most commonly in cast and wrought form. Typical mechanical properties at $20-25°C$ of selected magnesium alloys in various cast forms are given in

Table 11, in extruded forms in Table 12, and in sheet and plate forms in Table 15. Alloys containing rare-earth metals, or rare earths and yttrium, have good strength retention at temperatures up to 315°C and higher. The strength of the other alloys diminishes rapidly above 150°C.

Properties of castings are determined using test bars cut from castings or on separately cast test bars. The properties of sections cut from actual castings may be only about 75% of the separately cast test bar values, due to slower solidification rates which result in large grain size and a consequent reduction of tensile properties. Properties of wrought alloy are determined on sections cut from extrusions, sheet, forgings, etc, in accordance with ASTM E55 sampling procedures. Magnesium alloys do not have the sharp yield point characteristic of carbon steels. Instead, the alloys yield gradually when stressed and the term yield strength is used. It has been defined as the stress at which the stress–strain curve intersects a line parallel to the modulus line offset 0.2% on the strain axis. The slope of this line is known as the Young's modulus. In cast form, the tensile and compressive yield strengths of magnesium alloys are substantially equal. In most wrought alloys, however, the compressive yield strength is less than that of the tensile yield.

Magnesium alloys have a Young's modulus of elasticity of approximately 45 GPa (6.5×10^6 psi). The modulus of rigidity or modulus of shear is 17 GPa (2.4×10^6 psi) and Poisson's ratio is 0.35. Poisson's ratio is the ratio of transverse contracting strain to the elongation strain when a rod is stretched by forces at its ends parallel to the rod's axis.

Sand and permanent-mold castings in magnesium alloys are produced in a large variety of sizes and shapes for many uses. Typical alloys with good casting qualities containing aluminum and zinc are AZ63A, AZ91C, and AZ92A. The last provides the optimum combination of high yield strength and moderate elongation. Casting alloys containing zirconium and zinc, such as ZK51A and ZK61A, have been developed for their improved properties, including a reduced tendency for microporosity. Alloys containing rare earths, such as EZ33A and QE22, respectively, are specified for elevated temperature service. Yttrium–rare-earth alloys such as WE54A and WE43A, introduced in recent years, offer still further improved elevated temperature properties with the added advantage of enhanced corrosion performance in salt water exposures.

12.4. Heat Treatment.   Heat treatment improves the properties (87) of magnesium castings. In solution heat treatment (ASTM T4), the casting is heated to the proper temperature and held long enough for the precipitated compound to dissolve. Air quenching upon completion of the solution heat-treatment cycle prevents precipitation or reforming of the constituents. Controlled precipitation by artificial aging following solution heat treatment is designated as T6 temper. This treatment increases tensile yield strength and hardness. An artificial aging treatment consists of simply heating the as-cast product for a few hours at a suitable intermediate temperature. This treatment, designated as T5, relieves internal stresses that are likely to result during cooling after casting. Such a treatment improves mechanical properties and decreases the possibility of warping after machining or permanent distortion when used at elevated temperatures.

Casting alloy M11630 (AZ63A) is heat treated in a furnace at 260°C until it is the same temperature as the furnace. The temperature is then raised gradually over a two hour period to 390°C and the casting held at this temperature for about 10 hours and then air cooled. This provides solution heat treatment (T4 temper). For artificial aging (T6 temper), the solution-heat treated casting is heated further for 16 hours at 175°C. Heat treatment of AZ92A alloy castings requires different temperatures. For the solution-heat treatment, the alloy is soaked at 410°C for 18 hours, whereas for artificial aging the casting is heated at 230–290°C for 2–6 hours. Because of the higher temperature for M11920 (AZ92A) treatments, the furnaces should be equipped to circulate the heated air and should contain about 0.7% sulfur dioxide or 0.5% SF_6 to avoid excessive oxidation during the solution heat-treating cycle.

Alloy M16630 (ZE63A) which contains rare-earth metals and zinc, is designed to take advantage of a newer heat-treatment technique involving inward diffusion of hydrogen and formation of zirconium hydride. The alloy is heated in hydrogen at 480°C for 10, 24, or 72 hours for 6.3, 12.7, or 19 mm sections, respectively, to complete the formation of zirconium hydride. It is then quenched and aged for 48 hours at 140°C.

For the manufacture of die castings, the alloy M11916 (AZ91D), which contains aluminum and zinc, is most commonly used because of its excellent stiffness and strength at normal ambient temperatures. Alloys M10602 (AM60B) or AM50X1, which contain aluminum and manganese, are used where ductility is desired, and M10410 (AS41A), which contains silicon, or developmental alloy AE42 are used where good long-time yield strength (or creep resistance) is needed at elevated temperatures. Heat treating is not used on magnesium die castings.

For common wrought applications, alloys AZ31B, AZ61A, AZ80A, and ZK60A are employed. When wrought magnesium alloys are in tempers other than as fabricated, these are treated at the mill rather than by the customer. ZK60A and AZ80A are produced in the T5, artificially aged temper for maximum strength, whereas AZ31B sheet and plate is produced in the O (fully annealed) or the H24 or H26 (strain hardened and partially annealed) tempers. Magnesium is usually press-forged, although hammer forging is possible. Forged commercial alloys include AZ31B, AZ61A, AZ80A, and ZK60A.

In Europe, the same types of alloy systems as in the United States are employed.

12.5. Metallography. Most commercial magnesium alloys are either of the solid solution or hypoeutectic type, where intermediary phases are second constituents. The phase diagrams in Figures 10–12 show binary systems of some common alloying elements. Figure 13 is a phase diagram of the widely used ternary system comprised of magnesium, aluminum, and zinc (89).

Under equilibrium conditions, magnesium can contain as much as 12.7% aluminum in solid solution at the eutectic temperature. However, the slow diffusion of aluminum to the grain boundary leads to a coring effect in primary crystals and a hard-phase magnesium–aluminum compound(17:12) [12254-22-7], $Mg_{17}Al_{12}$, or β-(MgAl). Thus aluminum occurs in magnesium alloys both in solid solution and as the intermediary intermetallic phase. The latter is clear white and in slight relief in polished and etched samples. In as-cast alloys, the

hard phase occurs in massive form, but when precipitated from solid solution a lamellar structure is formed similar to pearlite in steel. When produced by aging at low temperatures, it appears as fine particles.

In commercial alloys, zinc is usually dissolved in the magnesium matrix and in the hard magnesium–aluminum phase when aluminum is present. Zinc additions to magnesium–aluminum alloys change the eutectic structure to a so-called divorced eutectic, characterized by the presence of massive compound particles surrounded by a magnesium-rich solid solution.

Grain size and other structural characteristics of magnesium alloys are most easily determined by polishing and etching. These characteristics are classified by reference to a series of charts that have been devised to express numerically the various structural characteristics. Magnesium alloys deform plastically by slip and twinning mechanisms, and polished and etched samples indicate prior working by the presence of lenticular twins, ie, having the shape of a double convex lens, within grains of deformed metal. The success of heat-treating operations can be followed by examining samples for decrease of the β-(MgAl) constituent on solution heat treatment, and by noting the character of precipitated β-(MgAl) after aging treatments.

Manganese appears as bluish gray angular crystals in the binary alloy if the crystals are formed during solidification of the alloy. In magnesium–aluminum alloys, the manganese appears as a manganese–aluminum binary phase, or as a manganese–aluminum–iron ternary phase formed with any iron contamination present in the alloy. Silicon is an impurity usually present as an intermetallic, light blue compound, magnesium silicide [22831-39-6], Mg_2Si. In magnesium–aluminum alloys containing more than about 0.2% silicon, the Mg_2Si develops an appearance of Chinese script. This is the form commonly found in die cast alloy AS41B. Tin is soluble in magnesium, and may be found in alloys in solid solution or as a dull grayish blue constituent that becomes tan to brown when etched. Calcium, if present in amounts greater than 0.1%, occurs as magnesium calcium compound(2:1) [12133-32-3], Mg_2Ca, unless aluminum is present, in which case calcium aluminide(1:2), Al_2Ca, forms instead.

12.6. Fabrication. Magnesium alloys are fabricated by common methods, including melting followed by casting, rolling, extrusion, and forging. Total energy required for the manufacture of magnesium sheet or extrusions has been estimated at 75 MJ/kg (32,090 Btu/lb) and 83 MJ/kg (35,980 Btu/lb), respectively (90). Further fabrication includes forming, joining, and machining after which standard assembly methods are used.

Magnesium alloys are produced from molten magnesium directly from magnesium cells or by remelting magnesium pigs or ingots in oil- or gas-fired steel pots or electric-induction furnaces (91,92). Alloying metals, especially aluminum and zinc, may be placed in a perforated steel basket and suspended in the molten magnesium which is held at about 700°C. Movement of the basket facilitates alloying by flushing, which minimizes the possibility of segregation of heavy constituents. Manganese is added either in the metallic or chloride form for the reduction of iron content through the formation of an insoluble intermetallic. After the alloying ingredients are added, the melt is allowed to stand to settle out impurities, including the iron–manganese phase. The metal can then be cast in ingot molds to produce the alloy ingot used for the various casting processes. In

high production alloying operations, the magnesium ingots are melted in multi-pot systems or reverberatory furnaces and the liquid metal is then transferred by pumping. A multipot system may consist of a complex of melting, alloying, settling, holding, and casting pots from which the metal is ladled or pumped into ingot molds.

Magnesium alloys containing zirconium and rare earths are often made up in the casting pot in the foundry because remelting can result in substantial loss of these alloying metals. Rare-earth metals generally are added as mischmetal (mixed rare-earth metals). Zirconium can be added as a magnesium–zirconium alloy called a zirconium hardener.

Salt-based fluxes are employed to prevent excessive oxidation of the melt and improve its purity. They contain a mixture of chlorides, including potassium chloride [7447-40-7] and magnesium, as well as calcium fluoride and magnesium oxide. Since the early 1980s, many foundries have adopted the use of sulfur hexafluoride, SF_6, at approximately 0.3 to 0.5% in air, or air/CO_2 mixtures, to inhibit excessive oxidation of magnesium melts. This practice, combined with developing fluxless refining methods, has dramatically improved the corrosion performance of cast products by eliminating the source of salt contamination which often leads to serious corrosion of machined castings (65,93,94).

The extrusion process starts with a cast extrusion billet that is made by casting in thick-walled iron or steel molds, or preferably by means of the direct-chill casting process which gives a fine grain and prevents compound segregation. Billets that have been machined to remove the casting skin are preheated at 315–455°C, depending on the alloy, placed in the container of the extrusion press, and then by means of a hydraulic ram are forced through a steel die to provide the desired shape. Certain magnesium alloys containing only small amounts of alloying constituent may be extruded at a rate as high as 30.5 m/min. Other alloys and more difficult configurations may have a limiting extrusion speed of only one or two meters per minute. The reduction in cross-sectional area from the original ingot to the final extruded section must be relatively high, 20:1 or greater, to obtain desired properties in the extrusion. Additional improvement in properties of certain alloys can be obtained after extrusion by a heat treatment, such as artificial aging, which causes precipitation of intermetallic compounds and thus improves yield strength but with some sacrifice in ductility.

