MAGNESIUM COMPOUNDS

1. Introduction

Magnesium is the eighth most abundant element in the earth's crust and the third most abundant element in seawater. More than sixty magnesium-containing minerals are known. The most important can be divided into three classes according to their commercial importance: the carbonates magnesite [1317-61-9], $MgCO_3$, and dolomite [17069-72-6], $CaCO_3 \cdot MgCO_3$; the salts and double salts found in oceanic deposits, including carnallite [1318-27-0], $KCl \cdot MgCl_2 \cdot 6H_2O$; kieserite, $MgSO_4 \cdot H_2O$; langbeinite, $K_2SO_4 \cdot 2MgSO_4$; and epsomite, $MgSO_4 \cdot 7H_2O$; and the silicates such as olivine [1317-71-1], $(Mg,Fe)_2SiO_4$; serpentine [12168-92-2] (chrysotile), $Mg_6(OH)_6Si_4O_{11} \cdot H_2O$; antigorite [12135-86-3], $Mg_6(OH)_8Si_4O_{10}$; talc [14807-96-6], $Mg_3(OH)_2Si_4O_{10}$; and sepiolite [15501-74-3], $Mg_3Si_4O_{11} \cdot 4H_2O$. Magnesium also occurs as the hydroxide brucite [1317-43-7], $Mg(OH)_2$, and in combination with aluminum as spinel [1302-67-6], $MgAl_2O_4$. There are hundreds of magnesium compounds known, varying from chlorophyll [1406-65-1] to asbestos [1332-21-4]. Only those compounds produced commercially are discussed herein.

2. Magnesium Acetate

2.1. Properties. Anhydrous magnesium acetate [142-72-3], a white, crystalline, deliquescent solid, occurs in two forms: α-$Mg(C_2H_3O_2)_2$, formed by the reaction of MgO and concentrated acetic acid (13–33%) in boiling ethyl acetate, and β-$Mg(C_2H_3O_2)_2$ which is formed using 5–6% acetic acid. Of commercial interest is magnesium acetate tetrahydrate [16674-78-5], $Mg(C_2H_3O_2)_2 \cdot 4H_2O$, a colorless to white crystalline solid obtained from aqueous solution. The tetrahydrate is the only stable phase below 68°C, the transition point of the anhydrous salt. A monohydrate [60582-92-5], $Mg(C_2H_3O_2)_2 \cdot H_2O$, can be prepared from the reaction of MgO and acetic acid in slightly hydrated isobutyl alcohol. Physical properties of magnesium acetate and its hydrates are given in Table 1.

The solubility of magnesium acetate is shown in Figure 1. Aqueous solutions of magnesium acetate are characterized by very high viscosities that are generally attributed to acetate association. As the concentration of anhydrous magnesium acetate rises from 20.1 to 43.6%, the relative viscosity increases 45-fold at 25°C (4,5). Anhydrous magnesium acetate may be prepared by heating the tetrahydrate to 134°C. The anhydrous salt melts at about 320°C, though decomposition starts at about 300°C. Upon decomposition, the residue is magnesium oxide and the volatile products include acetone, acetic acid, carbon dioxide, and steam.

2.2. Handling and Safety. Magnesium acetate is hygroscopic and should be stored in a cool, dry place. Personal protective equipment to be used when handling magnesium acetate includes chemical safety goggles, chemical resistant gloves, and a NIOSH/MSHA approved respirator. To keep exposure to respirable dust to a minimum, mechanical exhaust is required. Although magnesium acetate is a relatively low hazard chemical, intravenous poisoning can occur if this material is not handled properly. Magnesium acetate is incompatible with strong oxidizers. When heated to decomposition, acrid smoke and irritating fumes may evolve (6,7).

2.3. Uses. The largest use for magnesium acetate is in the production of rayon fiber, which is used for cigarette filter tow (see FIBERS, REGENERATED CELLULOSICS). During the acetylation of cellulose (qv), sulfuric acid is present as a catalyst and some cellulose is sulfated. In a subsequent hydrolysis step, the sulfate cellulose hydrolyzes first. Sulfuric acid is evolved and neutralized by the magnesium acetate, presumably through the formation of magnesium sulfate (see CELLULOSE ESTERS).

Magnesium acetate also has uses as a dye fixative in textile printing, as a deodorant, disinfectant, an antiseptic in medicine, and as a reagent chemical (see DISINFECTANTS AND ANTISEPTICS; TEXTILES) (8).

3. Magnesium Alkyls

Magnesium alkyl compounds RMg, RMgR, or RMgR′, along with other compounds are useful as polymerization catalysts (9). These compounds should not be confused with alkyl magnesium halides or the much discussed ether solvated Grignard reagents. Magnesium alkyls may, however, be prepared from Grignard reagents (see GRIGNARD REACTIONS) (10).

3.1. Properties. Magnesium alkyls are white, crystalline, pyrophoric solids that react vigorously with water, alcohols, and other compounds containing an active hydrogen (11). Magnesium alkyls, soluble in ether solutions but insoluble in benzene and some alkane solutions, decompose at 170–200°C (12). The molecular weights of unsolvated compounds fall in the range of 100–200, but the molecular weights in solution, as determined by cryoscopic methods, are in the range of 1,000–10,000. The low solubility and high molecular weights in solution are attributed to extensive association resulting from the electron-deficiency of the magnesium (13).

3.2. Reactions. The most noted magnesium alkyl reactions involve the solvated Grignard reagents. The more common reactions involving unsolvated magnesium alkyl are as follows (14,15).

$$\textit{Oxidation}\quad \mathrm{RMg} + \mathrm{O_2} \rightleftharpoons \mathrm{RMg}\cdot\mathrm{O_2} \tag{1}$$

$$\textit{Hydrolysis}\quad \mathrm{R{=\!=}RMg} + 2\ \mathrm{H_2O} \longrightarrow \mathrm{Mg(OH)_2}+\text{alkane} \tag{2}$$

$$\textit{Peroxide addition}\quad \mathrm{RMg} + \mathrm{ROOMg} \longrightarrow 2\ \mathrm{ROMg} \tag{3}$$

$$\textit{Polymerformation}\quad 2\ \mathrm{RMgR} + \text{heat} \longrightarrow \mathrm{RMgRC{=\!=}CH_2Mg} + \text{alkane} \tag{4}$$

$$\textit{Alkane formation}\quad \mathrm{RMgR} \longrightarrow \text{alkane} + \mathrm{RC{=\!=}CMg} \tag{5}$$

$$\textit{Magnesium hydride formation}\quad \mathrm{RMgR} + \text{heat} \longrightarrow \mathrm{MgH_2} + \text{alkene} \tag{6}$$

3.3. Preparations. Magnesium alkyls may be prepared from a Grignard reagent according to the following disproportionation reaction:

$$2\ \mathrm{RMgX} + \text{dioxane} \longrightarrow \mathrm{R_2Mg} + \mathrm{MgX_2} \tag{7}$$

Magnesium halide and alkyl magnesium halide precipitate and the alkyl magnesium compound remains in solution. Filtration (qv) followed by drying the filtrate yields solid magnesium alkyl (11). Another preparation method is that of metal exchange using mercury alkyl in ether.

$$\mathrm{RHgR} + \mathrm{Mg} \longrightarrow \mathrm{RMgR} + \mathrm{Hg} \tag{8}$$

Magnesium alkyls can also be prepared by reaction of alkyl iodide and a calcium–magnesium alloy in ether.

3.4. Uses.

Magnesium alkyls are used as polymerization catalysts for alpha-alkenes and dienes, such as the polymerization of ethylene (qv), and in combination with aluminum alkyls and the transition-metal halides (16–18). Magnesium alkyls have been used in conjunction with other compounds in the polymerization of alkene oxides, alkene sulfides, acrylonitrile (qv), and polar vinyl monomers (19–22). Magnesium alkyls can be used as a liquid detergents (23). Also, magnesium alkyls have been used as fuel additives and for the suppression of soot in combustion of residual furnace oil (24).

4. Magnesium Bromide

Magnesium bromide [7789-48-2], $MgBr_2$, is found in seawater, some mineral springs, natural brines, inland seas and lakes such as the Dead Sea and the Great Salt Lake, and salt deposits such as the Stassfurt deposits. In seawater, it is the primary source of bromine (qv). By the action of chlorine gas upon seawater or seawater bitterns, bromine is formed (see CHEMICALS FROM BRINE).

$$\mathrm{MgBr_2} + \mathrm{Cl_2} \longrightarrow \mathrm{MgCl_2} + \mathrm{Br_2}$$

4.1. Properties.

Magnesium bromide hexahydrate [13446-53-2], $MgBr_2 \cdot 6H_2O$, which crystallizes from an aqueous solution at temperatures above 0°C, is highly hygroscopic and isomorphous with $MgCl_2 \cdot 6H_2O$. It is also formed by the reaction of magnesium carbonate and hydrobromic acid (25). Physical properties of anhydrous magnesium bromide and the hexahydrate are shown in Table 2; solubilities are shown in Figure 2 (29). The solubility of magnesium bromide is 101 g/100 mL of water at 20°C; the solubility of the hexahydrate is 160 g/100 mL of 95% ethanol at 20°C (27).

Magnesium bromide is soluble in alcohols and forms addition compounds with numerous organic substances such as alcohols. The hexamethanolate, $MgBr_2 \cdot 6CH_3OH$, and the ethanolate, $MgBr_2 \cdot C_2H_5OH$, both exist. By gradually adding bromine to a cold mixture of magnesium powder and dry ether, the dietherate of magnesium bromide diethylether [17950-53-7], $MgBr_2 \cdot 2C_4H_{10}O$, is formed. Other compounds form with ammonia. For example, the compound magnesium bromide hexammoniate [75198-46-8], $MgBr_2 \cdot 6NH_3$, is easily prepared from anhydrous $MgBr_2$ and ammonia gas. Thermal decomposition of the hexammoniate yields the diammoniate [75198-47-9], $MgBr_2 \cdot 2NH_3$, and monoammoniate [75198-48-0], $MgBr_2 \cdot NH_3$.

Magnesium bromide forms double salts with potassium bromide, KBr, and ammonium bromide, NH_4Br, which are isomorphous with carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$. Basic bromides such as magnesium bromide oxide dodecahydrate [75300-54-8], $MgBr_2 \cdot 3MgO \cdot 12H_2O$, and magnesium bromide oxide hexahydrate [75300-55-9], $MgBr_2 \cdot 3MgO6H_2O$, have been reported.

4.2. Uses. Magnesium bromide is used in medicine as a sedative in treatment of nervous disorders, in electrolyte paste for magnesium dry cells, and as a reagent in organic synthesis reactions.

5. Magnesium Carbonate

Chemical reactions in the system $MgO{-}CO_2{-}H_2O$ result in a series of normal carbonates which include the following mineral species: magnesite [13717-00-5], $MgCO_3$; barringtonite [5145-48-2], $MgCO_3 \cdot 2H_2O$; nesquehonite [14457-83-1], $MgCO_3 \cdot 3H_2O$; and lansfordite [61042-72-6], $MgCO_3 \cdot 5H_2O$. These reactions also produce a series of basic, ie, hydroxyl-containing, magnesium carbonates having the general formula $x MgCO_3 \cdot y Mg(OH)_2 \cdot z H_2O$. This basic carbonate series includes artinite [12143-96-3], $MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$; hydromagnesite [12072-90-1], $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$; dypingite [12544-02-4], $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ (30); and an unnamed octahydrate [75300-49-1], $4MgCO_3 \cdot Mg(OH)_2 \cdot 8H_2O$ (31,32). Hydromagnesite is the most stable of the basic carbonates at ambient temperatures, humidities, and partial pressures of CO_2.

In its natural form magnesite is a member of the calcite group of rhombohedral carbonates. It is the most common species of the naturally occurring magnesium carbonate minerals. The other magnesium carbonate species are rare in occurrence compared to magnesite (33). Because of the similar sizes of the ionic radii of magnesium and iron, magnesite forms a complete solid solution series with the mineral siderite [14476-16-5], $FeCO_3$. The mineral which forms the species intermediate between magnesite and siderite is known as breunnerite, $(Mg,Fe)CO_3$.

5.1. Properties. The physical properties of the normal magnesium carbonates are given in Table 3, those of the basic magnesium carbonates in Table 4. Magnesium carbonate is insoluble in CO_2-free water. The solubility products, K_{sp}, for magnesium carbonate and some hydrates follow (34).

Compound	Solubility product, K_{sp}
magnesite	1.0×10^{-5}
$MgCO_3 \cdot H_2O$	2.7×10^{-5}
barringtonite	2.3×10^{-5}
nesquehonite	8.9×10^{-6}

The relatively high solubility of magnesium bicarbonate, $Mg(HCO_3)_2$, at low temperature and high partial pressures of CO_2 permits the separation of magnesium compounds from impurities. The high degree of solubility of magnesium bicarbonate was first utilized in the mid-nineteenth century in the Pattison process to prepare pure magnesium compounds from calcined dolomite [17069-72-6] (38).

Normal, hydrated, and the basic magnesium carbonates react with acids to yield salts which can be recovered by crystallization (39). Magnesium carbonate forms many double salts, some of which are listed in Table 5.

Because of this solid solution, natural magnesite contains varying amounts of iron which can affect the ultimate use of the material. Small amounts of calcium and manganese may also be present.

5.2. Production.

Naturally occurring magnesite is widely distributed throughout the earth's crust and is used as a starting raw material for the production of magnesia, MgO, and other magnesium compounds (41,42). It occurs as crystalline magnesite, and in the cryptocrystalline forms. Economically exploitable deposits of natural magnesium carbonate occur in many countries. World production is estimated at 650×10^3 t/yr, including 500×10^3/yr from China (43). World magnesite reserves are shown in Table 6. In addition to those estimates shown, magnesite deposits occur in Spain, Pakistan, and the Sudan. Deposits of less than 1×10^6 metric 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 metric tons of magnesite (15×10^6 metric tons magnesium) reserve base in the United States is divided as follows: in Nevada, 88%, including 27×10^6 metric tons 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.

Benefication. The purity of naturally occurring magnesite ores are quite variable. The ores can range from nearly pure magnesite to magnesite intermixed with other carbonate mineral species, quartz, clay minerals, and other aluminosilicates. The purity of the mined ore can be increased by several processes of mineral benefication (see MINERAL RECOVERY AND PROCESSING). Selective mining practices can produce a relatively good quality of industrial-grade magnesium carbonate. Ores can also be upgraded by means of heavy media separation. High quality magnesium carbonate is produced by means of froth flotation (qv) (45).

5.3. Manufacture.

Although magnesium carbonate ($MgCO_3$) occurs naturally as magnesite, magnesium carbonate used in the United States is synthetically manufactured. The chemical essentially is used in two forms—light and heavy, the difference is the number of water molecules that are included in the compound. Light magnesium carbonate has the empirical formula $(MgCO_3)_3 \cdot Mg(OH)_2 \cdot 3H_2O$, and heavy magnesium carbonate has the formula $(MgCO_3)_3 \cdot Mg(OH)_2 \cdot 4H_2O$. In the United States, magnesium carbonate is recovered from a brine solution by the addition of a soluble carbonate, such as sodium carbonate, to precipitate the magnesium carbonate. Magnesium carbonate also can be manufactured by saturation of dolomite with aqueous carbon dioxide under pressure. Increasing the temperature precipitates calcium carbonate. After filtration, the solution is heated to near boiling, so that H_2O and any remaining CO_2 are vaporized, and magnesium carbonate precipitates, usually as light magnesium carbonate.

5.4. Health and Safety Factors. Magnesium carbonates and its basic hydrated forms have minimal toxicological effects when encountered at normal exposure levels. However, in response to the possible adverse effects of long-term exposure to magnesium carbonate dust, the ACGIH has established a TLV–TWA of 10 mg/m^3 for magnesite dust that contains no asbestos (qv) fibers and less than 1% free silica (46). These compounds are best utilized within a conscientiously applied program of industrial hygiene (qv).

5.5. Uses. USP-grade magnesium carbonate is used in pharmaceuticals as an inert vehicle and an adsorbent. Heavy magnesium carbonate is used in concentrations up to 45% in tablets as an inert material to aid in drug delivery. Light magnesium carbonate can be used in concentrations of 0.5% to 1.0% as a liquid absorbent, particularly for flavorings in tablets. One of its most visible uses is as an antacid (see PHARMACEUTICALS). Magnesium carbonate is also used in cosmetic manufacturing. Because of its fine texture and high absorbency, light magnesium carbonate is an excellent carrier and retainer of perfumes. It also can be added to loose powders to provide fluffiness; in most cases it is blended with talc in quantities from 1 to 5%. The USP grade of magnesium carbonate is used as an additive to table salt to keep it free flowing. About 25% of magnesium carbonate is used annually in the United States for pharmaceuticals and cosmetics (47).

In the rubber industry, which accounts for about 30% of the total annual magnesium carbonate consumption, the material is used as a reinforcing agent. It also is used as a smoke suppressant in rubber and some plastics compounds to replace some of the alumina trihydrate that is traditionally used. The replacement of about 12.5% of the alumina trihydrate with magnesium carbonate increases the quantity of char that is formed in a fire. It also decreases the rate of flame spreading and the quantity of smoke generated (see FLAME RETARDANTS). The remaining 45% of magnesium carbonate consumption is as an extender for titanium dioxide in paint, in lithographing inks, and as a precursor for other magnesium-based chemicals.

Because the uses for magnesium carbonate are essentially in mature markets, with the exception of flame retardants, significant growth in U.S. consumption is not expected. In flame retardants, magnesium carbonate competes with magnesium hydroxide; most of the growth in flame retardants is expected in magnesium hydroxide.

6. Magnesium Chloride

6.1. Properties. Magnesium chloride [7786-30-3], $MgCl_2$, is one of the primary constituents of seawater and occurs in most natural brines and salt deposits formed from the evaporation of seawater. It occurs infrequently in nature as the mineral bischofite [13778-96-6], $MgCl_2 \cdot 6H_2O$. Large deposits of oceanic origin contain the mineral carnallite [1318-27-0], $KCl \cdot MgCl_2 \cdot 6H_2O$. Magnesium chloride, one of the most commercially important magnesium compounds, is available in the anhydrous and hexahydrate forms. Both are deliquescent and form saturated solutions on standing in a moist atmosphere. The physical properties of these compounds are given in Table 7. The step by step thermal dehydration of the hexahydrate goes through various hydrates (48,49): from $95 - 110°\mathrm{C} MgCl_2 \cdot 6H_2O \longrightarrow MgCl_2 \cdot 4H_2O + 2H_2O$, $MgCl_2 \cdot 4H_2O \longrightarrow MgCl_2 \cdot 2H_2O + 2H_2O$; from $135 - 180°\mathrm{C} MgCl_2 \cdot 4H_2O \longrightarrow Mg(OH)Cl + HCl + 3H_2O$, $MgCl_2 \cdot 2H_2O \longrightarrow MgCl_2 \cdot H_2O + H_2O$; from $185 - 230°\mathrm{C} MgCl_2 \cdot 2H_2O \longrightarrow Mg(OH)Cl + HCl + H_2O$; and $> 230°\mathrm{C} MgCl_2 \cdot H_2O \longrightarrow MgCl_2 + H_2O$, $MgCl_2 \cdot H_2O \longrightarrow Mg(OH)Cl + HCl$, $Mg(OH)Cl \longrightarrow MgO + HCl$.

Magnesium chloride also forms hydrates containing 8 and 12 molecules of water of hydration. The solubility for $MgCl_2$ in water is shown in Figure 2 (29) from which it can be seen that the hexahydrate is the only stable hydrate in the range of temperatures from 0 to 100°C.

Anhydrous magnesium chloride is soluble in lower alcohols. In 100 g of methanol, its solubility is 15.5 g at 0°C and 20.4 g at 60°C. In ethanol, the solubility is 3.61 g at 0°C and 15.89 g at 60°C. Upon cooling, anhydrous $MgCl_2$ forms addition compounds with alcohols of crystallization such as magnesium chloride hexamethanolate [57467-93-0], $MgCl_2 \cdot 6CH_3OH$, and magnesium chloride hexaethanolate [16693-00-8], $MgCl_2 \cdot 6C_2H_5OH$. Both of these alcoholates are deliquescent.

Magnesium chloride forms double salts with potassium and ammonium chlorides. Carnallite is an important source of $MgCl_2 \cdot 6H_2O$. Magnesium chloride hexammoniate [68374-23-2], $MgCl_2 \cdot 6NH_3$, can be formed by the reaction of anhydrous magnesium chloride and ammonia gas in a closed system, or by the action of ammonia on an aqueous solution of $MgCl_2$ and ammonium chloride, NH_4Cl, upon subsequent cooling to−30°C. Thermal decomposition of $MgCl_2 \cdot 6NH_3$ yields the diammoniate [68374-24-3], $MgCl_2 \cdot 2NH_3$, and the monoammoniate [68374-25-4], $MgCl_2 \cdot NH_4$.

6.2. Preparation and Manufacture. Magnesium chloride can be produced in large quantities from (*1*) carnallite or the end brines of the potash industry (see Potassium compounds); (*2*) magnesium hydroxide precipitated from seawater; (*3*) by chlorination of magnesium oxide from various sources in the presence of carbon or carbonaceous materials; and (*4*) as a by-product in the manufacture of titanium (see Titanium and titanium alloys).

Magnesium chloride is obtained from mother liquors resulting from the recovery of potassium chloride from carnallite. These liquors contain up to 28% magnesium chloride and have been regarded as a waste product because it is costly to obtain pure magnesium chloride from them. The liquor is purified by raising the concentration of the magnesium chloride through evaporation (qv) until potassium chloride, sodium chloride, sodium sulfate, and magnesium sulfate crystallize out and are removed. Ferrous iron is removed by oxidation using potassium chlorate at 158°C and precipitated with lime. Evaporation of the purified liquor to a density of 1.435 yields, upon cooling the solution, impure magnesium chloride as a glassy mass. The solution can be solidified on rotating cooling drums from which the salt layer can be removed by scrapers (50). Repeat recrystallization yields pure $MgCl_2 \cdot 6H_2O$.

To recover magnesium chloride from brines, the water from the Great Salt Lake is pumped to a series of solar evaporation ponds where water evaporates to concentrate the brine. The first salt to precipitate as the water evaporates is sodium chloride. The next group of salts to precipitate is a mix of double salts containing potassium and magnesium. Depending on brine concentration, temperature, and other factors, kainite, schoenite, and carnallite may be precipitated. Sodium sulfate is then precipitated from the cooled brine in the winter (even though it is no longer harvested for sale). The final product remaining dissolved in the brine is magnesium chloride. In general, an equilibrium is reached at about 35% $MgCl_2$ concentration by weight in the brine. Although most of the sodium and potassium have been removed from the brine at this stage, it still contains some dissolved sulfate. The purity of this brine is sufficient for some applications, or it may be further purified if necessary. Purified brine then may be further processed to produce the hexahydrate solid. The overall production cycle takes about two years to complete (51). A typical analysis of brine is shown in Table 8.

When magnesium oxide is chlorinated in the presence of powdered coke or coal (qv), anhydrous magnesium chloride is formed. In the production of magnesium metal, briquettes containing $CaCl_2$, KCl, NaCl, MgO, and carbon are chlorinated at a temperature such that the electrolyte or cell melt collects at the bottom of the chlorinator, enabling the liquid to be transferred directly to the electrolytic cells.

Another way of preparing anhydrous magnesium chloride is by a two-stage dehydration of magnesium chloride hexahydrate. In the first stage, concentrated magnesium chloride brine is spray-dried to a point where the residual water content is between 1 and 2 molecules. The partially dehydrated product can sometimes be chlorinated in the presence of carbon because the intermediate hydrate often contains some oxychloride. In the final stage of dehydration, the intermediate hydrate is treated with hydrogen chloride or chlorine gas. The anhydrous salt is then melted and cast into blocks which are packed so as to exclude all air (52).