Magnesium sheet and plate are fabricated by rolling slab which is made by the direct-chill casting process. Several separate operations are needed. First, in breakdown rolling, the slabs are heated in a two-step preheating oven to a temperature of 425–480°C. The slab is then reduced in thickness by repeated passes through the rolls of a hot mill. The original slab is reduced in thickness to about 6.4 mm without reheating. Following breakdown and reheating, the sheet is transferred to a finishing mill and rolled with intermittent steps to the final desired thickness and temper. Additional operations, such as shearing at various stages in production, acid cleaning, wire brushing, chrome pickling, or oil finishing, may be required depending on the final product.

Magnesium forgings usually are made by the press-forging process in closed dies or, less often, by hammer forging (92). The size of forgings is limited only by

the size of available equipment. A magnesium canister forging made for the Echo satellite program weighed 104 kg.

The earliest method of fabrication used for magnesium alloys, still commonly used as of 1994, is sand casting (92,95). Inhibitor agents are added to green sand or resin-bonded sand to prevent excessive reaction with atmospheric nitrogen, oxygen, or moisture in the sand mold. Inhibitor agents usually include sulfur, boric acid [10043-35-3], diethylene glycol [111-46-6], and ammonium fluorosilicate [16919-19-0]. A typical molding sand might contain 0.7% sulfur, 1% boric acid, and 5% ammonium fluorosilicate. Sand cores may contain inhibitors mixed with the sand or the cores may be sprayed with inhibitors after baking.

A wide variety of parts are made by die casting (96,97). Magnesium's low heat content per unit volume and its limited tendency to wet the die permits high casting speeds with extended die life relative to aluminum die casting. The cold-chamber process has been used widely for many years but the hot chamber process has assumed a significant share of the magnesium die casting market during the 1990s. However, recent developments in metering devices allow the delivery of the exact amount of metal required to the shot well of cold chamber die casting machines. This development may support their competitive use for larger castings for some years to come. Typically, the energy required to produce a finished die casting, including normal processing efficiencies, is reported to be $21-45$ MJ/kg $(9,000-19,160$ Btu/lb) (90,98).

Thixotropic injection molding offers a competitive technology for the magnesium die casting industry and has some unique advantages such as no molten metal handling or associated losses, rapid start-up and shutdown, improved die life, reduced porosity relative to die casting, and tighter part tolerances, and reduced scrap rates. The process, which is modeled after the plastics injection molding process, employs a granular alloy feed. The feed is heated under argon in the machine's screw injector to a temperature between the alloys' solidus and liquidus temperatures. Under the continuous mixing imparted by the screw, the material is converted to a thixotropic state at which point the material is injected into a mold of similar design to a standard high pressure die casting mold (99,100).

Magnesium sheet or extrusions can be formed by many methods (88,99,101). Bending around large radii is usually involved. Relatively minor deformations can be performed at room temperature. However, the formability is greatly improved at $200-315°C$, and most forming operations are carried out in this temperature range. This increased formability at elevated temperature is due to magnesium's hexagonal close-packed structure. When the metal is heated, additional slip planes become available within the metal lattice allowing improved plastic deformation characteristics. In high speed mechanical presses, draws are made in one step at up to 59% reduction and at speeds up to 24 m/min (102). Magnesium alloys are also formed by bending, stretch forming, spinning, impact extruding, drop-hammer forming, and other common methods.

Parts are assembled by joining methods including arc welding, electric-resistance welding, brazing, soldering, riveting, bolting, and adhesive bonding (103–107). Because of rapid heat transfer, magnesium cannot be satisfactorily

cut with an oxy-fuel gas flame in the same manner as steel. Welding (qv) is best accomplished by the gas−metal arc processes which prevent the formation of magnesium oxide or nitrides. Helium [7440-59-7] or argon are the preferred protective gases. In gas−tungsten arc welding, a tungsten [7440-33-7] electrode maintains the arc which melts the magnesium filler rod. Gas−metal arc welding uses a coil of magnesium wire that functions as both an electrode and filler rod. This method is sometimes described as consumable electrode-arc welding. The gas−metal arc welding processes are preferred over gas welding because they do not use a corrosive flux. Magnesium can be welded with oxy-fuel gases but a chloride-base flux is necessary to prevent oxidation. This flux is corrosive and difficult to remove completely after welding. Therefore, gas welding of magnesium alloys is limited to emergency repairs. Spot welding is the most popular method of electric-resistance welding. Forge welding and stud welding can also be used. Magnesium alloys are also joined by furnace, flux-dip, and torch brazing. Soldering is avoided because of the brittle joint that is formed (see SOLDERS AND BRAZING ALLOYS).

Riveting is another method of making mechanical joints in magnesium. Aluminum alloy 5056 (A95056) rivets in the H32 temper are commonly used, although rivets of 6053-T61 (A96053) or 6061-T6 (A96061) can be substituted. These aluminum alloys minimize the possibility of galvanic corrosion. Rivets of steel, brass, copper, and certain aluminum alloys should not be brought in contact with magnesium because of serious galvanic corrosion. Rivet holes in magnesium should be drilled rather than punched and squeeze rivets are preferred over pneumatic riveting hammers. The latter are more likely to damage the magnesium sheet by overdriving. Many small rivets are preferred over a few of large diameter. Optimum rivet-joint design calls for a minimum spacing in any direction of three times the rivet diameter. Similarly, a minimum edge distance of 2.5 times the rivet diameter is suggested. Riveted joints should be protected with a sealing compound to prevent water entrapment. A coat of chromate-pigmented primer is often used for this purpose.

In some applications, adhesive bonding has become a popular method of joining magnesium sheet. For example adhesive bonding is used when joining material too thin to be effectively riveted or welded. A large variety of adhesives (qv) are available, most of which require elevated ($\geq 90°C$) temperature curing. Curing times range from a few minutes to an hour or more. Certain adhesives require the application of pressure but usually contact is sufficient. The shear strength of adhesive bonded joints ranges from about 7 to 28 MPa (1000−4000 psi). Most bonded joints hold up to 65°C. Some epoxy phenolic adhesives have good joint strength retention up to 260°C.

12.7. Machining. Magnesium is the easiest of all structural metals to machine (108). Because of this machinability, it is sometimes used in applications where a large number of machining operations are required. The machinability of magnesium alloys relative to that of other metals based on the lowest power required to remove 16 cm^3 of metal and when magnesium is assigned a value of unity, is (108):

Metal	Relative power required
magnesium alloys	1.0
aluminum alloys	1.8
brass	2.3
cast iron	3.5
mild steel	6.3
nickel alloys	10.0

Some of the advantages of excellent machinability include reduced machining time, resulting in higher productivity for the machine tools and thus lower capital investment; greatly increased tool life; an excellent surface finish with a single large cut; well-broken chips which minimize handling costs; and less tool buildup.

Dry machining is strongly encouraged owing to the fact that the value of turnings or chips produced are significantly higher as a result of ease with which these can be recycled through remelting or through use as a desulfurization reagent. Where chip removal is required, a combination of air- and screw-driven conveyors can be employed. If a coolant or cutting fluid must be used for a particular operation, mineral oil is usually preferred over water-based coolants. This is due to the fact that magnesium reacts with water to some degree, over time, producing hydrogen gas and magnesium hydroxide. As a result, wet chips should be treated with caution in order to prevent ignition of the evolved hydrogen, and to prevent partial drying of the wet mass, which may result in spontaneous ignition due to the heat evolved in the reaction in combination with poor heat-transfer characteristics of the partially dried mass. If wet chips are generated, the chips should be kept fully submerged in excess water and stored in a well-ventilated, remote location until they can be properly recovered or safely destroyed (108−111). Despite the hazards associated with water-based coolants, well-inhibited coolants have been employed in some applications for a number of years, with few poblems.

Coolants or cutting fluids containing animal or vegetable oil must be avoided. The carboxylic acid functions present can undergo reaction with the magnesium on standing.

12.8. Corrosion and Finishing. With few exceptions, magnesium exhibits good resistance to corrosion at normal ambient temperatures unless there is significant water content in the environment in combination with certain contaminants. The reaction which typically occurs is described by the equation

$$Mg + 2\,H_2O \longrightarrow Mg(OH)_2(s) + H_2(g) \tag{19}$$
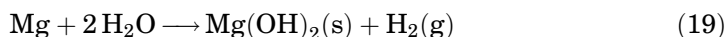
In neutral and alkaline environments, the magnesium hydroxide product can form a surface film which offers considerable protection to the pure metal or its common alloys. Electron diffraction studies of the film formed in humid air indicate that it is amorphous, with the oxidation rate reported to be less than 0.01 μm/yr. If the humidity level is sufficiently high, so that condensation occurs on the surface of the sample, the amorphous film is found to contain at least some crystalline magnesium hydroxide (brucite). The crystalline magne-

sium hydroxide is also protective in deionized water at room temperature. The aeration of the water has little or no measurable effect on the corrosion resistance. However, as the water temperature is increased to 100°C, the protective capacity of the film begins to erode, particularly in the presence of certain cathodic contaminants in either the metal or the water (112,113).

In extended atmospheric exposures of magnesium and magnesium alloys, the reaction of the magnesium hydroxide with acid gases, such as CO_2 and SO_2, has been reported to play an important role in the stability and composition of the film present. X-ray diffraction analysis of the oxidation product present on unalloyed magnesium ingot reveals it consists of a mixture of crystalline hydroxycarbonates of magnesium such as hydromagnesite [12275-04-6], $MgCO_3 \cdot Mg(OH)_2 \cdot 9H_2O$, nesquehonite [5145-46-0], $MgCO_3 \cdot 3H_2O$, and lansfordite [5145-47-1], $MgCO_3 \cdot 5H_2O$. In the case of the common commercial wrought alloy, AZ31B (magnesium, 3% aluminum, 1% zinc, 0.2% manganese) analysis of the adherent corrosion product by x-ray diffraction revealed only two crystalline phases: hydromagnesite and hydrotalcite [12304-65-3], $Mg_6Al_2(OH)_{16} CO_3 \cdot 4H_2O$. In an industrial atmosphere with high SO_2 content, traces of magnesium sulfate hexahydrate [10034-99-8], $MgSO_4 \cdot 6H_2O$, and magnesium sulfite hexahydrate [13446-29-2], $MgSO_3 \cdot 6H_2O$, were detected in addition to the hydroxycarbonate products for unalloyed ingot. It was suggested that SO_2 exposures accelerate the corrosion of magnesium through the conversion of the protective hydroxide and carbonate compounds to the highly soluble sulfate and sulfite, which are then eroded (112,114).

Corrosion by Various Chemicals and Environments.   In general, the rate of corrosion of magnesium in aqueous solutions is strongly influenced by the hydrogen ion [12408-02-5] concentration or pH. In this respect, magnesium is considered to be opposite in character to aluminum. Aluminum is resistant to weak acids but attacked by strong alkalies, while magnesium is resistant to alkalies but is attacked by acids that do not promote the formation of insoluble films.

With regard to salts, neutral or alkaline fluorides form insoluble magnesium fluoride, and consequently magnesium alloys are resistant to them. Chlorides are usually corrosive even in solutions having pH values above that required to form magnesium hydroxide. Acid salts are generally destructive but chromates, vanadates, and phosphates form films that usually retard corrosion except at elevated temperatures. Most mineral acids attack magnesium rapidly. Hydrofluoric acid, except at low concentration and elevated temperature, is an exception to this rule. Chromic acid [11115-74-5] has a low rate of attack except when chlorides or sulfates are present. Chromic acid solutions of about 20% are used to clean corroded samples, since this solution dissolves the magnesium oxidation products without significantly attacking the base metal (115). Most organic acids attack magnesium alloys readily.

Contaminant Effects.   Magnesium alloys have long had a reputation for poor corrosion performance, particularly in salt water exposures. The importance of metal composition in determining the susceptibility to salt water attack has been recognized since the 1930s and 1940s. However, the first complete definition of the compositional limits required for some common commercial alloys was only established within the 1980s (116–120). A summary of the effects of 14 separate elements on the salt water corrosion performance of magnesium

was published in 1942 (121). Of the four elements having the most degrading effects, iron, nickel, copper, and cobalt [7440-48-4], the first three are common contaminants of standard commercial alloys. It is these elements that in large part have led to magnesium's poor reputation for salt water corrosion durability (116–120). When these elements are controlled at levels lower than established limits, referred to as tolerance limits, for a specific alloy composition, the salt water corrosion rates may be reduced by more than 100-fold in accelerated ASTM B117 salt spray testing. Figure 14 illustrates the effect of reduced levels of iron, nickel, and copper on the corrosion rates of high pressure die cast AZ91 alloy, versus cold-rolled carbon steel, and 380 die cast aluminum alloy (116,117). As may be noted, the corrosion performance of the alloy having each of the three critical contaminants at low levels is better than that of both the carbon steel and die cast aluminum alloy which were simultaneously tested.

Since 1982, five high pressure die casting and three sand casting alloys have been introduced commercially having high purity corrosion performance. The die casting alloys are AZ91D, AM60B, AS41B, AM50A, and AE42X1 (see Table 10). The sand casting alloys are AZ91E, WE54A, and WE43A (see Table 11). The introduction of these alloys has played a significant part in the growth of the magnesium alloy business. In the North American die casting industry, alloys grew at an average compound rate of almost 18%/yr in the period 1983–1993.

Magnesium is resistant to pure alkalies in solutions of pH 10.2 or greater, even when metals cathodic to magnesium are present as impurities. Magnesium is resistant to dilute alkalies even in boiling solutions, and to 50% caustic solutions up to about 60°C. At higher temperatures there may be serious attack. Fruit juices and sour milk attack magnesium due to their acid content. Ethylene glycol solutions are considered essentially noncorrosive at room temperature; however, the rate of attack increases with temperature and inhibitors are recommended above 100°C. Magnesium alloys have been used for oil and gasoline tanks, but pitting can result from the presence of tetraethyllead and ethylene dibromide when water is present, unless inhibitors are used (see CORROSION AND CORROSION CONTROL).

Table 14 indicates the compatibility of magnesium with a variety of chemicals and common substances. Because the presence of even small amounts of impurities in a chemical substance may result in significantly altered performance, a positive response in the table only means that tests under the actual service conditions are warranted (123). Other factors which may significantly alter magnesium compatibility include the presence of galvanic couples, variations in operating temperatures, alloy composition, or humidity levels.

Organic compounds normally cause little or no corrosion of magnesium. Tanks or other containers of magnesium alloys are used for phenol [108-95-2], methyl bromide [74-96-4], and phenylethyl alcohol [60-12-8]. Most alcohols cause no more than mild attack, but anhydrous methanol attacks magnesium vigorously with the formation of magnesium methoxide [109-88-6]. This attack is inhibited by the addition of 1% ammonium sulfide [12135-76-1], or the presence of water.

Magnesium is not attacked seriously by dry chlorine [7782-50-5], iodine [7553-56-2], bromine, or fluorine [7782-41-4] gas. However, the presence of

water promotes attack. Similarly, sulfur dioxide, ammonia, and fluorine-containing refrigerants do not attack in the absence of water.

Some tests indicate that magnesium alloys are resistant to loam soil. However, in the presence of chlorides, corrosive attack may be serious particularly if galvanic couples are present as a result of coupling to iron structures.

Galvanic Corrosion.   Galvanic corrosion is an electrochemical process with four fundamental requirements: (*1*) an anode (magnesium), (*2*) a cathode (steel, brass, or graphite component), (*3*) direct anode to cathode electrical contact, and (*4*) an electrolyte bridge at the anode and cathode interface, eg, salt water bridging the adjacent surfaces of steel and magnesium components. If any one of these is lacking, the process does not occur (124,125).

The most common means of controlling galvanic attack on magnesium is through minimizing the electrochemical potential difference between the magnesium and the other metal. For steel fasteners, tin, cadmium [7440-43-9], and zinc electroplates have long been recognized for their ability to reduce the galvanic attack induced by the fastener when compared to bare steel. The relative effectiveness of these electroplates has generally been accepted to be in descending order as listed. Not all methods of deposition are equivalent, however. Certain proprietary zinc- and aluminum-filled polymers, as well as some ion vapor deposited aluminum coatings, applied to steel fasteners may actually produce more damage than the untreated steel fastener itself. This has been attributed to two possible causes: either the high surface area involved with each of the particulate coatings, or the contamination of the particulate surface with active cathodic contaminants such as iron, nickel, or graphite. Another point of interest is that a simple inorganic chromate treatment applied to a cadmium or zinc electroplate, used to preserve its brightness, has been found as effective in further retarding the galvanic attack on magnesium as was a coating of epoxy resin. This is consistent with the known inhibitive effects of chromate on the cathodic reduction process and has been observed with other fastener coatings as well (124−126).

In addition to selecting compatible metals or electroplates for use with magnesium assemblies, there are several other methods of controlling galvanic corrosion of magnesium parts. One method is to electrically isolate the magnesium component from the cathodic material. In many applications, however, this is not a practical alternative due to the mechanical, electrical, or cost requirements. Another alternative is to paint the cathodic material. This provides a barrier against electrolyte contact with the cathode. However, this is not easily accomplished in many cases because of the permeability of coatings by moisture and the generation of hydrogen and hydroxyl ion on the cathode surface. The combined effect is to strip all but the most alkali-resistant coatings. A third possibility is a design which prevents pooling of the electrolyte in critical areas of fasteners and interfaces with other cathodic components. This is an effective method of control since it both limits the electrolyte resistance and the duration of its presence because thin films of an aqueous electrolyte have both lower conductivity and higher rates of drying, so that the time of conductivity is minimized in applications where exposure to electrolytes is an intermittent event. A final alternative is to use compatible shims or washers in association with joints and fasteners. This control technique works well where exposure to the electrolyte

is again intermittent and surfaces are well drained. By using a shim or washer that extends 3–6 mm beyond the interface of the cathodic material with the magnesium surface, the electrolyte path is extended to a range where the resistance of typical aqueous salt water electrolytes is sufficiently high to significantly retard the electrochemical activity. This compatible material may be a nonconductive ceramic, a polymeric material, or a compatible metal, such as an aluminum 5052 or 6061 alloy. The use of an aluminum washer beneath the head of a steel fastener that extends 3–6 mm beyond the radius of the bolt head is a simple effective method of control of the galvanic attack associated with fasteners in magnesium (124–126).

High Temperature Corrosion.   The rate of oxidation of magnesium alloys increases with time and temperature. Additions of beryllium, cerium [7440-45-1], lanthanum [7439-91-0], or yttrium as alloying elements reduce the oxidation rate at elevated temperatures. Sulfur dioxide, ammonium fluoroborate, as well as sulfur hexafluoride inhibit oxidation at elevated temperatures.

Finishing Requirements.   Magnesium parts are finished by the usual steps of cleaning, chemical treatment, anodizing, electroplating, and painting (122,127) (see METAL SURFACE TREATMENTS). Cleaning may be either mechanical or chemical. Sand blasting, grit blasting, and hydroblasting are used on sand and permanent-mold castings. Sand and grit blasting must be followed by acid pickling in order to remove embedded blast media if optimum corrosion performance is desired. Grinding, sanding, wire brushing, and barrel or bowl abrading are other common mechanical cleaning methods. When dust is generated, an approved dust collector is required because mixtures of fine magnesium dust and air can burn or explode. Magnesium surfaces are cleaned by acid pickling, and numerous pickling bath compositions are available. Grease and oil are removed with solvent cleaners by dipping, vapor degreasing, or with emulsion-type cleaners. Another cleaning method is soaking in hot alkaline cleaner. Yet another is making the magnesium part to be cleaned the cathode in an alkaline bath and applying direct current of $105 - 403 \, \text{A/m}^2$ at 6 V. Most magnesium alloys, unlike aluminum, are unaffected by strong alkaline cleaners, with the exception of alloy ZK60A, which is attacked in baths containing 2% or more sodium hydroxide.

Many chemical treatments are available. Some provide decorative finishes, others provide a limited degree of protection, or serve as a base for subsequent paint coats. The choice of a chemical treatment is influenced by cost, ease of application, metal loss during treatment, and durability. Traditional chemical treatments for magnesium are described in Military Specification MIL-M-3171 and ASTM D1732 (128,129). These treatments, however, are generally based on chromate solutions, which are under increasing environmental regulation. While chromate-based formulations remain the best choice overall for magnesium alloys, particularly in critical applications, they offer little advantage over selected phosphate formulations when employed with the new high purity alloys (130,131). Some effective anodic treatments are available for magnesium alloys (132): the conventional treatments are covered in Military Specification MIL-M-45202 (133), while some promising new anodizing treatments have been described (134–136). The popular chemical dip treatment, known as the ferric nitrate [10421-48-4] bright pickle, provides a thin decorative bright finish

which has good conductivity. It consists of a simple dip, after cleaning, in a solution containing chromic acid, ferric nitrate, and potassium fluoride. Parts are immersed for 15 s to 3 min, depending on the amount of tarnish on the magnesium surface (122,137).

Electroplating of magnesium is used successfully in several commercial applications. Caution should be used when using these coatings on components exposed to corrosive environments or electrolytes. The process requires a preliminary dip in an aqueous solution containing zinc sulfate monohydrate [7446-19-7] and tetrasodium pyrophosphate [7722-88-5] to form a thin coating of metallic zinc on the magnesium surface. This is followed by a copper strike (a preliminary, very thin coating) after which parts may be electroplated in standard plating baths. Any metal that can be electrodeposited can be applied successfully to magnesium alloys. An electroless nickel process permits the deposition of a coating of nickel directly on magnesium by immersion in a special electroless nickel bath. No current is required. This process can be used as a final electroplated coating or as a strike coating over which standard electroplates such as bright nickel, chromium [7440-47-3], tin, cadmium, and zinc can be applied (see ELECTROLESS PLATING) (122,137).