A one-step, low energy process was developed by Magnesium International Corp. for producing anhydrous magnesium chloride. This process involved the reaction of magnesite and chlorine gas in the presence of carbon monoxide in a packed-bed reactor at 900°C to produce magnesium chloride and carbon dioxide. Carbon dioxide is withdrawn from above the packed bed and liquid magnesium chloride is collected at the bottom of the reactor and tapped periodically for transfer to electrolytic cells (53,54). The process can be represented by

$$MgCO_3 + CO + Cl_2 \longrightarrow MgCl_2 + 2CO_2$$

6.3. Uses.

The largest use for magnesium chloride brine is as a suppressant for dust on dirt roads, construction sites, unpaved parking lots, mines, and quarries. A corrosion inhibitor may be added to the brine to reduce corrosion on structures, such as steel surfaces, that are associated with the sites where the brine is used. The inhibitor forms a protective coating so that the brine will not corrode metal surfaces. Magnesium chloride brine also may be used to melt ice on road surfaces, sometimes in conjunction with an abrasive such as sand. Brines also have applications in oil-well completion fluids, as a component of some herbicides, and in regeneration of ion-exchange resins.

Magnesium chloride hexahydrate is almost exclusively used for melting ice. It is used in conjunction with, or in place of, salt for removal of ice and snow from sidewalks and roadways. Magnesium chloride has a lower freezing point than salt and is generally less corrosive to asphalt and cement, but it is significantly more expensive. In most cases, salt is used as the major melting agent for ice and snow, but if the surface that is being treated is expensive to maintain, the additional cost for magnesium chloride can be justified.

Weather plays an important role in the outlook for magnesium chloride. In the production process, weather in the Great Salt Lake area affects the salinity of the brines. Excessive snow or rainfall can dilute the lake. When the salinity of the lake is decreased by dilution, more water must be evaporated to produce the same quantity of salts. As a result, the length of the production cycle is increased. Snow and rainfall amounts also affect the demand for magnesium chloride. Obviously, the demand for magnesium chloride increases in winters with heavy snowfall and decreases in years with little snowfall. However, since municipalities often purchase snow removal products before winter starts in response to snow predictions, if there is a light snowfall in one year, the products bought for that year can be used for the next winter, reducing the municipalities' buying requirements. Rainfall amounts in the West affect the need for magnesium chloride as a dust suppressant. Heavy rainfall leads to decreased consumption, and dry weather results in increased consumption. Because of the unpredictability of the weather, it is difficult to predict the demand for magnesium chloride. With increasing environmental concerns, however, magnesium chloride hexahydrate demand is likely to increase for removal of ice and snow. Its lower level of corrosiveness is becoming more attractive to municipalities and homeowners despite its higher cost.

Magnesium Hydroxide. Another important use of magnesium chloride is in the preparation of oxychloride cements, $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, for flooring (nonsparking), wall plaster compositions, fire-resistant panels, fireproofing of steel beams, and grinding wheels. These cements (known as Sorel cements) are vermin resistant flooring cements used in industrial buildings. The cements are produced on-site by adding a 20% solution of $MgCl_2$ in water and a dry mix consisting of magnesium oxide, fillers (eg, wood fiber), and fine aggregates. After a few hours of setting, the cements form a dense but smooth-textured stonelike product (55). For example,

$$5MgO + MgCl_2 + 13H_2O \longrightarrow 5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$$

The phase diagram in Figure 3 represents equilibria in the $MgO \cdot MgCl_2 \cdot H_2O$ system at room temperature (56).

Magnesium chloride is also used in the processing of sugar beets (see SUGAR, BEET SUGAR) and textiles (qv), in water treatment, as a fireproofing agent for wood, as a dust control agent in mines and on haul roads, as an ingredient of floor-sweeping compounds, refrigeration brines, and fire-extinguishing agents.

Anhydrous magnesium chloride, along with magnesium bromide and magnesium iodide, is used in a process for producing organometallic compositions such as alkyllithium compounds used as reagents in the preparation of pharmaceuticals (qv) and special chemicals (57). Molten magnesium chloride has been used in the preparation of pure crystalline ceramic powders such as crystalline cordierite, forsterite, enstatite, and spinel (58). The introduction of $MgCl_2$-supported $TiCl_3$ (Ziegler-Natta) catalysts has changed the manufacturing technology of polypropylene because of greatly enhanced catalytic productivity (59). Also as a catalyst, $MgCl_2 \cdot 6H_2O$ is used in finishing to increase strength properties of cotton fabric (60).

7. Magnesium Fluoride

7.1. Properties. Magnesium fluoride [7783-40-6],MgF_2, is a fine white crystalline powder with low chemical reactivity. This relative inertness makes possible some of its uses, eg, stable permanent films to alter light transmission properties of optical and electronic materials. The reaction withsulfuric acid is so sluggish and incomplete that magnesium fluoride is not a suitable substitute forcalcium fluoride in manufacturing hydrogen fluoride. Magnesium fluoride resists hydrolysis to hydrogen fluoride up to 750°C (61). Bimetallic fluorides, such as $KMgF_3$[28042-61-7], are formed on fusion of MgF_2 alkali metal and ammonium fluorides (62). Chemical and physical properties are listed in Table 9. MgF_2 is birefringent and only mildly affected by high energy radiation, making possible optics for the uv region.

7.2. Manufacture. Magnesium fluoride is manufactured by the reaction ofhydrofluoric acid andmagnesium oxide or carbonate:

$$MgO + 2\ HF \longrightarrow MgF_2 + H_2O$$

$$MgCO_3 + 2\ HF \longrightarrow MgF_2 + CO_2 + H_2O$$

Formation of a gelatinous precipitate that is difficult to filter can be avoided by addition of magnesium oxide to the acid solution. In order to increase particle size it is often necessary to keep the solution hot for several hours; however, this problem is avoided by heating an intimate mixture ofammonium bifluoride with magnesium carbonate to 150–400°C (71). Particles of MgF_2 similar in size to those of the magnesium carbonate are obtained.

$$MgCO_3 + NH_4HF_2 \xrightarrow{150-400^\circ C} MgF_2 + NH_3 + CO_2 + H_2O$$

The same results are obtained by addingmagnesium carbonate to an aqueous solution ofammonium bifluoride and ammonium hydroxide and warming to 60°C (72). The resulting precipitate is ammonium magnesium fluoride[35278-29-6] which settles rapidly.

$$MgCO_3 + 3\ NH_4F\ (aq) \longrightarrow NH_4MgF_3 + (NH_4)_2CO_3$$

$$NH_4MgF_3 \xrightarrow[4\ h]{620^\circ C} MgF_2 + NH_3 + HF$$

Magnesium fluoride is a by-product of the manufacture of metallic beryllium and uranium. The beryllium or uranium fluorides are intimately mixed with magnesium metal in magnesium fluoride-lined crucibles. On heating, a Thermite-type reaction takes place to yield the desired metal and MgF_2 (73). Part of the magnesium fluoride produced in this reaction is then used as a lining for the crucibles used in the process.

$$BeF_2 + Mg \longrightarrow Be + MgF_2$$

Magnesium fluoride optical crystals are made by hot-pressing (74) high quality MgF_2 powder. The optical quality powder is made by the NH_4HF_2 method described (71) or by reaction of magnesium bicarbonate and hydrofluoric acid (75). Lead fluoride can also be used in purification of MgF_2 for optical crystals (76).

7.3. Health and Safety Factors. The lethal dose of MgF_2 to guinea pigs by ingestion is 1000 mg/kg (77).

7.4. Uses. Established uses of magnesium fluoride are as fluxes in magnesium metallurgy and in the ceramics industry. A proposed use is the extraction of aluminum from arc-furnace alloys with Fe, Si, Ti, and C (78). The molten alloy in reacting with magnesium fluoride volatilizes the aluminum and magnesium which are later separated above the melting point of MgF_2. A welding (qv) flux for aluminum (79) as well as fluxes for steel (80) contain MgF_2.

Optical windows of highly purified magnesium fluoride which transmit light from the vacuum ultraviolet (140 nm) into the infrared (67) are recommended for use as ultraviolet optical components for use in space exploration.

8. Magnesium Hydroxide

8.1. Properties. The physical properties of magnesium hydroxide are listed in Table 10. The crystalline form of magnesium hydroxide is uniaxial hexagonal platelets (Fig. 4). Magnesium hydroxide begins to decompose thermally above 350°C, and the last traces of water are driven off at higher temperatures to yield magnesia.

Upon exposure to the atmosphere, magnesium hydroxide absorbs moisture and carbon dioxide. Reactive grades are converted to the basic carbonate $5MgO \cdot 4CO_2 \cdot xH_2O$ over a period of several years. Grades that resist carbonization at high temperature and humidity have been reported (81).

The reactivity of magnesium hydroxide is measured primarily by specific surface area in units of m^2/g and median particle size in μm. Reactivity ranges from low, $1-2$ m^2/g, 5 μm, eg, Kyowa's product; to high, $60-80$ m^2/g, 5–25 μm, eg, Barcroft's CPS and CPS-UF powders. Higher reactivity tends to lower capital and operating costs for users as a result of shorter reaction times in their processes.

8.2. Occurrence. Magnesium hydroxide [1309-42-8], $Mg(OH)_2$, occurs naturally as the mineral brucite [1317-43-7]. Brucite, usually found as a low temperature, hydrothermal vein mineral associated with calcite, aragonite, talc, or magnesite, appears as a decomposition product of magnesium silicates associated with serpentine, dolomite, magnesite, and chromite. Brucite also occurs as a hydrated form of periclase, and is found in serpentine, marble, chlorite schists, and in crystalline limestone. At one time brucite was recovered commercially from deposits at Wakefield, Quebec and Nye County, Nevada; both operations have since ceased.

8.3. Production.

Production from Magnesium Salts. Magnesium hydroxide is produced from aqueous solutions of magnesium salts. To precipitate and recover magnesium hydroxide from solutions of magnesium salts, a strong base is added. The more commonly used base is calcium hydroxide [1305-62-0], derived from lime [1305-78-8], CaO, or dolime [50933-69-2], CaO·MgO. Lime and dolime are calcination products of limestone and dolomite, respectively (see LIME AND LIMESTONE). Calcination of crushed and sized dolomite or limestone is done in rotary or shaft kilns controlled to drive off all CO_2 without deactivating the material. Theoretical precipitant requirements per kilogram of $Mg(OH)_2$ are approximately 0.97 kg lime or 0.83 kg dolime. Sodium hydroxide is used as a precipitant if a product having low CaO content is desired.

In seawater–dolime and brine–dolime processes, calcined dolomite or dolime, CaO·MgO, is used as a raw material. Dolime typically contains 58% CaO, 41% MgO, and less than 1% combined SiO_2, R_2O_3, and CO_2 where R is a trivalent metal ion, eg, Al^{3+} or Fe^{3+} (82). Roughly one-half of the magnesia is provided by the magnesium salts in the seawater or brine and the other half is from dolime (83). Plant size is thus reduced using dolime and production cost is probably lower.

Raw $MgCl_2$ brines at Ludington and Manistee, Michigan typically contain 51.6 g/L of equivalent MgO (66). This magnesium oxide equivalent represents approximately 4% $Mg(OH)_2$ by weight. Brine at Midland, Michigan typically contains one-third the equivalent MgO of Ludington and Manistee brines. The equivalent magnesia content of delivered brine may be 3 to 8% lower because of dilution at the well head to prevent salting out in the well tubulars (82). Seawater typically contains the equivalent of 2.2 g/L of MgO, present as $MgCl_2$ and $MgSO_4$ (83). Typical compositions of deep-well brine and seawater are compared in Table 11.

The reactions (84) for the brine process are (*1*) calcination of dolomite; (*2*) slaking of dolime; and (*3*) precipitation of $Mg(OH)_2$:

$$CaMg(CO_3)_2 \longrightarrow CaO + MgO + 2CO_2\ (g) \quad \Delta H = +305.5\ \text{kJ}\ (73.02\ \text{kcal})$$

$$CaO + MgO + 2\ H_2O(l) \longrightarrow Ca(OH)_2 + Mg(OH)_2 \quad \Delta H = -84\ \text{kJ}\ (-20\ \text{kcal})$$

$$\begin{aligned} &Ca(OH)_2 + Mg(OH)_2 + MgCl_2(aq) \longrightarrow 2\ Mg(OH)_2 + CaCl_2(aq) \\ &\quad \Delta H_{298} = -14.4\ \text{kJ}\ (3.44\ \text{kcal}) \end{aligned}$$

A flow diagram for the brine process is given in Figure 5. Dolime and brine are metered in fixed proportion to a slaking reactor where the temperature and chemistry are controlled to meet product purity and trace element specifications. A faster settling and more filterable precipitate results from a reduction in the reactivity of the precipitant, ie, lime or calcined dolomite, by control of the slaking conditions and degree of burn. Recirculation of a fraction of the precipitated slurry into the thickener or the continuous addition of flocculating agents (qv) boosts the settling rates of magnesium hydroxide. Improved settling and filtering characteristics reduce capital expenditures and operating costs.

Improvements in settling characteristics must be balanced against final product purity. This latter can be reduced by addition of settling aids (flocculants) or occlusion of residual unreactive lime. Clarification following thickening maximizes recovery of solids. Underflow slurry from the thickeners is dewatered, washed, and repulped to produce magnesium hydroxide of high bulk density and high purity.

Approximately 65 to 80% of the total $Mg(OH)_2$ yield is formed in the slaking reactor via the parallel reactions given in equations (13) and (14). The remaining 20 to 35% is formed by hydration of remaining dolime-borne MgO in equation (13) (66). The theoretical yield from 1 kg of dolime is approximately 1.2 kg of magnesium hydroxide, excluding impurities. Trace impurities include CaO, SiO_2, Fe_2O_3, Al_2O_3, SO^{-2}_3, Cl^-, and B. Sources of CaO are $CaCl_2$, $Ca(OH)_2$, $CaCO_3$, and $CaSO_4$, the last three being functions of the dolime. The brine is the source of the boron.

Calcium chloride in the spent brine includes the residual quantity in the raw brine plus $CaCl_2$ produced in equation (14). Approximately 0.84 kg of by-product calcium chloride are produced per kg of magnesium hydroxide via the brine–dolime process.

The key difference between the brine process and seawater process is the precipitation step. In the latter process (Fig. 6) the seawater is first softened by adding small amounts of lime to remove bicarbonate and sulfates, present as $MgSO_4$. Bicarbonate must be removed prior to the precipitation step to prevent formation of insoluble calcium carbonate. Removal of sulfates prevents formation of gypsum, $CaSO_4 \cdot 2H_2O$. Once formed, calcium carbonate and gypsum cannot be separated from the product.

An alternative pretreatment for seawater is acidification of the bicarbonate followed by degasification to remove the carbon dioxide generated. The precipitation step for the seawater process is given by (85):

$$\begin{aligned} 2\ Ca(OH)_2 + 2\ Mg(OH)_2 + MgCl_2(aq) + MgSO_4 + 2\ H_2O(l) &\longrightarrow 4Mg(OH)_2(s) \\ + CaCl_2(aq) + CaSO_4 \cdot 2H_2O(s) \qquad \Delta H &= -22.6\ \text{kJ}\ (-5.40\ \text{kcal}) \end{aligned}$$

The softened seawater is fed with dry or slaked lime (dolime) to a reactor. After precipitation in the reactor, a flocculating agent is added and the slurry is pumped to a thickener where the precipitate settles. The spent seawater overflows the thickener and is returned to the sea. A portion of the thickener underflow is recirculated to the reactor to seed crystal growth and improve settling and filtering characteristics of the precipitate. The remainder of the thickener underflow is pumped to a countercurrent washing system. In this system the slurry is washed with freshwater to remove the soluble salts. The washed slurry is vacuum-filtered to produce a filter cake that contains about 50% $Mg(OH)_2$. Typical dimensions for equipment used in the seawater process may be found in the literature (83).

Other Processes. Dead Sea Periclase (DSP, Mishor Rotem, Israel) converts magnesium chloride into MgO by spray-roasting, then hydrates the MgO to $Mg(OH)_2$. The $Mg(OH)_2$ is washed and drum filtered. DSP purchases the brine from Dead Sea Works, which collects and stores enriched brine from the southern margins of the Dead Sea (85).

The Austrian manufacturer Magnifin Magnesiaprodukte GmbH uses a magnesite acidification process to produce a high purity magnesium hydroxide for flame retardant/smoke suppressant applications (87). Magnesite is acidified to produce $MgCl_2$ and subsequent MgO of 99% purity, which is converted to magnesium hydroxide by hydration.

Magnesium hydroxide can also be produced by slaking or pressure hydrating various reactive grades of magnesium oxide. The reaction is highly exothermic ($\Delta H_{298} = -40.86$ kJ/mol (-9.77 kcal/mol)) to produce crystalline form at stoichiometric water addition;$\Delta H_{298} = -43.03$ kJ/mol (-10.28 kcal/mol) including heat of solution, at standard state $m = 1$) and may require a heat sink to prevent boiling of the reaction mixture. A 30% by weight suspension of MgO in 20°C water boils in the absence of any heat sink. The time to reach boiling is dependent on the reactivity of the MgO raw material, and this time can be only several hours for the more reactive grades of MgO. Investigations of the kinetics of formation of magnesium hydroxide by hydration of MgO have been reported (88).

8.4. Shipment.

Magnesium hydroxide is produced and shipped in aqueous slurry or as dry powder.

Slurry. Dow Chemical was the first producer of a stabilized slurry product. National Magnesia, American Premier, and Martin Marietta Magnesia Specialties, have followed with slurry formulations. The slurry is shipped in totes, bulk trucks, or bulk railcars. Railcars equipped with air spargers for agitation are available from some manufacturers for improving unloading of slurry. Approximate container loadings are given in Table 12.

Bulk density is 1.49 kg/L for 57% solids slurry with a $Mg(OH)_2$ loading of 0.85 kg/L. The properties of some magnesium hydroxide slurries are given in Table 13.

Slurry Storage and Handling. Bulk quantities of slurry are stored in agitated or recirculated storage tanks. Agitation is necessary to resuspend settled solids. Slurry stability can be characterized by agitation requirements ranging from several hours per week for very stable products to 2 h/d for medium stability products to constant agitation for low stability products. Guidelines for storing and agitating slurries such as magnesium hydroxide and for estimating agitation requirements have been presented in detail in the literature (87,89).

Instrumentation and control guidelines for processes utilizing magnesium hydroxide and other slurries have been outlined (90). An experimental determination of the accuracy of magnetic flow meters for magnesium hydroxide slurries flowing in pipelines (qv) has been reported (64).

Powder. Magnesium hydroxide powder can be produced by drying the $Mg(OH)_2$ filter cake from the various production processes. Powders having particle sizes comparable to the $Mg(OH)_2$ solids in the slurry can be obtained by spray drying the slurry. Slaking reactive MgO followed by spray drying also produces a $Mg(OH)_2$ powder. The minimum purity specification is typically 95–98% by weight $Mg(OH)_2$. The loose bulk density typically ranges from 0.4 to

0.6 g/cm^3. The properties of some commercial grades of magnesium hydroxide powders are given in Table 14.

Packaging of magnesium hydroxide powders is usually in paper bags of 10 to 25 kg size. Bulk shipments may be made in 1 t supersacks. Magnesium hydroxide powder is hygroscopic and should be protected against exposure to moisture by use of lined bags. Magnesium hydroxide powder can be dusty, and appropriate precautions against dust exposure should be taken during handling (see POWDERS, HANDLING).

8.5. Analytical Methods. Many of the procedures for technical analyses of magnesium hydroxide are readily available from the principal producers. These procedures should be carefully reviewed. Site-specific variations in procedure steps and mechanics, especially for chemical activity, can bias results and inadvertantly disqualify an otherwise acceptable product.

Particle Size. Wet sieve analyses are commonly used in the 20 μm (using microsieves) to 150 μm size range. Sizes in the 1–10 μm range are analyzed by light-transmission liquid-phase sedimentation, laser beam diffraction, or potentiometric variation methods. Electron microscopy is the only reliable procedure for characterizing submicrometer particles. Scanning electron microscopy is useful for characterizing particle shape, and the relation of particle shape to slurry stability.

Surface Area. Surface area is measured by determining the quantity of nitrogen gas that adsorbs on the particle/crystal surfaces of a dry sample. Determination of surface area by measuring adsorption at gas–solid interfaces is covered extensively in the literature (85). Instruments such as the FlowSorb 2300 are used to control the adsorption/desorption within specific conditions of temperature and pressure.

Mineral and Chemical Composition. X-ray diffraction is used to determine the mineral composition of an $Mg(OH)_2$ sample. Induced coupled plasma (icp) spectrophotometry is used to measure the atomic concentrations present in a sample. X-ray fluorescence analysis is another comparative instrumental method of determining chemical composition.

Chemical Activity. The activity of magnesium hydroxide is measured using a citric acid activity (CAA) test. The CAA is determined by measuring the time required for a given weight of a particular magnesium hydroxide to provide hydroxyl ions sufficient to neutralize a given weight of citric acid.

Loss on Ignition. The loss on ignition (LOI) test is used to approximate the percent of magnesium hydroxide present in a sample and to determine extent of hydration. When the magnesium hydroxide sample is heated to 1000°C, all of the magnesium hydroxide and trace impurities of magnesium carbonate are converted to magnesium oxide. Some chlorides and sulfates are also decomposed. The relative difference in sample weight before and after heating approximately represents the quantity of water given up by the $Mg(OH)_2$. Assuming that complete dehydration of the $Mg(OH)_2$ occurs and the starting sample is dry, the theoretical LOI for a 100% sample of $Mg(OH)_2$ is 30.85%.

Slurry Viscosity. Viscosities of magnesium hydroxide slurries are determined by the Brookfield Viscometer in which viscosity is measured using various combinations of spindles and spindle speeds, or other common methods of viscometry. Viscosity decreases with increasing rate of shear. Fluids, such as magnesium hydroxide slurry, that exhibit this type of rheological behavior are termed pseudoplastic. The viscosities obtained can be correlated with product or process parameters. Details of viscosity determination for slurries are well covered in the literature (91,92).

8.6. Health and Safety Factors.

Magnesium hydroxide is not absorbed by the skin. Dry magnesium hydroxide may irritate the eyes, skin, nasal passages, and respiratory tract. Routes of body entry are skin contact, eye contact, inhalation, and ingestion. No LD_{50} values for $Mg(OH)_2$ are available.

If $Mg(OH)_2$ is heated above 1700°C, magnesium oxide fumes may volatilize. Inhalation of freshly generated MgO fumes may result in metal fume fever. Ingestion of $Mg(OH)_2$ generally causes purging of the bowels, although swallowing a large amount of $Mg(OH)_2$ may lead to bowel obstruction. No data is available regarding chronic exposure to $Mg(OH)_2$.

$Mg(OH)_2$ powder is classified by OSHA as a nuisance dust. ACGIH categorizes the powder form as particulates not otherwise classified. Exposure limits are as follows (93): ACGIH 10 mg/m^3, OSHA 5 mg/m^3 (respirable), and 15 mg/m^3 (total). Magnesium hydroxide is reported in the EPA TSCA inventory (94).

8.7. Uses.

After discounting the portion of magnesium hydroxide that is used to produce dead-burned magnesia, the largest use for magnesium hydroxide in the United States is for environmental applications. This portion of the market, which includes industrial water treatment, heavy-metals removal, and flue-gas desulfurization, accounts for about more than half of total U.S. consumption. For water treatment, magnesium hydroxide is supplied as a suspension containing about 58% solids, and it is used primarily to lower the pH of acidic solutions. In this market it competes with other acid-neutralizing compounds; the most common are lime and caustic soda. Magnesium hydroxide has advantages and disadvantages when compared to the other materials in this use. One of the advantages is that it is a pH buffer, and wastewater treated with it will not exceed a pH of 9.5 even if excess magnesium hydroxide is added. In contrast, excess addition of lime can raise the pH to 12, and excess caustic soda addition can raise the pH to 14. In these cases, back additions of acid are necessary to lower the pH. Magnesium hydroxide also has a higher basicity per unit added than either lime or caustic soda; for equivalent neutralization, 0.72 metric ton of magnesium hydroxide can replace 1 metric ton of lime. Magnesium hydroxide is better than lime or caustic soda at removing some metals such as lead and trivalent chromium. Metal hydroxides that are precipitated with magnesium hydroxide rather than caustic soda or lime tend to form larger crystals, resulting in lower sludge volumes and hence, lower disposal costs. The solids formed through precipitation by magnesium hydroxide have a cakelike consistency, rather than that of a gel as do the solids formed by caustic soda precipitation; the cake is easier to handle (95).