Painting, like chemical treating, may be used to apply a decorative finish or as a means of protection against corrosion (see PAINT). Proper preparation of the metal surface and careful choice of priming materials are important factors for the performance of the paint coating. Primers for magnesium are based on such alkali-resistant vehicles as poly(vinyl butyral) [9003-62-7], polyvinyl, epoxy, polyurethane [26778-67-6], acrylic resins, and baked phenolic resins. Zinc chromate or titanium dioxide [1317-70-0] are often chosen as commercial pigments for the corrosion-inhibiting action they provide. Finishes are selected for their compatibility, ease of application, and performance in service. Baking rather than air drying is preferred since it improves adhesion of the primer and durability of the finish coats. Powder coatings are employed effectively for a growing number of magnesium applications. The adhesion and alkali resistance of many powder epoxy coatings are so good that in some applications parts are simply mechanically cleaned and powder coated without a chemical pretreatment (138). Porcelain enamels can be applied at relatively low temperatures to magnesium alloys (see ENAMELS, PORCELAIN OR VITREOUS). Such enamels are available in attractive colors and textures. They provide excellent adhesion and resist chemical attack and abrasion. The popular AZ31B alloy lends itself readily to the process. Porcelain enamels are not suggested for alloys that have low melting point eutectics, such as AZ61A, AZ80A, and ZK60A.

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Table 1. **World Magnesite, Reserves and Reserve Base,** $\times$ **10^6 t of contained Mg**[a]

Country	Reserves	Reserve Base[b]
Australia	na	na
Austria	15	20
Brazil	45	65
China[c]	750	1000
Greece	30	30
India	30	45
Korea, North[c]	450	750
Russia[c]	650	730
Serbia and Montenegro	5	10
Slovakia[c]	20	30
Spain	10	30
Turkey	65	160
United States	10	15
other countries	420	480
Total[d]	*2500*	*3400*

[a] *Source*: U.S. Geological Survey.

[b] The reserve base includes demonstrated resources that are currently economic (reserves), marginally economic (marginal reserves), and some of those that are currently subeconomic (subeconomic resources).

[c] Estimated; na = not available.

[d] Data may not add to totals shown because of independent rounding.

Table 2. **U.S. Historical Salient Magnesium Statistics, 10^3 t**

Year	Primary production	New scrap	Old scrap	Imports	Exports	Government Stockpile releases	Stocks, year end	Apparent consumption	Net import reliance[a] as percent of apparent consumption
1955	55	5	4	2	8	—	27	47	NE
1960	36	5	4	−2	5	—	24	48	17
1965	74	9	3	3	17	2	14	71	NE
1970	102	8	3	3	32	13	12	88	NE
1975	109[b]	16	9	7	30	—	36	60	NE
1980	154[b]	21	16	3	51	—	45	117	NE
1985	136	18	24	8	37	—	39	123	NE
1990	139	23	31	27	52	—	26	145	NE
1995	142	35	30	35	38	—	12	171	NE
1996	133	41	30	47	41	—	17	162	NE
1997	125	50	31	65	41	—	13	185	16

[a] Defined as imports − exports + adjustments for government and industry stock changes (NE = net exporter).
[b] Derived from production reported by the International Magnesium Association and the Canadian Department of Natural Resources.

43

Table 3. **U.S. Imports for Consumption and Exports of Magnesium, t**[a]

	1990	1995	1996	1997	Principal Sources or Destinations, 1997
Imports for consumption					
metal (HTS 8104.11.0000)	16,100	6,480	17,300	19,700	Russia, 57%; Israel, 17%
waste and scrap (HTS 8104.20.0000)	4,080	11,500	3,340	3,990	Canada, 56%; Netherlands, 8%
alloys (magnesium content) (HTS 8104.19.0000+8104.30.0000)	5,340	15,900	24,600	41,000	Canada, 72%; China, 17%; Russia, 8%
sheet, tubing, ribbons, wire, powder, and other (magnesium content) (HTS 8104.90.0000)	1,200	867	1,280	510	Canada, 59%; Mexico, 31%
Total[b]	26,800	34,800	46,600	65,100	Canada, 51%; Russia, 22%; China, 14%; Israel, 5%
Exports					
metal (HTS 8104.11.0000)	41,900	21,500	17,000	17,100	Netherlands, 52%; Japan, 27%; Australia, 10%
waste and scrap (HTS 8104.20.0000)	967	3,540	8,500	11,200	Canada, 98%
alloys (gross weight) (HTS 8104.19.0000+8104.30.0000)	4,630	6,080	6,970	9,180	Canada, 59%; Netherlands, 28%
sheet, tubing, ribbons, wire, powder, and other (gross weight) (HTS 8104.90.0000)	4,350	7,200	7,970	2,960	Canada, 24%; Mexico, 18%; Netherlands, 15%
Total[a]	*51,800*	*38,300*	*40,500*	*40,500*	Canada, 44%; Netherlands, 30%; Japan, 13%

[a] *Source*: Bureau of the Census.
[b] Data are rounded to three significant digits; may not add to totals shown.

Table 4. **Properties of Magnesium**

Properties	Value	Refs.
atomic weight	24.31	
melting point, °C	650	
boiling point, °C	1103	
crystal structure	close-packed hexagonal, no phase transformations	
lattice parameters at 20°C, nm		
a_0	0.3203	
c_0	0.5199	
axial ratio	1.624	3
density, g/cm^3		
at 20°C	1.738	4
400°C	1.682	
650°C (s)	1.61	
650°C (l)	1.58	
volume contraction, %		
at solidification	3.97–4.2	(5, 6)
from 650 to 20°C as solid	1.8–2	(5, 6)
electrical resistivity, $\Omega \cdot m \times 10^{18}$		
at 0°C	4.10	6
20°C	4.45	
50°C	4.92	
300°C	9.02	
600°C	14.12	
heat of fusion, 20°C, kJ/kg[a]	386	6
heat of sublimation, 20°C, kJ/kg[a]	6109	
heat of vaporization, 20°C, kJ/kg[a]	5272	
specific heat, J/(kg · K)[a]		
at 20°C	1025	
100°C	1034	
surface tension, 20°C, mN/m(= dyn/cm)	563	5
viscosity at melting, mPa · s(= cP)	1.25	6

[a] To convert J to cal, divide by 4.184.

Table 5. **Primary Magnesium Metal Production Capacities 1997**[a]

Country and Company	Process and Raw Material[b]	Capacity, t/yr
Brazil (Brasmag) Rima Industrial	silicothermic (D)	10,600
Canada		
Timminco Metals, Ltd.	silicothermic (D)	9,000
Norsk Hydro A/S	electrolytic (M)	43,000
China[c]		
Baotou 202 Factory	unknown	3,500
Chaoyang Rich Magnesium Co.	unknown	4,000
Dencheng Ferroalloy Factory	unknown	1,000
Fushun Aluminum Plant	electrolytic (M)	5,000
Guangshui Magnesium Metal Plant	unknown	2,000
Guigang Magnesium Plant	unknown	1,000
Hengyang Magnesium Plant	silicothermic (D)	3,000
Hubei Province	unknown	600
Huinong Xian Smelter	unknown	1,000
Jinzhou Ferroalloy Plant	unknown	1,000
Mian Xian Magnesium Plant	unknown	500
Minhe Magnesium Plant	electrolytic (M)	5,000
Nanjing Ube Magnesium Co.	silicothermic (D)	4,000
Ningxia Metal Magnesium Works	unknown	1,400
Tongxin Magnesium Factory	unknown	1,700
Wenxi Yin Guang Magnesium Industry Group	unknown	9,600
Yellow River Magnesium Co.	unknown	1,500
Yinchuan Smelter	unknown	1,000
Ynidu Magnesium Product Co.	unknown	1,500
France		
Sofrem (Pechiney)	silicothermic (D)	17,000
India		
Southern Magnesium and Chemicals Ltd.	silicothermic (D)	900
Israel		
Dead Sea Works Ltd.	electrolytic (C)	27,500
Kazakstan		
Ust'-Kaminogorsk	electrolytic (C)	65,000
Norway		
Norsk Hydro A/S	electrolytic (B)	35,000
Russia		
Solikamsk Magnesium Works	electrolytic (C)	20,000
Avisma	electrolytic (C)	62,000
Serbia and Montenergo		
Magnohrom	silicothermic (D)	5,000
Ukraine		
Kalush	electrolytic (C)	24,000
Zaporzhye Titanium and Magnesium Co.	electrolytic (C)	30,000
United States		
Dow Chemical Co.[d]	electrolytic (S)	65,000
Magnesium Corp. of America (MagCorp)	electrolytic (B)	40,000
Northwest Alloys Inc. (Alcoa)	silicothermic (D)	40,000

[a] Source: U.S. Geological Survey.
[b] Raw-material source: (B)—brines, (C)—carnalite ($MgCl_2 \cdot KCl \cdot 6H_2O$), (D)—dolomite ($MgCO_3 \cdot CaCO_3$), (M)—magnesite ($MgCO_3$), (S)—seawater.
[c] Press reports indicate that there are more than 500 magnesium plants in China, with a total annual capacity of 200,000 t
[d] Plant closed in November 1998.

Table 6. **Primary Magnesium Metal Production Capacities: Proposed Facilities**[a]

Country and Company	Process and Raw Material[b]	Capacity, t/yr	Scheduled Completion Data
Australia			
Australian Magnesium Corp.	Electrolytic (M)	60,000	2002
Crest Magnesium NL	Electrolytic (M)	95,000	2002
Congo (Brazzaville)			
Magnesium Alloy Corp.	Electrolytic (C)	58,000	2005
Canada			
Gossan Resources	Silicothermic (D)	50,000	No date
Magnola Metallurgy Inc.	Electrolytic (asbestos tailings)	58,000	2001
Netherlands			
Antheus Magnesium Development Programme Delfzijl	Electrolytic (B)	40,000–50,000	2005

[a] *Source*: U.S. Geological Survey.
[b] Raw-material source: (B)—brines, (C)—carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$), (D)—dolomite ($MgCO_3 \cdot CaCO_3$), (M)—magnesite ($MgCO_3$), (S)—seawater.

Table 7. **1999 U.S. Tariff Rates**[a]

HTS No.	Description	Normal Trade Relations	Special[b]
8104.11.00	Unwrought magnesium, containing ≥99.8 wt% magnesium	8% ad valorem	Free (A*, CA, E, IL, J, MX)
8104.19.00	Unwrought magnesium, other	6.5% ad valorem	Free (A+, CA, E, IL, J, MX)
8104.20.00	Waste and scrap	Free	
8104.30.00	Raspings, turnings and granules, and powders	4.4% ad valorem	Free (A+, CA, E, IL, J, MX)
8104.90.00	Other magnesium metal	14.8 ¢/kg on magnesium content +3.5% ad valorem	Free (A, B, CA, E, IL, J, MX)

[a] *Source*: U.S. International Trade Commission.
[b] *Key*: A, A* or A+—Generalized System of Preferences; B—Automotive Products Trade Act; CA and MX—North American Free Trade Agreement; E or E*—Caribbean Basin Economic Recovery Act; IL—United States-Israel Free Trade Area; and J or J*—Andean Trade Preference Act.

Table 8. **Primary Magnesium Shipments, by End Use, t**[a]

Use	1983					1990					1997				
	Area 1: U.S. and Canada	Area 2: Latin America	Area 3: Western Europe	Area 4: Africa and Middle East	Area 5: Asia and Oceania	Area 1: USA and Canada	Area 2: Latin America	Area 3: Western Europe	Area 4: Africa and Middle East	Area 5: Asia and Oceania	Area 1: USA and Canada	Area 2: Latin America	Area 3: Western Europe	Area 4: Africa and Middle East	Area 5: Asia and Oceania
aluminum alloying	52,700	2,200	31,900	2,400	21,600	60,000	1,000	37,800	3,800	28,000	72,750	3,100	35,000	4,100	31,200
nodular iron	4,000	100	4,000		800	5,600	800	4,900	100	3,000	6,500	400	2,700		300
desulfurization	10,300		2,300		800	19,900	400	7,600		100	31,100	400	15,300	200	950
metal reduction	7,500		1,200		500	6,600		1,000		1,200	3,800		1,100		100
electrochemical	6,100		700		800	7,400	700	600	100	800	5,400	400	1,500	600	1,000
chemical	4,600	500	1,500		1,600	1,800		3,300		2,000	1,300		2,700		2,700
die casting	4,800	6,800	14,000		1,400	15,800	8,700	10,100		1,700	68,600	3,200	19,800	200	3,500
gravity casting	600		1,200		200	800		2,400		100	700		1,400		
wrought products	6,500		400		200	6,000		500		200	3,300		100		100
other[b]	1,500		400		7,400	3,400		500		3,300	42,500	200	800		1,100
Total	98,600	9,600	57,600	2,400	35,300	127,300	11,600	68,700	4,000	40,400	235,950	7,700	80,400	5,100	40,950

[a] Source: International Magnesium Association.
[b] Includes shipments to secondary producers and shipments to China and the former Soviet Union.

Table 9. **Use of Magnesium Die Castings in North America–Produced Vehicles**[a]

Model Year	Total Weight, lb	Total Vehicle Weight, %
1977	1	0.03
1978	1	0.03
1979	1	0.03
1980	3	0.10
1985	2.5	0.08
1987	2.5	0.08
1988	4	0.13
1990	3	0.10
1991	3	0.10
1992	3.5	0.11
1993	4.5	0.14
1994	5	0.16
1995	5	0.16
1996	5.5	0.17
1997	6	0.18
1998	6.5	0.20
1999	7.0	0.21

[a] *Source*: American Metal Market.

Table 10. **Chemical Compositions and Physical Properties of Magnesium Cast and Wrought Alloys**[a]

Alloy		Nominal composition, %[b]						Physical properties			
ASTM	UNS	Temper	Al	Mn	RE[c]	Zn	Other	Density at 20°C, g/cm^3	Melting point,[d] °C	W/(m · K)[e]	μΩ · cm[f]
Sand and permanent-mold castings											
AM100A	M10100	-T6	10.0	0.2				1.81	465	58.3	12.4
AZ63A	M11630	-F	6.0	0.2		3.0		1.82	455	59.2	12.2
		-T4								52.2	14.0
		-T5								65.1	11.0
		-T6								61.0	11.8
AZ81A	M11810	-T4	7.6	0.2		0.7		1.80	510	50.3	15.0
AZ91C,E	M11914,-18	-F	8.7	0.2		0.7		1.80	470	53.6	13.6
		-T4								44.3	16.2
		-T6								56.2	12.9
AZ92A	M11920	-F	9.0	0.2		2.0		1.83	445	52.2	14.0
		-T4								44.3	16.8
		-T5								58.3	12.4
		-T6								58.3	12.4
EZ33A	M12330	-T5			3.0	2.7	0.7 Zr	1.80	545	99.0	7.0
QE22A	M18220	-T6			2.2		2.5 Ag	1.82	550	102.2	6.8
WE43A	M18430	-T6			3.0		4.0 Y	1.84	543	51	14.8
WE54A	M18410	-T6			3.5		5.2 Y	1.85	549	52	17.3
ZE41A	M16410	-T5			1.2	4.2		1.84	510	123.1	5.6
ZE63A	M16630	-T6			2.6	5.7	0.7 Zr	1.87	515	123.1	5.6
ZK51A	M16510	-T5				4.6	0.7 Zr	1.81	550	108.3	6.4
ZK61A	M16610	-T6				6.0	0.8 Zr	1.83	520		
Die castings											
AM50A	M10500	-F	5.0	0.4				1.78	543	62	12.5
AE42X1		-F	4.0	0.3	2.0			1.79	565	68	
AM60A,B	M10600,-02	-F	6.0	0.2				1.79	541	62	12.5
AS41A,B	M10410,-12	-F	4.2	0.3			1.0 Si	1.77	566	68	
AZ91B,D	M11912,-16	-F	9.0	0.2		0.6		1.80	470	51.2	14.1

Table 10 (*Continued*)

| Alloy | | Nominal composition, %[b] | | | | | | Physical properties | | | |
ASTM	UNS	Temper	Al	Mn	RE[c]	Zn	Other	Density at 20°C, g/cm^3	Melting point,[d] °C	W/(m · K)[e]	μΩ · cm[f]
					Sheet and plate						
AZ31B	M11311	-F	3.0			1.0		1.77	565	76.9	9.2
AZ31B,C	M11311,-12	-H24	3.0	0.3		1.0		1.77	565	76.9	9.2
		-H26	3.0	0.3		1.0		1.77	565	76.9	9.2
		-O	3.0	0.3		1.0		1.77	565	76.9	9.2
AZ61A	M11610	-F	6.5	0.2		1.0		1.80	510	57.9	12.5
		-O	6.5	0.2		1.0		1.80	510		
				Extruded bars, rods, solid and hollow shapes, and tubes							
AZ80A	M11800	-F	8.5			0.5		1.80	490	47.3	15.6
		-T5	8.5			0.5		1.80	490	59.2	12.2
ZK60A	M16600	-F				5.7	0.55 Zr	1.83	520	117.6	6.0
		-T5				5.7	0.55 Zr	1.83	520	121.0	5.7

[a] Refs. 85 and 86.
[b] Balance Mg.
[c] The solidus temperature (lower limit of alloy melting range).
[d] Rare earths.
[e] Thermal conductivity, at 20°C.
[f] Electrical resistivity at 20°C.

52

Table 11. **Mechanical Properties of Magnesium Casting Alloys**[a]

Alloy			Tensile strength, MPa[b]	Tensile yield strength, MPa[b]	Elongation in 51 mm, %
ASTM	UNS	Temper			
Sand and permanent-mold castings					
AM100A	M10100	-F	152	83	2
		-T4	276	90	10
		-T5	152	110	2
		-T61	276	152	1
AZ63A	M11630	-F	200	97	6
		-T4	276	97	12
		-T5	200	103	4
		-T6	276	131	5
AZ81A	M11810	-T4	276	83	15
AZ91C,E	M11914,-18	-F	165	97	2.5
		-T4	276	90	15
		-T6	276	131	5
AZ92A	M11920	-F	172	97	2
		-T4	276	97	10
		-T5	172	117	1
		-T6	276	152	3
EZ33A	M12330	-T5	159	110	3
QE22A	M18220	-T6	276	207	4
WE43A	M18430	-T6	252	190	7
WE54A	M18410	-T6	275	171	4
ZE41A	M16410	-T5	207	138	3.5
ZE63A	M16630	-T6	276	186	5
ZK51A	M16510	-T5	276	165	8
ZK61A	M16610	-T6	276	179	5
Die castings					
AM60A,B	M10600,-02	-F	220	130	8
AS41A,B	M10410,-12	-F	210	140	6
AZ91B,D	M11912,-16	-F	230	158	3

Table 11 (*Continued*)

Compressive yield strength, MPa[b]	Bearing strength, MPa[b]	Bearing yield strength, MPa[b]	Shear strength, MPa[b]	Impact strength Charpy, J[c]	Hardness[d]	
					Brinell[e]	Rockwell E
Sand and permanent-mold castings						
83			124	0.8	53	64
90	476	310	140	2.7	52	62
110					58	70
131	560	470	145	0.9	69	80
97	415	275	125	1.4	50	59
97	410	270	124	3.4	55	66
97	455	275	130	3.5	55	66
131	475	355	138	1.5	73	83
83	400	241	165	6.1	55	66
97	415	275		0.8	60	66
90	415	255	150	4.1	55	62
131	460	360	165	1.4	70	77
97	345	315	125	0.7	65	76
97	470	315	140	2.7	63	75
117	345	317	140		69	80
152	540	460	180	1.1	81	88
110	310	275	135		50	59
207					78	
187			162		85	
171			150		85	
138	485	355	150	1.4	62	72
165	485	350	150		65	77
					70	
Die castings						
160			140	3	63	75

[a] Properties determined on separately cast test bars using 0.2% offset of method; Ref. 85.
[b] To convert MPa to psi, multiply by 145.
[c] To convert J to ft·lbf, divide by 1.356; Ref. 86.
[d] See HARDNESS.
[e] 500-kg load, 10-mm ball.

Table 12. **Mechanical Properties of Magnesium Extrusions**[a]

Alloy					Tensile strength, MPa[b]	Tensile yield strength, MPa[b]
ASTM	UNS	Temper	Least dimension, mm	Area, cm^2		
Bars, rods, and shapes						
AZ31B	M11311	-F	under 6.3		260	195
			6.3–38.1		260	200
			38.1–63.5		260	195
			63.5–127		260	195
AZ61A	M11610	-F	under 6.3		315	230
			6.3–63.5		310	230
			63.5–127		310	215
AZ80A	M11800	-F	under 6.3		340	250
			6.3–38.1		340	250
			38.1–63.5		340	240
			63.5–127		330	250
AZ80A	M11800	-T5	under 6.3		380	260
			6.3–38.1		380	275
			38.1–63.5		365	270
			63.5–127		345	260
ZK60A	M16600	-F		under 12.9	340	260
				12.9–19.3	340	255
				19.3–32.3	340	248
				32.3–259	330	255
ZK60A	M16600	-T5		under 12.9	365	305
				12.0–19.3	360	295
				19.3–32.3	350	290
Hollow and semihollow shapes						
AZ31B	M11311	-F			250	165
AZ61A	M11610	-F			285	165
ZK60A	M16600	-F			315	235
		-T5			345	275
Tube			wall thickness,[d] mm	OD,[e] cm[f]		
AZ31B	M11311	-F	0.7–6.3	15.2	250	165
			6.3–18.9	38.7	250	165
AZ61A	M11610	-F	0.7–18.9	38.7	285	165
ZK60A	M16600	-F	0.7–6.3	19.3	325	240
		-T5	0.7–6.3	19.3	345	275
		-T5	2.4–48	19.3–54.8	340	270

Table 12 (*Continued*)

Elongation, in 5.08 mm, %	Compressive yield strength, MPa[b]	Shear strength, MPa[b]	Bearing strength, MPa[b]	Bearing yield strength, MPa[b]	Brinell hardness[c]
Bars, rods, and shapes					
14	103	130	385	235	
15	95	130	385	230	49
14	95	130	385	230	
15	95	130	385	230	
17		160	450	260	
16	130	150	470	275	60
15	145	150	470	290	
12		150	470	330	60
11		150	470	330	60
11		150	470	330	60
9		150	470	330	60
8	235	165	415	395	82
7	240	165	415	400	82
6	220	165	455	370	82
6	215	165	470	365	82
14	230	165	525	385	75
14	195	165	525	345	75
14	185	165	525	340	75
9	160	165	515	305	75
11	250	180	545	405	82
12	215	180	540	365	82
14	205	170	530	360	82
Hollow and semihollow shapes					
16	85				46
14	110				50
12	170				75
11	200				82
Tube					
16	85				46
12	85				
14	110				50
13	170				75
11	205				82
12	180				

[a] Refs. 85 and 88.
[b] To convert MPa to psi, multiply by 145.
[c] Values are inclusive.
[d] OD = outer diameter.
[e] Values are maximum unless range is given.
[f] 500-kg load, 10-mm ball.