One principal disadvantage of magnesium hydroxide is its cost compared to that of other materials. Another disadvantage is its slower reaction rate, particularly when precipitating high concentrations of metals ($>$2000 ppm) or neutralizing weak organic acids. Most treatment systems in use today were originally designed to use lime or caustic soda, and as a result of magnesium hydroxide's slower reaction time, there may not be enough residence time in the system. In some cases, users must reconfigure their systems when switching to magnesium hydroxide.

Magnesium hydroxide slurry also competes with magnesium oxide where there are large neutralization requirements. Magnesium oxide has about two and a half times as much neutralizing capability as magnesium hydroxide per unit volume, and transportation costs for the oxide are generally lower than those for the hydroxide slurry. In addition, existing lime neutralization systems may be more easily converted to use of the magnesium oxide powder rather than the hydroxide slurry.

In flue-gas desulfurization, magnesium hydroxide is used in place of lime in a few applications. Most of the processes designed for industrial gas scrubbing use lime or calcium in some form. Scrubbing with lime produces gypsum products, which need to be landfilled in most cases. The volume of these waste products may be greater than the original waste volume, so lime may not be appropriate for all scrubbing applications. In these instances, magnesium hydroxide may be used. Landfilling, however, may not be as much of a problem in the future for lime scrubber wastes because significant research and development is underway to find applications for the by-product gypsum.

The second largest use for magnesium hydroxide is as a precursor for other magnesium chemicals. Magnesium hydroxide is also used in pharmaceuticals. The pharmaceutical grades of magnesium hydroxide include a 100% $Mg(OH)_2$ powder used in antacid tablets and a 30% $Mg(OH)_2$ paste used in liquid antacids such as milk of magnesia.

Like magnesium carbonate, magnesium hydroxide can replace alumina trihydrate in some flame retardants. Both alumina trihydrate and magnesium hydroxide function as flame retardants by releasing water vapor in an endothermic reaction that diverts the heat away from the flame, thereby reducing the formation of combustible gases. Alumina or magnesia remaining after the water is released is believed to have a high surface area available for absorbing smoke. Although the properties of alumina trihydrate and magnesium hydroxide are similar, magnesium hydroxide has a higher temperature stability. Magnesium hydroxide begins to decompose at about 330°C, compared to about 200°C for alumina trihydrate. This higher temperature stability makes magnesium hydroxide more attractive for specific flame retardant applications. Some thermoplastics, such as polypropylene or nylon–vinyl, require temperatures in processing that are high enough to begin decomposing alumina trihydrate. In addition, the high processing speed of lines that produce plastic insulation for wire and cable generates enough friction to begin decomposing alumina trihydrate. In these cases, magnesium hydroxide is the flame retardant of choice (96). Magnesium hydroxide particles have excellent properties as a flame retardant for synthetic resins (97).

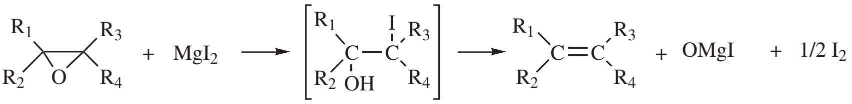
9. Magnesium Iodide

9.1. Properties. Magnesium iodide [10377-58-9] can exist as two deliquescent and heat sensitive compounds: the octahydrate [7790-31-0], $MgI_2 \cdot 8H_2O$, and the hexahydrate [75535-11-4], $MgI_2 \cdot 6H_2O$. The octahydrate is crystallized as a white powder from solutions between 8°C and 43°C and the hexahydrate from solutions above 43°C. The physical properties of both compounds are shown in Table 15, solubilities in water are shown in Figure 2 (29).

The octahydrate can be obtained from a solution of magnesium hydroxide in hydriodic acid and evaporation at room temperature, followed by cooling to 0°C to increase the yield. By heating $MgI_2 \cdot 8H_2O$ in a current of dry hydrogen iodide, HI, followed by dry nitrogen, N_2, the anhydrous salt MgI_2 is formed. This salt is extremely hydroscopic and decomposes in air with the formation of free iodine.

Magnesium iodide is soluble in alcohols and many other organic solvents, and forms numerous addition compounds with alcohols, ethers, aldehydes, esters, and amines. One example is magnesium iodide dietherate [29964-67-8], $MgI_2 \cdot 2C_4H_{10}O$, prepared by gradual addition of iodine to a mixture of magnesium and dry ether. Magnesium iodide dietherate, which occurs as white, needle-like crystals, is very hygroscopic and becomes yellowish after several hours, and then brown after a day because of separation of iodine. The action of water upon magnesium iodide dietherate leads to the formation of the octahydrate salt, $MgI_2 \cdot 8H_2O$.

9.2. Uses. Magnesium iodide is used in the deoxygenation of oxiranes into olefins and iodine. This step is important to organic chemistry because it helps in the structure elucidation of complex organic molecules (98). For example,



Magnesium iodide is also an effective electrophilic reagent for the cleavage of C—O bonds in aromatic and aliphatic carboxylic esters (99). In organic catalysis, the addition of MgI_2 to a catalyst compound containing CuI_2 and CuI increases the activity of the catalyst for removing SO_2 from gases to reduce air pollution (100).

Anhydrous MgI_2 is used in a process for producing organometallic and organobimetallic compositions, which are important in the preparation of pharmaceutical and special chemicals. An organic halide, an alkali metal, and magnesium halide react in a liquid hydrocarbon solvent (82).

10. Magnesium Nitrate

10.1. Properties. Anhydrous magnesium nitrate [10377-60-3], $Mg(NO_3)_2$, is very difficult to isolate. The commercial product is the deliquescent hexahydrate [13446-18-9], $Mg(NO_3)_2 \cdot 6H_2O$. As illustrated in the solubility curve in Figure 7, the hexahydrate is the stable solid phase between−18 and 55–56°C. Properties are given in Table 16 (1–4). The unit cell contains two formula units and the calculated density is 1.643 g/cm^3.

10.2. Manufacture. Magnesium nitrate is prepared by dissolving magnesium oxide, hydroxide, or carbonate in nitric acid, followed by evaporation and crystallization at room temperature. Impurities such as calcium, iron, and aluminum are precipitated by pretreatment of the solution with slight excess of magnesium oxide, followed by filtration. Most magnesium nitrate is manufactured and used on site in other processes.

Dehydration of the hexahydrate above its melting point is generally accompanied by hydrolysis and the formation of basic nitrates such as $Mg(NO_3)_2 \cdot 4Mg(OH)_2$ [76190-42-6]. At about 400°C magnesium nitrate is converted completely to magnesium oxide and oxides of nitrogen. All magnesium nitrates are soluble in methanol and ethanol and form addition compounds with urea, aniline, and pyridine. The basic nitrates $MgO \cdot 2Mg(NO_3)_2 \cdot 5H_2O$ [75300-53-7], $2MgO \cdot Mg(NO_3)_2 \cdot 5H_2O$ [75300-52-6], and $3MgO \cdot Mg(NO_3)_2 \cdot 11H_2O$ [75300-51-5] also exist.

10.3. Handling and Safety.

Magnesium nitrate should be stored in a cool, dry place because it is hygroscopic. Magnesium nitrate is an acute skin, eye, and respiratory irritant which can be absorbed into the body via inhalation and ingestion. Ingestion of magnesium nitrate may lead to the formation of methemoglobin. Personal protection to be used when handling magnesium nitrate includes chemical safety goggles, chemical resistant gloves, and a NIOSH/MSHA approved respirator. To keep exposure to respirable dust to a minimum, mechanical exhaust is required.

Magnesium nitrate is a strong oxidizer and is incompatible with strong reducing agents and strong acids. A mixture of aluminum powder, water, and metal nitrates may explode owing to a self-accelerating reaction. Magnesium nitrate mixed with alkyl esters may explode owing to the formation of alkyl nitrates. Magnesium nitrate reacts violently with dimethylformamide, causing fire and explosion hazards. When heated to decomposition (above 330°C), magnesium nitrate may give off toxic and corrosive nitrous vapors (101,102).

10.4. Uses.

A soluble form of magnesium nitrate is used as a fertilizer in states such as Florida where drainage through the porous, sandy soil depletes the magnesium (see FERTILIZERS). Magnesium nitrate is also used as a prilling aid in the manufacture of ammonium nitrate. A 0.25–0.50% addition of magnesium nitrate to the process improves the stability of the prills and also improves durability and abrasion resistance.

Another use for magnesium nitrate is as an alternative to sulfuric acid in the purification of nitric acid. A process developed by Hercules Powder (103) combines molten magnesium nitrate containing ca 70% anhydrous $Mg(NO_3)_2$ and ca 30% water, and 60% nitric acid. These are fed to the middle of a dehydration tower. A vapor containing 90–95% nitric acid is taken from the top of the tower and distilled. The solution of 50–55% magnesium nitrate is removed from the bottom of the tower, reconstituted to 72%, and recirculated through the dehydration tower (104,105). The tower and circulation equipment must be kept above 100°C, the freezing point of liquid magnesium nitrate (104).

11. Magnesium Oxide

11.1. Properties.

Magnesium oxide, MgO, also known as magnesia [1309-48-4], occurs in nature only infrequently as the mineral periclase, most commonly as groups of crystals in marble. The principal commercial forms of magnesia are dead-burned magnesia (periclase), caustic-calcined (light-burned magnesia), hard-burned magnesia, and calcined dolomite. These materials are usually formed by the thermal decomposition or chemical reaction of various magnesium compounds including magnesite ore, magnesium hydroxide, magnesium chloride, and synthetic magnesium carbonate. Physical properties of periclase are given in Table 17 (28,34,106–109).

The properties of magnesia produced by thermal decomposition are determined by the calcination time, temperature, the nature of the magnesium-containing precursor, and other chemical compounds in the process. Increasing calcination time and temperature increases the crystallite size of the magnesia, simultaneously decreasing the surface area and reactivity of the product. Typical production conditions and resulting properties of magnesias produced from magnesium hydroxide are shown in Table 18.

Light-burned, ie, caustic-calcined magnesia is characterized by small crystallite size, relatively large surface area, and moderate to high chemical reactivity. It readily dissolves in dilute acids, and hydrates upon exposure to moisture or water. The most reactive grades combine with moisture and carbon dioxide eventually to form basic magnesium carbonates. Reactivity of light-burned magnesia is often quantified by specific surface area, iodine number, rate of reaction in acetic acid, and rate of reaction with citric acid.

Hard-burned magnesia is characterized by moderate crystallite size and moderately low chemical reactivity. Hard-burned magnesia is readily soluble only in concentrated acids.

Dead-burned magnesia, characterized by large crystallite size and very low chemical reactivity, is resistant to the basic slags employed in the metals refining industry. It reacts very slowly with strong acids, and does not readily hydrate or react with carbon dioxide unless finely pulverized.

Pure-fused magnesia is produced at extremely high (> ca 2750°C) temperatures using graphite electrodes in an electric arc furnace. Fused magnesia has extremely large crystal size and may have single crystals weighing 200 g or more. The chemical stability, strength, and abrasion resistance of fused magnesia surpass those of either light-burned or dead-burned magnesia.

11.2. Manufacture. There are many processes for producing magnesium oxide. Martin Marietta Magnesia Specialties, Inc. mines dolomitic limestone in Woodville, Ohio (see Fig. 8). The limestone is calcined at a high temperature under controlled conditions to produce calcined dolomite or dolime [50933-69-2] which upon reaction with magnesium chloride-rich brine produces magnesium hydroxide and calcium chloride. The insoluble magnesium hydroxide is then separated from the liquid calcium chloride carrier and calcined under controlled conditions. The various grades of magnesia range from very reactive light-burned to nonreactive dead-burned.

Another process, in use globally, involves the mining, crushing, sizing, and subsequent calcination of natural magnesite. The chemical purity of the magnesia produced is dependent on the mineralogical composition of the natural magnesite. This magnesia is often less pure than magnesia produced by other processes.