Table 13. **Mechanical Properties of Magnesium Sheet and Plate**[a]

Alloy				Tensile strength, MPa[b]	Tensile yield strength, MPa[b]	Elongation, in 5.08 mm, %	Compressive yield strength, MPa[b]	Shear strength, MPa[b]	Bearing strength, MPa[b]	Bearing yield strength, hardness[c]
ASTM	UNS	Temper	Thickness, mm							
Sheet and plate										
AZ31B	M11311	-H24	0.4–6.3	290	220	15	180	200	530	47
			6.3–9.5	275	200	17	160	195	495	45
			9.5–12.7	270	185	19	130	185	485	40
			12.7–25.4	260	165	17	110	180	470	37
			25.4–50.8	255	160	14	95	180	455	35
			50.8–76.2	255	145	16	85	180	455	33
Sheet and plate										
AZ31B	M11311	-O	0.4–1.5	255	150	21	110	180	455	37
			1.5–6.3	255	150	21	110	180	455	37
			6.3–12.7	250	150	21	90	170	448	34
			12.7–50.8	250	150	17	85	170	448	33
			50.8–76.2	250	145	17	75	170	448	32
Plate										
AZ31B	M11311	-H26	6.3–9.5	275	205	16	165	195	495	46
			9.5–11.1	275	195	13	150	195	495	44
			11.1–12.7	275	195	13	150	195	495	44
			12.7–18.9	275	195	10	130	195	495	40
			18.9–25.4	270	180	10	125	195	485	39
			25.4–38.1	260	170	10	110	185	470	37
			38.1–50.8	260	170	10	100	180	470	36

[a] Refs. 85 and 88.
[b] To convert MPa to psi, multiply by 145.
[c] 500-kg load, 10-mm ball.

Table 14. **Behavior of Magnesium in Contact with Chemicals**[a]

Chemical	Concentration, %[b]	Service test warranted[c]
acids, most	any	no
acid salts	any	no
alcohols, except methyl	100	yes
ammonia, gas or liquid	100	yes
arsenates, most	any	yes
benzene [71-43-2]	100	yes
brake fluids, most	100	yes
bromides, most	any	no
butter	100	no
camphor [76-22-2]	100	yes
carbon tetrachloride [56-23-5]	100	yes
carbonated water	any	no
cement	100	yes
chlorides, most	any	no
chromates, most	any	yes
chromic acid	any	yes
cyanides, most	any	yes
dry-cleaning fluids	100	yes
ethers	100	yes
fats, cooking, acid-free	100	yes
fluorides, most	any	yes
fruit juices and acids	any	no
gasoline	100	yes, if inhibited
gelatin	any	yes
glycerol, [56-81-5]	100	yes
hydrocarbons	100	yes
hydrofluoric acid	5–60	yes
hydrogen peroxide [7722-84-1]	any	no
iodides	any	no
kerosene	100	yes
lard	100	yes
lime	100	yes
methyl chloride [74-87-3]	100	yes
milk, fresh and sour	100	no
naphtha [8030-30-6]	100	yes
nitrates, all	any	no
oils, acid- and chloride-free	any	yes
oxygen	100	yes
permanganates, most	any	yes
phenol	100	yes
phosphates, most	any	yes

Chemical	Concentration, %[b]	Service test warranted[c]
refrigerants, fluorinated	100	yes
rubber and rubber cements	100	yes
seawater	100	no
steam	100	no
sugar solutions, acid-free	any	yes
sulfur	100	yes
toluene [108-88-3]	100	yes
turpentine [8006-64-2]	100	yes
urea [57-13-6]	100	yes
vinegar	any	no
waxes, acid-free	100	yes

[a] Ref. 122.

[b] 100% refers to pure substance in dry or liquid form; concentrations less than 100% refer to water solutions of the chemical.

[c] Resistance is indicated by yes, ie, laboratory tests have shown enough promise to warrant test under actual service conditions.
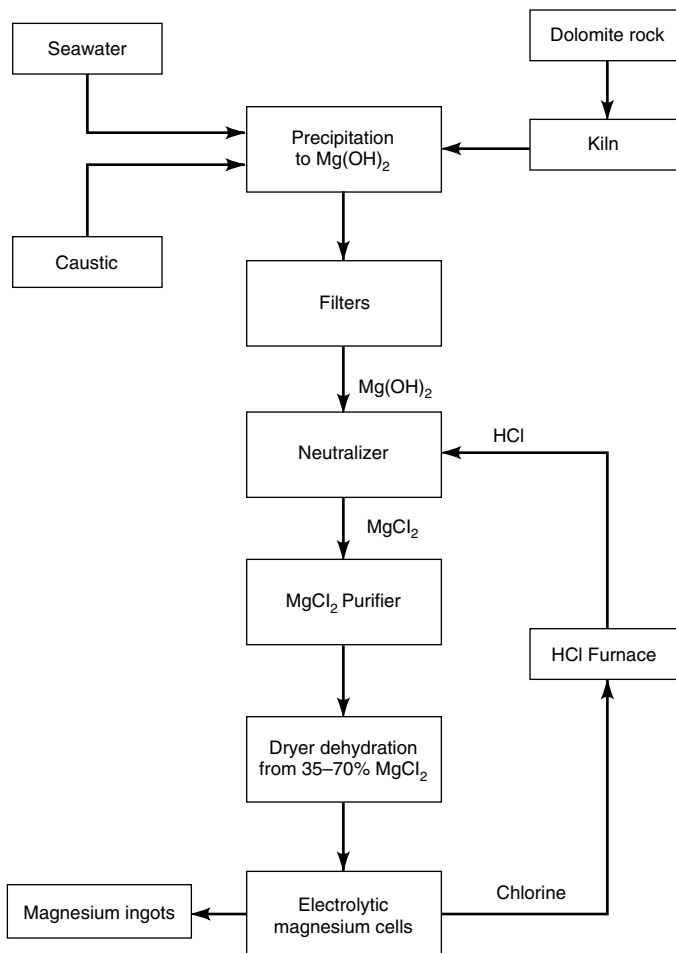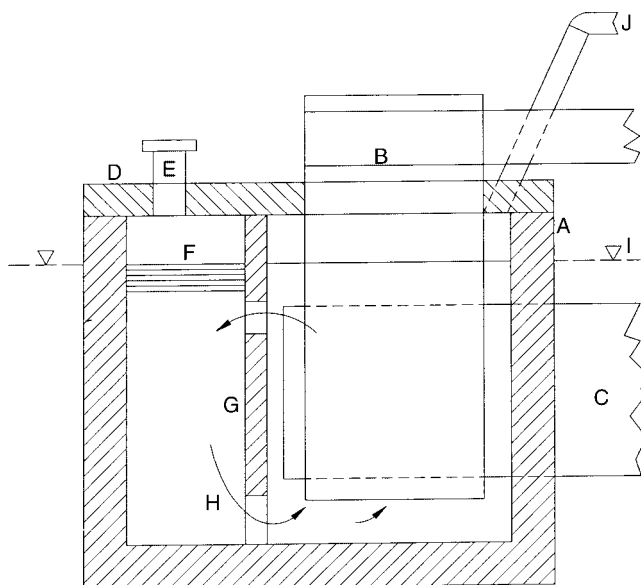
Fig. 1. The Dow seawater process.
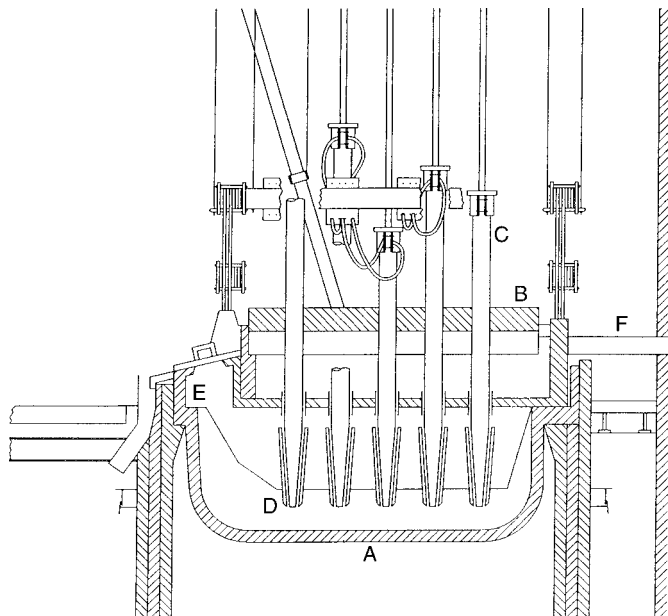
Fig. 2. The Dow magnesium cell. The steel container, A, is equipped with a ceramic cover, B, through which graphite anodes, C, pass. The magnesium is deposited on the cathode, D, and is diverted as it rises into the collection sump, E. The chlorine is withdrawn through a vent, F.
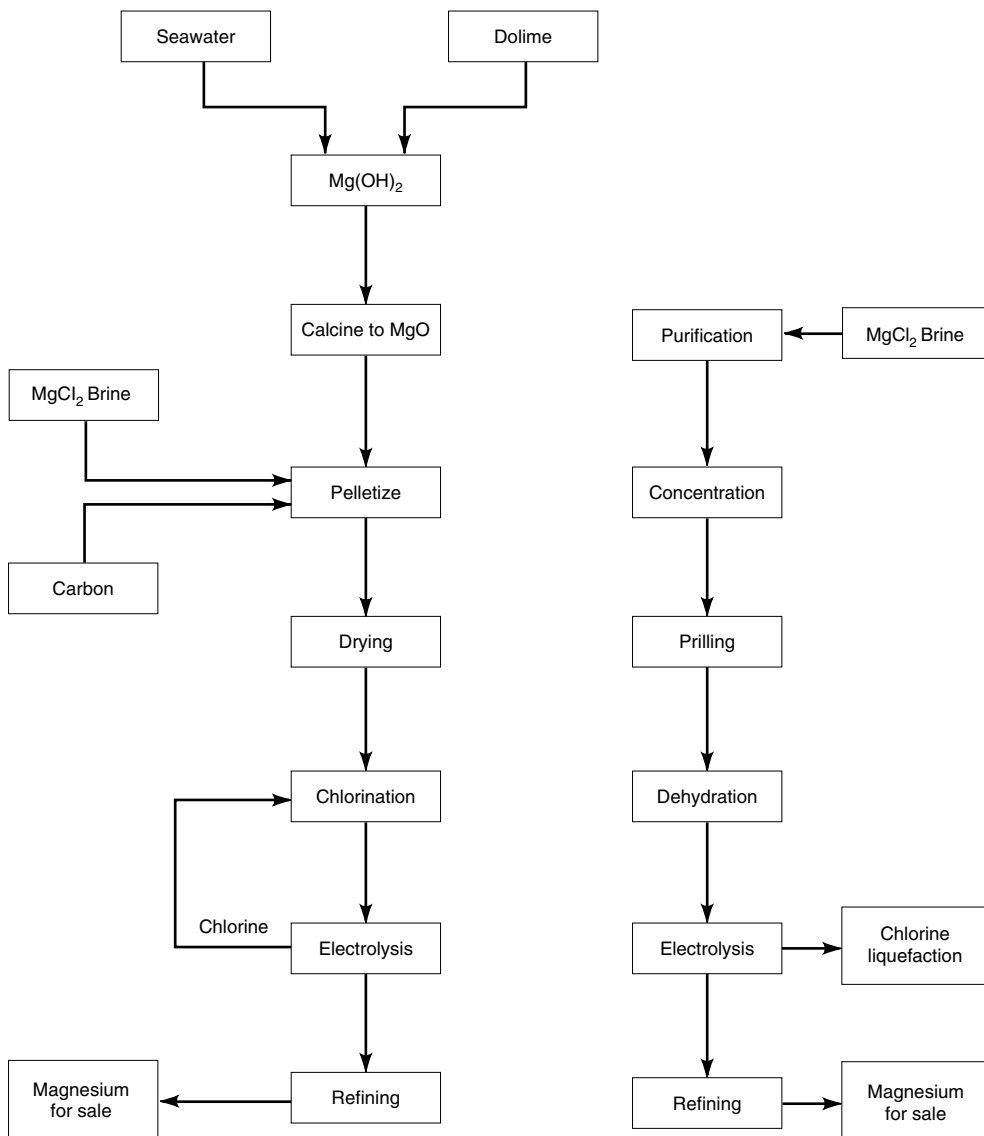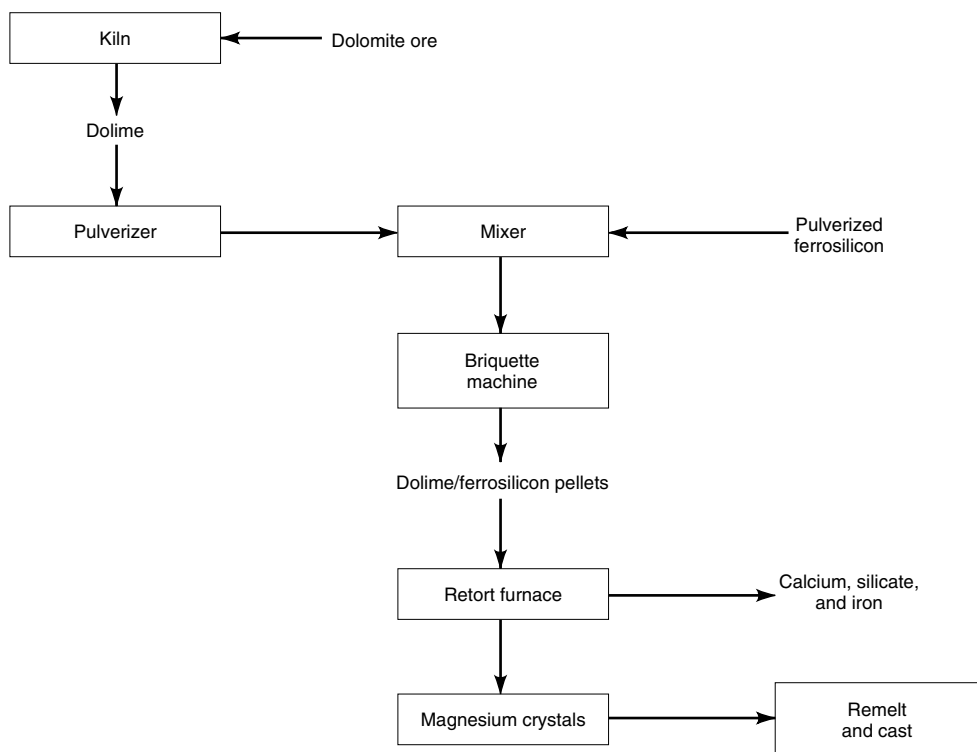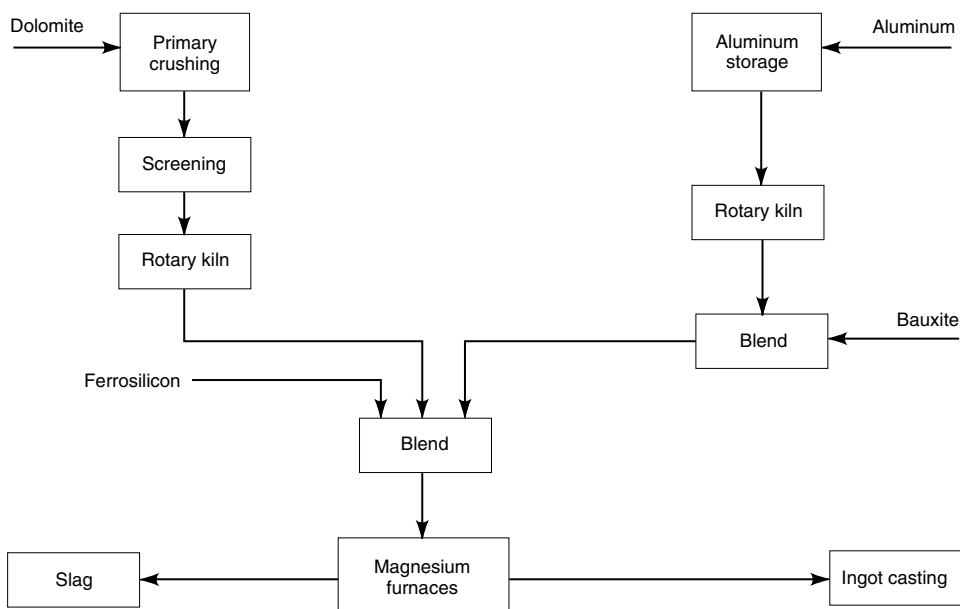
Fig. 3. The Norsk Hydro process.

Fig. 4. The Norsk Hydro cell. Refractory material, A; graphic anode, B; steel cathode, C; refractory cover, D; metal outlet, E; metal, F; partition wall, G; electrolyte flow, H; electrolyte level, I; and chlorine outlet, J.
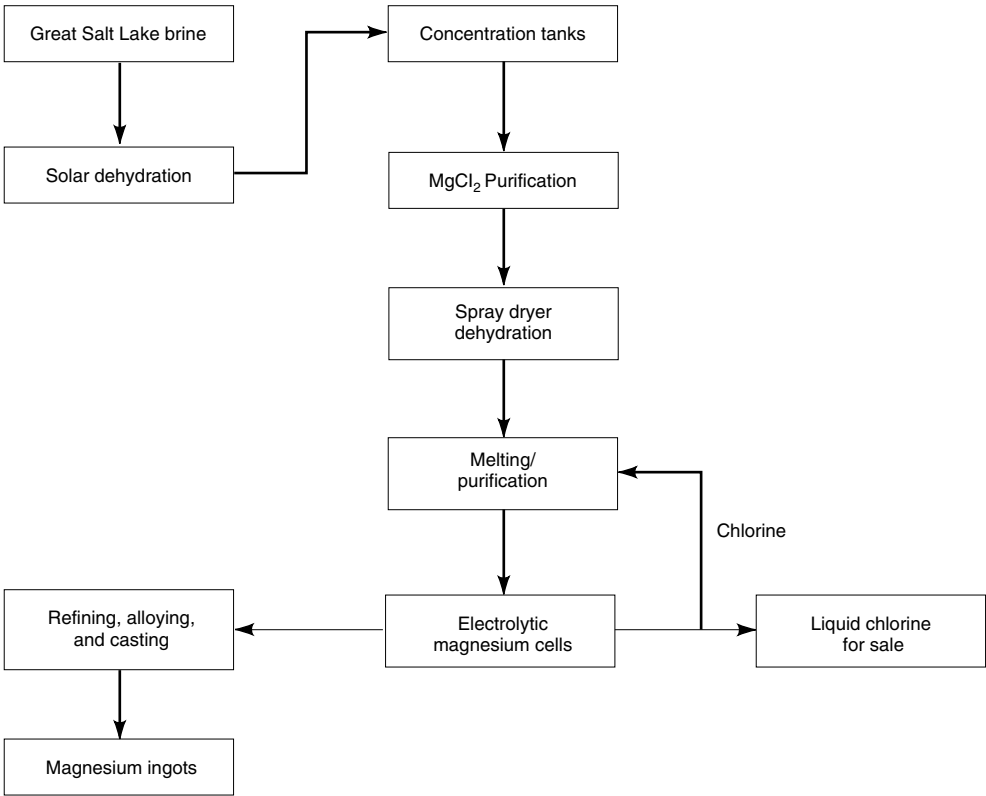
Fig. 5.   The Magcorp brine process.

Fig. 6.   The Pidgeon ferrosilicon magnesium process.