The seawater process (41,110–113) used by American Premier, National Magnesia Chemicals, and others, involves decarbonating limestone or dolomite to the point where all CO_2 is removed without converting the resulting magnesia to a chemically inactive form. Reaction of filtered seawater, treated to remove bicarbonate and/or sulfate, and dolime is followed by seeding with magnesium hydroxide to promote crystal growth. Upon formation of magnesium hydroxide, flocculants are added and the magnesium hydroxide precipitate is allowed to settle while the spent seawater is disposed to the sea. The precipitate is washed, filtered, and dried to obtain magnesium hydroxide which is calcined to produce light-burned, hard-burned, or dead-burned magnesium oxide.

Dead Sea Periclase Ltd., on the Dead Sea in Israel, uses yet another process to produce magnesium oxide. A concentrated magnesium chloride brine processed from the Dead Sea is sprayed into a reactor at about 1700°C (114,115). The brine is thermally decomposed into magnesium oxide and hydrochloric acid. To further process the magnesia, the product is slaked to form magnesium hydroxide which is then washed, filtered, and calcined under controlled conditions to produce a variety of MgO reactivity grades.

11.3. Health and Safety Factors. Magnesium oxide (fume) has a permissible exposure limit (PEL) (116) (8 hours, TWA), of $10\,\text{mg/m}^3$ total dust and $5\,\text{mg/m}^3$ respirable fraction. Tumorigenic data (intravenous in hamsters) show a TD_{LO} of 480 mg/kg after 30 weeks of intermittent dosing (117), and toxicity effects data show a TC_{LO} of $400\,\text{mg/m}^3$ for inhalation in humans (118). Magnesium oxide is compatible with most chemicals; exceptions are strong acids, bromine pentafluoride, chlorine trifluoride, interhalogens, strong oxidizers, and phosphorous pentachloride.

11.4. Uses. Refractory magnesia represents the largest tonnage use of magnesium in compounds. The iron and steel industry is the largest consumer of these products in the United States and most other magnesia-consuming countries. Dead-burned magnesia from magnesite, seawater, or well and lake brines is used as a principal constituent in metallurgical furnace refractory products.

In 2002, the largest end use for caustic-calcined magnesia was in preparation of intermediates (36%) (119).

Caustic-calcined magnesia has uses in many market segments. In water treatment, magnesia is used to remove silica and heavy metals from industrial wastewater. It also is used as a neutralizing agent for some wastewater streams. Caustic-calcined magnesia is used for removal of SO_2 from industrial flue gases; the magnesium oxide reacts with the SO_2 to form magnesium sulfate. Magnesia competes with calcium compounds in this application. In 2002, environmental applications accounted for 34% of U.S. shipments of caustic-calcined magnesia.

Magnesia is also used in agricultural applications for animal feed and fertilizer. Magnesium serves as a structural part of the chlorophyll molecule, a compound necessary for plant photosynthesis. Without sufficient magnesium, either from the soil or from fertilizer application, plants can die. Corn, potatoes, cotton, citrus, tobacco, and sugar beets are among the crops that are highly responsive to magnesium fertilization (120).

Pasture fertilization with magnesium-containing fertilizers also is important in animal nutrition. Grazing ruminants, such as cattle and sheep, require magnesium in their diet to guard against hypomagnesia, also known as grass tetany, a potentially fatal disease. This disease most often occurs in cool weather when the animals are grazing on grass that has had a quick growth spurt. Two of the most popular methods of introducing magnesium in cattle diets are to incorporate the magnesium with molasses in a liquid lick, or adding caustic-calcined magnesia to purchased feed. In 2002, agricultural applications (fertilizers and animal feed) accounted for 22% of U.S. shipments of caustic-calcined magnesia.

An important use of caustic-calcined magnesia is in the production of magnesium oxychloride and oxysulfate cements, which are used primarily as flooring in industrial and institutional buildings. Magnesia also is used as a stabilizer or vulcanizing agent in rubber. Fused and boron-free magnesia or periclase are used for insulation of heating elements in electric furnaces and appliances.

In the manufacturing industry, caustic-calcined magnesia is used in the production of rayon, fuel additives, and rubber. Caustic-calcined magnesia is used to produce magnesium acetate, which is used for neutralization purposes in producing rayon fiber. Caustic-calcined magnesia is a starting material for the production of magnesium overbased sulfonates, which are used as acid acceptors and sludge dispersants in crankcase lubricating oils and as a fuel additive. Magnesium oxide also may be injected into oil-fired utility boilers where it reacts with vanadium salts to form a magnesium vanadate; this alleviates slagging and corrosion problems caused when using high-vanadium fuels. In water-base oil well drilling muds, magnesia is used as a buffer, for viscosity control, and as a corrosion inhibitor. In the rubber industry caustic-calcined magnesia is used as a vulcanizing agent in the curing of rubbers and elastomers.

Most of the end markets for caustic-calcined magnesia are mature, and there is little room for significant growth. The exception to this is the environmental market, where applications in water treatment are growing. Caustic-calcined magnesia competes with magnesium hydroxide in this market. Caustic-calcined magnesia has some advantages compared with magnesium hydroxide in this use. Magnesium oxide has more neutralizing capacity per unit volume, transportation costs are generally lower, and existing systems may be more easily converted from lime to magnesia.

12. Magnesium Peroxide

12.1. Properties. Industrial production of magnesium peroxide [14452-57-4], MgO_2, involves the reaction of magnesium oxide and hydrogen peroxide (qv). A product containing not more than 50% MgO_2 is obtained (121). Another process using magnesium hydroxide yields a product containing up to 60% magnesium peroxide (121). Most users prefer magnesium peroxide having residual $Mg(OH)_2$. Magnesium peroxide is stable in a range of oxygen partial pressures wider than those where MgO is stable. Magnesia is calculated to be stable at oxygen partial pressures $>3.6 \times 10^{-188}$ Pa (3.6×10^{-200} atm) at 25°C (106). Decomposition of MgO_2 has been observed to occur at temperatures from 245 to 375°C (121,122).

12.2. Uses. Magnesium peroxide is used mainly in medicine for treating hyperacidity in the gastric intestinal tract, and in the treatment of metabolic diseases such as diabetes and ketonuria. It is also used in the preparation of toothpaste and antiseptic ointments. All of these uses involve a mixture of magnesium peroxide, magnesium oxide, magnesium hydroxide, and an admixture of magnesium carbonate. Magnesium peroxide is also used in bleaching and agricultural applications (see BLEACHING AGENTS).

13. Magnesium Phosphate

13.1. Properties. An aqueous solution of monoammonium phosphate [10361-65-6] reacts with MgO to form ammonium magnesium phosphate hexahydrate [15490-91-2], $NH_4MgPO_4 \cdot 6H_2O$. Several other species of hydrated phosphates are created during this reaction which takes place quickly and produces compounds that have desirable properties as cementing agents. The hexahydrate is the most prevalent. Properties are given in Table 19.

13.2. Uses. *Investment Castings.* Magnesium phosphate compounds are used as cementing agents for the refractory material used in high temperature dental investment castings (see DENTAL MATERIALS) (123,124). The initial ammonium magnesium phosphate compound develops strength within several hours of the onset of the cementing reaction. The casting is then dried in stages in order to develop further strength and to minimize shrinkage. Dehydration takes place initially at 50°C then proceeds up to 160°C, producing ammonium magnesium phosphate monohydrate [16674-60-5], $NH_4MgPO_4 \cdot H_2O$. The crystal structure changes during this drying step. Magnesium acts as the bonding atom between the corners of PO_4^{3-} tetrahedra. Further heating from 300 to 650°C drives off the ammonia to produce $Mg_2P_2O_7$ [13446-24-7] which results in a further reorientation of the crystal structure. Final heating of the casting to 1040°C develops the greatest strength as the compound reorients to anhydrous magnesium phosphate [10043-83-1], $Mg_3(PO_4)_2$ where three magnesium atoms act as the bonding atoms between two PO_4^{3-}tetrahedra. At this stage the processing of the dental investment is complete. These phosphate-bonded investment casting are used for the formation of noble metal alloy dental appliances. A discussion of magnesium phosphate investment cements is available (125).

Magnesium Phosphate Cements. The reaction of magnesia and various forms of ammonium phosphate has great utility in the production of fast setting concrete (126). Acceptable levels of concrete strength are developed within several hours of the initial reaction. Onset times can be varied by controlling the ratio of phosphate to polyphosphate in the starting aqueous mixture (127). The ultimate strength of the concrete is attained over a 7–28 day period through dehydration and ammonia loss.

Rapid development of concrete strength finds utility in the highway construction industry, where repairs on high volume thoroughfares may be accomplished quickly using this material. Magnesium phosphate cements are also amenable to application by pneumatic gunning equipment. Pneumatic gunning is useful for application of the cements to vertical, rounded, or irregular surfaces such as sewer pipes and exposed steel.

Additional Uses. Magnesium calcium phosphates find use as nutrient supplements in animal feeds. Magnesium pyrophosphate [13446-24-7], $P_2O_7 \cdot 3H_2O$, spray dried at 100°C, takes on a fibrous form during the drying and dehydration process (128). This fibrous material is used as a strengthening agent in plastics. Granulated ammonium magnesium phosphate, $NH_4MgPO_4 \cdot H_2O$, is used as a slow-release fertilizer providing magnesium, nitrogen, and phosphorus.

14. Magnesium Sulfate

Magnesium sulfate [7487-88-9], $MgSO_4$, is found widely in nature as either a double salt or as a hydrate. The more important mineral forms are listed in Table 20.

14.1. Properties. Physical properties of anhydrous magnesium sulfate, kieserite, and epsomite, as well as physical properties of four less prominent hydrates, are listed in Table 21. The complexity of the $MgSO_4 \cdot H_2O$ system is apparent from Figure 9. Several metastable phases exist in very close proximity to stable phases, making equilibrium difficult to achieve. The magnesium sulfate hydrates tend to form supercooled solution and metastable solid phases, hence several hydrates may coexist in aqueous solution at a given temperature. Only the mono-, hexa-, and heptahydrates are stable. Ranges of stability are -5 to 48.2°C, 48.2 to 67.5°C, and >67.5°C, respectively. As can be seen from Figure 9, the monohydrate displays inverse aqueous solubility: solubility, g/100 g saturated solution, 37.1, 8, and 0.5, at temperatures of 67.5, 170, and 240°C, respectively. The hydrates begin thermal decomposition at approximately 150°C and are often hydrolyzed to oxysulfates which are analogous to the oxychlorides, concomitantly. Hydrates decomposing in the presence of concentrated sulfuric acid yield a stable anhydrous salt. This salt starts to decompose at about 900°C and decomposes completely at 1100°C, producing MgO, O_2, SO_2, and SO_3. $MgSO_4$ decomposes in the presence of carbon at about 750°C:

$$MgSO_4 + C \longrightarrow MgO + SO_2 + CO$$

Addition of alkali such as NaOH or $Ca(OH)_2$ to $MgSO_4$ solutions precipitates magnesium hydroxide. Addition of a soluble carbonate such as Na_2CO_3 precipitates nesquehonite [14457-83-1], $MgCO_3 \cdot 3H_2O$. Insoluble magnesium salts, eg, sulfite, phosphate, or stearate, are prepared by adding the appropriate soluble, (often alkali metal) reagent to a $MgSO_4$ solution.

The reaction of MgO and $MgSO_4$ solutions produces magnesium oxysulfate cements. Oxysulfate cements, defined as Mg salts precipitated in alkaline conditions, contain both hydroxide and sulfate salt components. The crystalline forms $MgSO_4 \cdot 3MgO \cdot 11H_2O$ [65496-31-3] and $MgSO_4 \cdot 5MgO \cdot 8H_2O$ have been isolated.

Magnesium sulfate forms many double salts, including naturally occurring minerals (Table 21). The sulfuric acid double salts $MgSO_4 \cdot H_2SO_4$ [10028-26-9], $MgSO_4 \cdot H_2SO_4 \cdot 3H_2O$ [75198-53-7], and $MgSO_4 \cdot 3H_2SO_4$ [39994-66-6] are crystallized from solutions of $MgSO_4$ in H_2SO_4. The amine double salts $MgSO_4 \cdot NH_3 \cdot 3H_2O$ [75198-54-8], $MgSO_4 \cdot 2NH_3 \cdot 4H_2O$ [75198-56-0], and $MgSO_4 \cdot 2NH_3 \cdot 2H_2O$ [75198-55-9] are products of $MgSO_4 \cdot 7H_2O$ and gaseous ammonia.