Fig. 7.   The Magnetherm process.
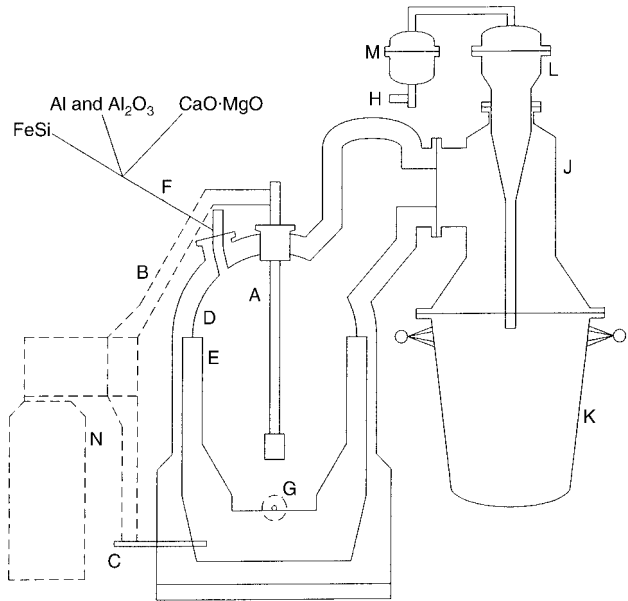
Fig. 8. Magnetherm reactor: central electrode, A; secondary circuit, B; grounding electrode, C; refractory lining, D; carbon lining, E; primary material feed, F; slag taphole to FeSi recovery, G; vacuum line, H; water spray ring, I; condenser, J; crucible, K; trap, L; filter, M; and transformer, N.
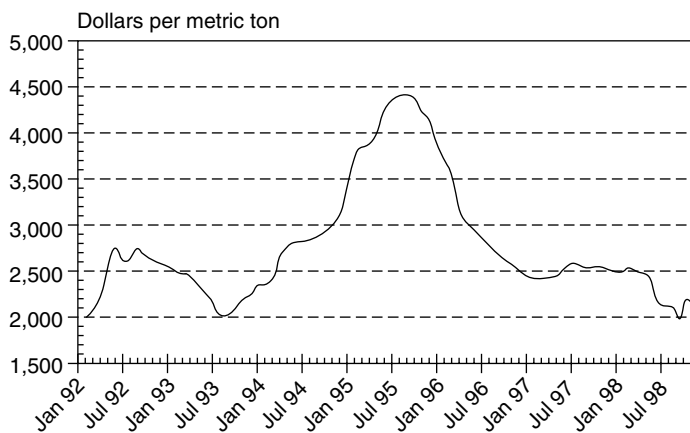
Fig. 9. Primary magnesium prices for 1992−1998.
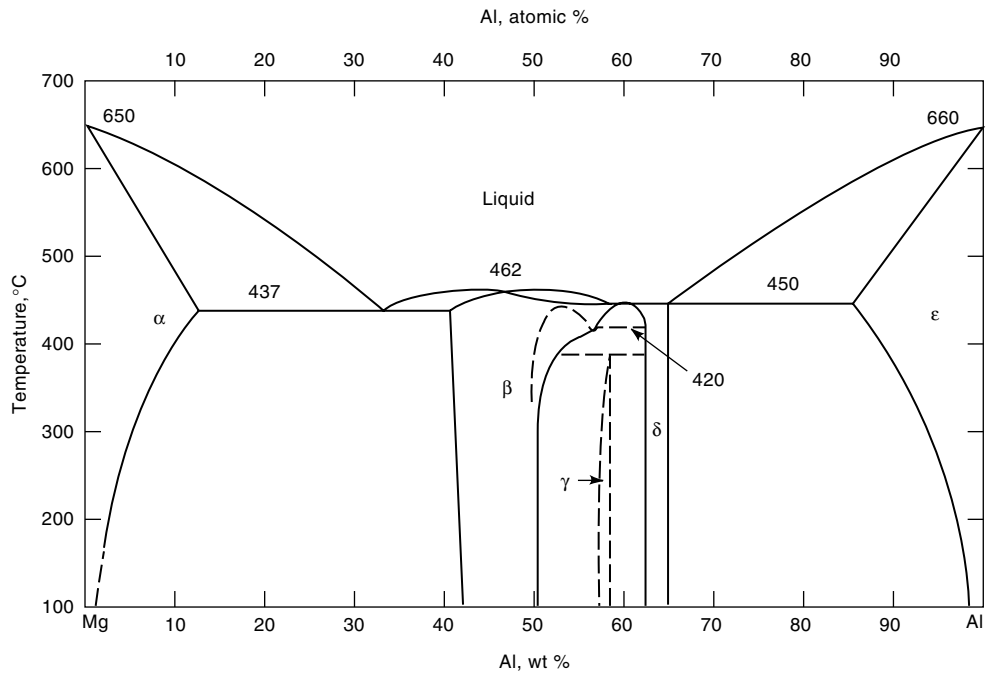
Fig. 10.   Aluminum−magnesium phase diagram (89).

Zn, atomic %
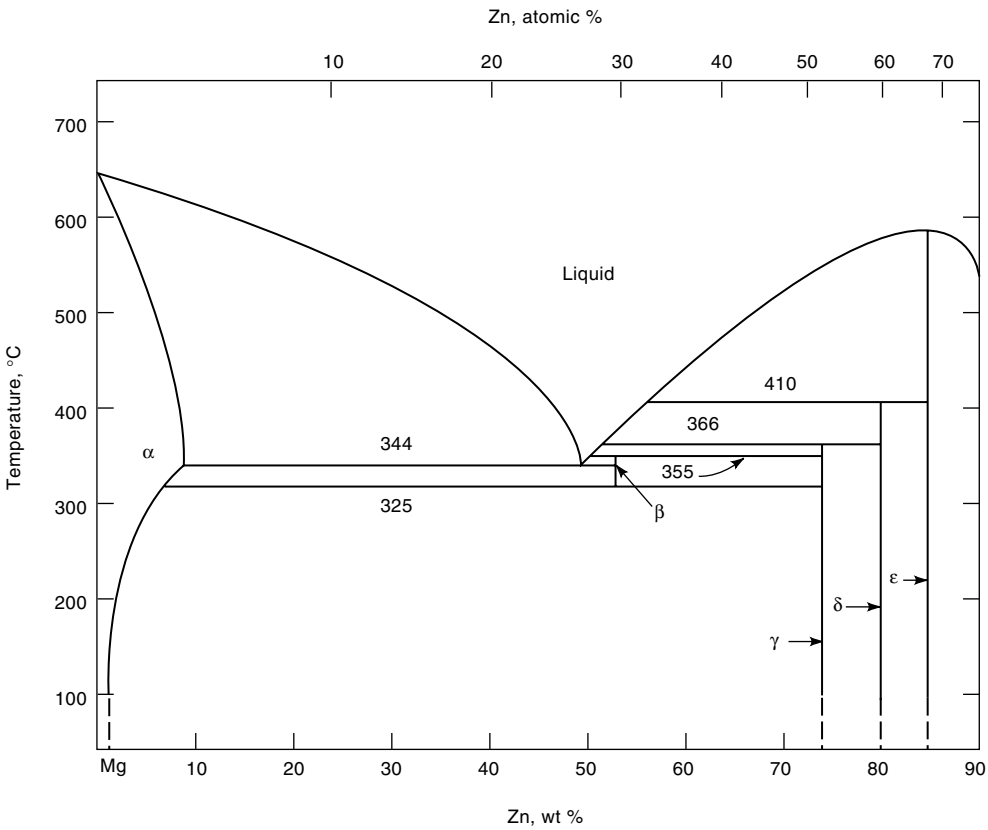
Fig. 11.   Magnesium–zinc phase diagram (89).
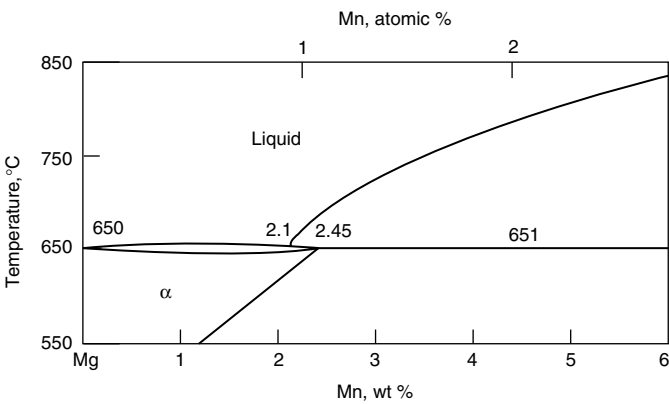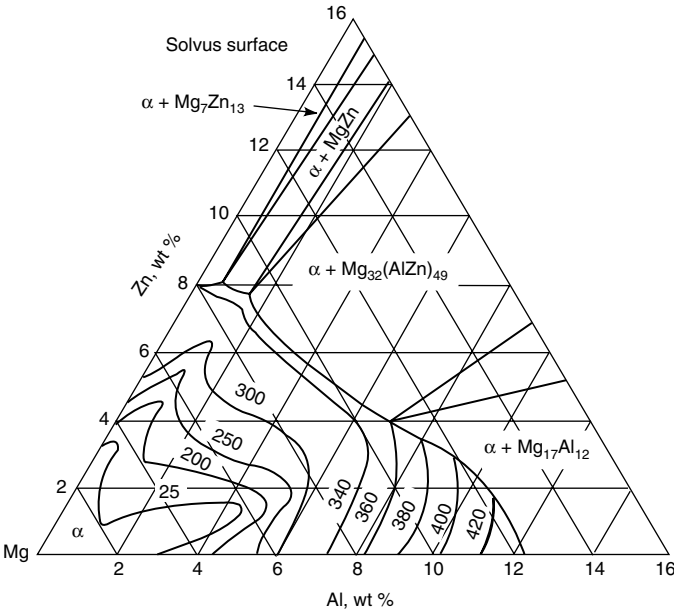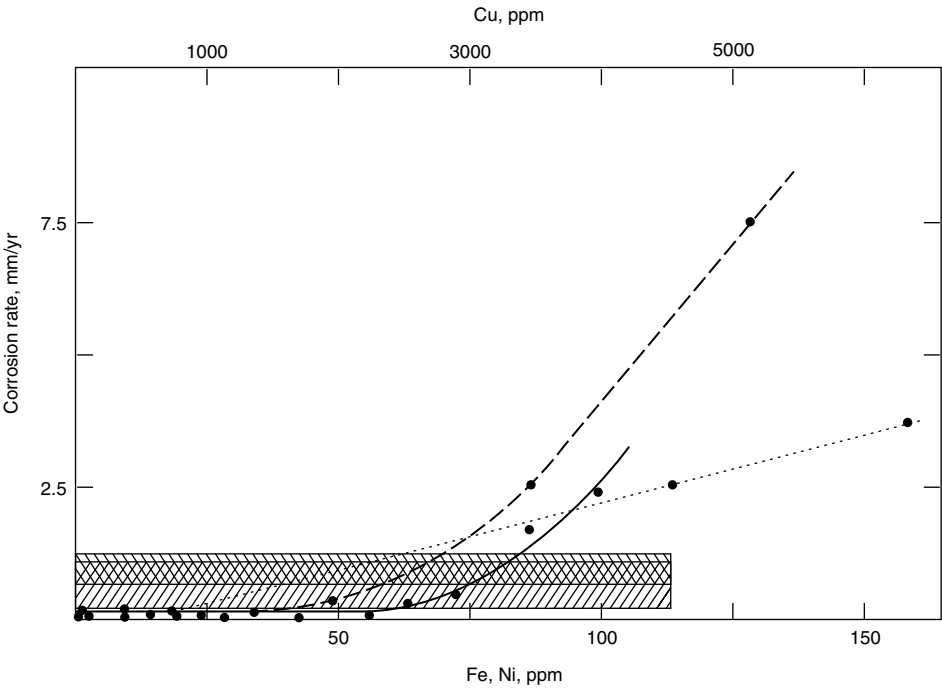
Mn, atomic %

Fig. 12.   Magnesium–manganese phase diagram (89).

Fig. 13. Aluminum−magnesium−zinc phase diagram (89).

Fig. 14. Effects of iron (—), nickel (- - -), and copper (. . .) contaminant levels on the salt-water corrosion performance of magnesium AZ91 alloy containing 0.23% Mn. Corrosion of carbon steel (▨) and 380 die cast Al (▨) is also shown (094).