14.2. Manufacture and Processing. Anhydrous $MgSO_4$ can be prepared only by dehydration of a hydrate. Crystallization from aqueous solution is not possible. Aqueous solutions of $MgSO_4$ can be prepared by dissolving

MgO, $Mg(OH)_2$, or $MgCO_3$ in sulfuric acid; or absorbing SO_2 using a $Mg(OH)_2$ slurry to form the soluble bisulfite, $Mg(HSO_3)_2$, followed by air oxidation to SO_4^{-2}.

Technical-grade epsom salt is prepared by dissolving MgO, $Mg(OH)_2$, or $MgCO_3$ in sulfuric acid. The reaction mixture is crystallized to separate the product. In one process $MgSO_4$ solution is recycled from crystallizers to a reaction vessel containing sulfuric acid and low reactivity MgO. After pH adjustment to slightly acidic conditions and a 4–5 h reaction time, a 34% $MgSO_4$ mother liquor at 82°C is produced. Iron is precipitated and insolubles are filtered from the mother liquor. Epsom salt is crystallized at 15°C and screened; the 24% $MgSO_4$ filtrate is recycled. The epsom salt crystals are dried at low temperature in a rotary oven. Following filtration, the 34% mother liquor can be diluted to 24% and sold as a solution. The theoretical yield is 1 t of epsom salt per ton MgO. The actual yield depends on particle size, reactivity, and purity of the MgO. The heat of reaction is often the determining factor for using MgO or $Mg(OH)_2$ as the reagent. The $Mg(OH)_2$ reaction generates only 65–75% of the heat that the MgO reaction does.

To prepare a USP-grade epsom salt, higher purity MgO or $Mg(OH)_2$ is used. USP and food grades require low chloride levels, limiting allowable chloride content of the MgO to 0.08 wt %. Trace impurities including iron and aluminum are precipitated using excess MgO. Following crystallization, the epsom salt is washed free of mother liquor.

14.3. Uses.

Natural and synthetic magnesium sulfate have a wide array of uses. The largest use for magnesium sulfate in all forms is for consumer goods. About 30% of magnesium sulfate is used in food additives and pharmaceuticals. Magnesium sulfate heptahydrate, epsom salts, is used for mineral baths and in medicine as a cathartic and analgesic soaking agent for bruises, sprains, localized inflammations, and insect bites. Magnesium sulfate is used as a micronutrient in some food products, and it is used in the production of high fructose corn syrup (HFCS). In the early 1980s, replacement of most or all of the sugar by HFCS in soft drinks was expected to increase the market for HFCS dramatically, and as a consequence, boost magnesium sulfate consumption by as much as 5% per year. Although some sugar has been replaced, the high estimates of growth for magnesium sulfate in this application did not materialize.

Industrial uses account for about 25% of U.S. magnesium sulfate demand. The primary component of industrial applications is the use of magnesium sulfate as a precursor to other chemicals. It also is used in drying and fluocculation applications and in catalyst preparation.

Animal feeds and fertilizers represent about 22% of the U.S. market for magnesium sulfate. Most applications for magnesium sulfate use synthetically produced material because of its higher purity. Purity requirements for animal feeds and fertilizers are not as stringent, so they use mainly the natural minerals, which are imported into the United States. The most effective way of preventing grass tetany is to provide magnesium to the pasture through fertilization. Magnesium also may be supplied in the form of epsom salts or kieserite that is added to the feed or drinking water.

In addition to pasture grasses, most crops require magnesium because magnesium is an essential constituent of the chlorophyll molecule. The average uptake of magnesium for field crops ranges from 10 to 30 lb/acre annually, with root crops requiring about double that of grain crops. Most nitrogen–phosphorus–potassium fertilizers have very little magnesium in them, so magnesium is supplied through foliar application of epsom salts, kieserite, sulfate of potash magnesia, or magnesium oxide. Magnesium fertilizer applications range from 20–50 lb/acre.

Pulp and paper processing accounts for about 14% of magnesium sulfate use in the United States. Magnesium sulfate is used by kraft pulp mills that use oxygen delignification on soft woods, but it is also used in conjunction with sodium silicate to increase the life of hydrogen peroxide in oxygen-based bleaching processes. Miscellaneous use, which represent about 9% of magnesium sulfate demand, include textiles, matches, photographic solutions, rubber coagulation, refractory bonding agent in bricks, and oxysulfate cements Figure 10 shows a process for cement board (129).

15. Magnesium Sulfite

15.1. Properties. The white hexahydrate [13446-29-2], $MgSO_3 \cdot 6H_2O$, is prepared by adding an excess of sulfur dioxide, SO_2, to a suspension of magnesium hydroxide, $Mg(OH)_2$, or basic magnesium carbonate, [12306-51-3], $5MgO \cdot 4CO_2 \cdot 5H_2O$. The formation of magnesium bisulfite (magnesium hydrogen sulfite), $MgHSO_3$, unisolable in solid form, in the presence of excess SO_2 increases the solubility of magnesium sulfite in the liquid phase. In dilute solutions of both magnesium sulfite and magnesium bisulfite, the solubility of magnesium sulfite increases with increasing temperature independent of $MgHSO_3$ concentration. The basic salt $11MgSO_3 \cdot 2Mg(OH)_2 \cdot 22H_2O$ forms as dilute solutions of magnesium sulfite are heated.

The $MgSO_3 \cdot H_2O$ system is shown in Figure 11 and the properties of the tri- and hexahydrate are listed in Table 22.

15.2. Uses. *Flue Gas Desulfurization.* The system $Mg(OH)_2 \cdot SO_2 \cdot H_2O$ is employed in the scrubbing process for removing SO_x from flue gases (see SULFUR REMOVAL AND RECOVERY) (130). The equilibria involved in scrubbing has been studied in detail (131).

Typically flue gas containing 50–200 ppm SO_x is scrubbed in a venturi absorber. The absorbing medium is an aqueous slurry of $Mg(OH)_2$ also containing magnesium sulfite [7757-88-2], $MgSO_3$, and $MgSO_4$. Centrifuging can be used to remove magnesium sulfite (usually a mixture of the tri- and hexahydrate), some unreacted $Mg(OH)_2$, and some adhering $MgSO_4$ from the slurry. The solids can be dried and calcined to recover MgO and SO_2 for reuse. MgO is reused in the scrubber, and SO_2 can be used to produce sulfuric acid (132).

Wood Pulping. The system $Mg(OH)_2 \cdot SO_2 \cdot H_2O$ is also used in acid bisulfite pulping. Compared to a calcium-based system which is not as amenable to regeneration of the pulping bisulfite (130), fewer technical problems are encountered in the digesters, evaporators, or recovery boiler of the Mg-based process. In the presence of excess SO_2, bisulfite forms in a 43% $MgSO_3$ solution, at 25°C and 101.3 kPa (1 atm) SO_2 pressure, to increase $MgSO_3$ solubility.

An acid bisulfite solution containing excess SO_2 is used as the pulping liquor in a few sulfite mills often devoted to dissolving pulp. By using excess sulfites, the lignin (qv) can be dissolved completely and removed leaving the cellulose behind. The black liquor that contains the inorganic salts and lignin after pulping can be concentrated to about 55% solids in multiple-effect evaporators and burned in a heat recovery boiler, at the same time recovering the pulping chemicals. Gases exiting the recovery boiler contain MgO that is recovered in cyclones and SO_2 that is absorbed in $Mg(OH)_2$ slurry.

16. Magnesium Sulfonates

Magnesium sulfonates are detergents containing magnesium carbonate or magnesium complexes as the metallic portion, and an oil-soluble magnesium-based substrate, dispersed as a colloid in petroleum oil. By definition a soap is commonly the sodium or potassium salt of a high molecular weight fatty acid. The term metallic soap refers to substitution of another metal for the sodium, in this case, magnesium.

Classification of detergents reflects their alkalinity. Magnesium sulfonates may be either neutral or overbased. Overbasing is the process of preparing oil-soluble detergents containing up to 30 times as much metal as the normal neutral detergents (133). These methods, discovered in the early 1950s, have led to the development of extensive patents. (More than 80 related U.S. patents have been issued since 1963.) The degree of overbasing is defined in part by total base number (TBN) which refers to the equivalent amount of potassium hydroxide, KOH, contained in the material. A base number of 100 corresponds to 2.14% Mg; for magnesium sulfonates a TBN of 300–400 is typical.

The overbasing process generally involves the addition of magnesium oxide to oil, solvent, a promoter, and water in a reflux vessel. Sulfonic acid is added to neutralize about 10% of the MgO. The resulting magnesium sulfonate acts as a crystal modifier to produce colloidal magnesium carbonate when carbon dioxide is bubbled through the mixture. The resulting product is equivalent to 10–16% MgO by weight. Approximately 90% of the magnesia is present as submicrometer, colloidal particles of $MgCO_3$, fine enough to preserve optical clarity. The magnesium sulfonate detergent accounts for the remaining 10% of magnesia. Filtration or centrifugation are used to remove any unreacted material or sludge followed by distillation to remove the solvent. In another process (134), noncarbonated magnesium sulfonates are prepared by heating a mixture of magnesium compounds, an oleophilic reagent containing a sulfonic acid, water, and an organic solubilizing agent above 30°C. The resulting product may be in liquid or in gel form.

Principal uses of magnesium sulfonates are as additives to engine oils, automatic transmission fluids, gear oils and industrial oils (see HYDRAULIC FLUIDS). In engine lubricating oils, in concentrations of 1–2%, the primary function is as a sludge dispersant and neutralizer of acidic contaminants from partially oxidized fuels, oil degradation products, and NO_x. The noncarbonated forms may be used also in corrosion-resistant coatings for metals, and as liquid fuel additives, in smoke suppression and in vanadium scavenging (134).

17. Magnesium Vanadates

Several forms of magnesium vanadates have been characterized. Some physical properties are summarized in Table 23 (26–28) (see also VANADIUM AND VANADIUM ALLOYS).

Fuels from areas having natural deposits of vanadium, such as Venezuela (131), may contain significant amounts of this metal which results in deposition of vanadium compounds in the boiler as the fuels are burned (see PETROLEUM). In 1963 the Long Island Lighting Co. (LILCO), Mineola, New York, began injecting magnesium oxide fuel additives to control corrosion and slagging problems in the power utility boilers and acid stack emissions. These additives produce magnesium vanadates and affect the type of slag produced, reducing slag adherence to heat-exchange surfaces, and facilitating removal (131).

The recovery of vanadium from these slags is of commercial interest because of the depletion of easily accessible ores and the comparatively low concentrations (ranging from less than 100 ppm to 500 ppm) of vanadium in natural deposits (131,132). In the LILCO applications the total ash contained up to 36% V_2O_5 (131). Vanadium is of value in the manufacture of high strength steels and specialized titanium alloys used in the aerospace industry (132,135). Magnesium vanadates allow the recovery of vanadium as a significant by-product of fuel use by electric utilities (see RECYCLING, NONFERROUS METALS).

17.1. Health and Safety Factors.

Magnesium vanadates, as vanadium compounds in general, are known irritants of the respiratory tract and conjunctiva. The threshold limit value (TLV) for vanadium compounds in air recommended by the National Institute of Occupational Safety and Health is 0.05 mg/m^3 based on a typical 8-h workday and 40-h workweek (16,131). Chronic inhalation can lead to lung diseases such as bronchitis, bronchopneumonia, and lobar pneumonia. These dust-related effects can be avoided by use of individual respirators in areas where exposure is likely.

18. Economic Aspects

Magnesium oxide is the most commercially important of the magnesium compounds. China was the largest producer from natural magnesite, accounting for nearly half of the magnesium oxide produced. The United States and Japan account for more than half of the world's magnesium compound production from seawater or brines. In Asian regions other than China or Japan, it is believed that natural ores are not available and that the producers manufacture magnesium chemicals from seawater, bittern, or purchased magnesium chemicals (136).

Refractories comprise the largest use of magnesium so the health of the industries that use magnesia-base refractories is the most important determinant in the U.S. consumption of magnesia. The iron and steel industry is the principal consumer of these refractories (119).

The market for magnesium hydroxide will continue to grow. Slurries for water treatment and powder for flame retardants have been at overcapacity, Slurries will grow at the rate of 3–5%/yr through 2006. Demand for powder is steady and should remain stable (119).

Magnesium sulfate imports from Germany have had an impact on the U.S. market. Magnesium sulfate is used in the consumer market for personal care products and as a secondary nutrient for garden lawns. The use of epsom salts should grow at the rate of 6%/yr. Use in agriculture (15% of total) is used in feed supplements for farm animals to prevent grass tetany (119).

Table 24 and 25 give salient economic data for the United States. Table 26 gives U.S. export data. Table 27 gives U.S. import data. Table 28 gives information on magnesium compounds shipped and used in the U.S.

Overall, worldwide consumption of magnesium chemicals has been consistent over the years and is not expected to change.

19. Environmental Concerns

Magnesite and dolomite normally can be mined without interfering with other land use. Mine drainage from open pit or underground operations does not contribute significantly to stream pollution, since the drained areas usually contain no significant amounts of soluble materials. Dust collectors and wet scrubbers are used to control stack gas dust emissions from plants calcining and dead-burning dolomite, magnesite, and magnesium hydroxide.

In metal and magnesia plants, based on seawater, the water is returned to the ocean after the magnesia is removed. Recent innovations have decreased the turbidity of the effluent, resulting in minimal changes to the ocean environment. None of the discharges from either natural or synthetic magnesia plants has a noxious quality, and their apperance can be made acceptable with modern treatment methods.

Most magnesium compounds are treated as nuisance-causing dusts in the workplace. The American Conference of Government and Industrial Hygienists has established threshold limit values (TLV) for magnesium oxide fume and magnesium carbonate. The TLV for both substances has been established at 10 parts per million. TLV's for magnesium chloride and magnesium sulfate have not been established (138). The Occupational Safety and Health Administration has set permissible exposure limits (PELs) for magnesium carbonate and magnesium oxide fume. The PEL for magnesium oxide fume was established at 10 mg/m^3 (total particulate), with a PEL of 5 mg/m^3 for the respirable particulate (139). The PEL for magnesium carbonate (magnesite) has been set at 15 mg/m^3 for the total particulate and 5 mg/m^3 for the respirable particulate (140).

Because of the chromium content in the material, magnesia-chrome bricks must be disposed of as a hazardous waste if an extract from a representative sample contains total chromium at a concentration greater than, or equal to, 5.0 mg/L. The waste can be treated by chemical leaching or washing to dilute the concentration, but these options are costly, and if washing is used, the waste water must also be treated. Another alternative for treatment is high temperature reprocessing, but few firms have the treatment facilities necessary for this operation (141).

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Table 1. **Physical Properties of Magnesium Acetates**[a]

Property	α-Mg-$(C_2H_3O_2)_2$	β-Mg-$(C_2H_3O_2)_2$	$Mg(C_2H_3O_2)_2\cdot H_2O$	$Mg(C_2H_3O_2)_2\cdot 4H_2O$	β–Mg—- $(C_2H_3O_2)_2\cdot 4H_2O$
mol wt	142.40	142.40	160.38	214.46	214.46
crystal system	orthorhombic	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$		$P2_1cn$ or Pmcn	$P2_1/A$	
lattice constants, nm					
a	1.127	1.034	1.175	0.8550	1.296
b	1.501	1.295	1.753	1.1995	0.7647
c	1.100	0.7726	0.6662	0.4807	1.017
angle, degree					
α		112.02			
β		94.53		95.37	113.84
γ		95.80			
Z[b]	12	6	8	2	4
density, g/cm^3					
calculated	1.524		1.553	1.453	1.545
observed	1.507	1.502		1.454	
mp, °C	323 dec			80	
color	white	white			

[a] Refs. 1–3.

[b] Number of formulas per unit cell.l

Table 2. **Physical Properties of Magnesium Bromide and Magnesium Bromide Hexahydrate**[a]

Property	$MgBr_2$	$MgBr_2 \cdot 6H_2O$
mol wt	184.13	292.22
crystal system	hexagonal	monoclinic
space group	$P\bar{3}m1$	C_2/m
lattice constants, nm		
a	0.3822	1.0286
b		0.7331
c	0.6269	0.6211
angle, β degree		93.34
Z[b]	1	2
density, calculated, g/cm^3	3.855	2.076
mp, °C	711	174.2
color	white	colorless
heat of formation, ΔH_{298}, kJ/mol[c]	−524.3	−2410.0
free energy of formation, ΔG_{298}, kJ/mol[c]	−503.8	2056.0

[a] Refs. 26–28.

[b] Number of formulas per unit cell.

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

Table 3. **Physical Properties of Magnesium Carbonates**[a]

Parameter	Magnesite	Barringtonite	Nesquehonite	Lansfordite
mol wt	84.32	120.35	138.37	174.4
crystal system	hexagonal	triclinic	monoclinic	monoclinic
space group	R3c		$P2_1/n$	$P2_1/n$
lattice constants, nm				
a	0.46332	0.9115	1.2112	
b		0.6202	0.539	
c	1.5015	0.6092	0.77697	
angle, degree				
α		94.00		
β		95.53	90.42	
γ		108.87		
Z[b]	6	4	4	
density, calculated, g/cm^3	3.009	2.825	1.837	1.730
hardness, Mohs'	3.5–5.0		2.5	2.5
color	white	colorless	colorless to white	white
melting point, °C	402–480[c]			
index of refraction	1.510, 1.700	1.458, 1.473, 1.501	1.412, 1.501, 1.526	1.456, 1.476, 1.502
heat of formation, ΔH_{298}, kJ/mol[d]	−1095.8			
free energy of formation, ΔG_{298}, kJ/mol[d]	−1012.1		−1726.3	−2199.5

[a] Refs. 3, 28, 33–37.

[b] Number of formulas per unit cell.

[c] Material decrepitates.

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

Table 4. **Physical Properties of Basic Magnesium Carbonates**[a]

Parameter	Artinite	Hydromagnesite	Dypingite	Octahydrate
mol wt	196.70	467.67	485.69	539.74
crystal system	monoclinic	monoclinic	monoclinic	
space group	C_2 or C_2/M	$P2_1/C$		
lattice constants, nm				
a	1.656	1.011		
b	0.315	0.894		
c	0.622	0.838		
angle, β degree	99.15	114.58		
Z^b	2	2		
density, calculated, g/cm^3	2.039	2.254		
hardness, Mohs'	2.5	3.5		
color	white	white	white	white to gray
index of refraction	1.488, 1.534, 1.556	1.458, 1.473, 1.501	1.412, 1.501, 1.526	1.456, 1.476, 1.502

[a] Refs. 3,28,33–37.

[b] Number of formulas per unit cell.

Table 5. **Double Salts of Magnesium Carbonate**[a]

Salt	CAS Registry number	Salt	CAS Registry number
$MgCO_3 \cdot MgCl_2 \cdot 7H_2O$	[11140-13-9]	$MgCO_3 \cdot K_2CO_3 \cdot 8H_2O$	[75198-51-5]
$MgCO_3 \cdot MgBr_2 \cdot 8H_2O$	[75198-49-1]	$MgCO_3 \cdot KHCO_3 \cdot 4H_2O$	[19154-48-4]
$MgCO_3 \cdot MgBr_2 \cdot 7H_2O$	[75198-50-4]	$MgCO_3 \cdot Rb_2CO_3 \cdot 4H_2O$	[75198-52-6]
$MgCO_3 \cdot NH_4CO_3 \cdot 4H_2O$	[22450-55-1]	$MgCO_3 \cdot Na_2CO_3$	[19086-68-1]

[a] Ref. 40.

Table 6. **World Magnesite Reserves and Reserve Base 10^3 t (contained Mg), 2003**[a]

Country	Reserves	Reserve base
Australia	100	120
Austria	15	20
Brazil	45	65
China	380	860
Greece	30	30
India	14	55
Korea, North	450	750
Russia	650	730
Slovakia	41	319
Spain	10	30
Turkey	65	160
United States	10	15
Other countries	390	440
Total[a,b]	2200	3600

[a] Ref. 44

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

Table 7. **Physical Properties of Magnesium Chloride**[a]

Property	$MgCl_2$	$MgCl_2 \cdot 6H_2O$
mol wt	95.22	203.31
crystal system	hexagonal	monoclinic
space group	$R\overline{3}m$	C_2/m
lattice constants, nm		
a	0.3632	0.9871
b		0.7113
c	1.7795	0.6079
angle, β degree,		93.74
Z[b]	3	2
density, calculated, g/cm^3	2.333	1.585
mp, °C	708	116–118 dec
index of refraction	1.675, 1.59	1.498, 1.505, 1.525
color	white lustrous	colorless
heat of formation, ΔH_{298}, kJ/mol[c]	−641.3	−2499.0
free energy of formation, ΔG_{298}, kJ/mol[c]	−591.8	−2115.0

[a] Refs. 26–28.

[b] Number of formulas per unit cell.

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

Table 8. **Magnesium Chloride Brine Characteristics**[a]

Chemical composition	Weight %
$MgCl_2$	28.0–35.0
Cl	19.8–27.0
Mg	6.8–9.2
SO_4	1.2–3.5
Na	0.2–1.0
K	0.1–0.8
Li	0.1–0.2
Br	0.1–0.2
Fe	5–10 ppm
specific gravity	1.27–1.36 g/L
bulk density	11 lb/gal

[a] From Reilly Industries Inc.

Table 9. **Chemical and Physical Properties of Magnesium Fluoride**

Property	Value	Reference
melting point, °C	1263	63
boiling point, °C	2227	63
standard heat of formation, kJ/mol[a]	−112.4	64
standard entropy of formation, J/(mol · K)[a]	178	65
heat of fusion, kJ/mol[a]	58.2	63
heat of vaporization, kJ/mol[a]	264	65
lattice energy, kJ/mol[a]	2920	65
heat capacity, 25°C, J/(mol · K)[a]	61.59	63
free energy of solution, kJ/mol[a]	40.2	65
density, g/cm^3	3.127	66
index of refraction[b]		
n_o[c]	1.37770	67
n_e	1.38950	67
crystalline form (sellaite)	tetragonal	66
a, nm	0.4623	
c, nm	0.3052	
solubility, g/100 g of solvent		
water, 25°C	0.013	68
hydrogen fluoride, 12°C	0.025	69
acetic acid, 25°C	0.681	70

[a] To convert kJ to kcal, divide by 4.184.

[b] *o*, ordinary;*e*, extraordinary.

[c] At 589 nm.

Table 10. **Physical Properties of Magnesium Hydroxide**[a]

Property	Value
mol wt	58.32
crystal system	hexagonal
space group	P $\overline{3}$ ml
lattice constants, nm	
a	0.3147
c	0.4769
Z[b]	1
density, g/cm^3	
$Mg(OH)_2$	2.36
brucite	2.38–3.40
index of refraction	1.559, 1.580
color	colorless to white
hardness, Mohs'	2.5
melting point, °C	
brucite	dec 268[c]
$Mg(OH)_2$	dec 350[c]
solubility,[d] mg/L	
25°C	11.7
100°C	4.08
solubility product, K_{sp}, at 25°C	5.61×10^{-12}
heat of formation,ΔH_{298}, kJ/mol[e]	−924.54
free energy of formation,ΔG_{298} kJ/mol[e]	−833.58
C_p,298, J/(mol · K)[e]	77.03

[a] Refs. 3,36.

[b] Number of formulas per unit cell.

[c] Begins to lose H_2O.

[d] There is only fair agreement between data of various authors. See Ref. 70.

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

Table 11. **Typical Composition of Michigan Brine and Seawater, g/L**[a]

Component	Michigan brine	Seawater
$MgCl_2$	8.2	4.176
$MgSO_4$		1.668
$MgBr_2$		0.076
$CaCl_2$	13.64	
$CaSO_4$		1.268
NaCl	5.45	27.319
KCl	0.48	
K_2SO_4		0.869
Br_2	0.2134	
specific gravity	1.264	1.024

[a] U.S. Bureau of Mines.

Table 12. **$Mg(OH)_2$ Container Loadings**

Container	Tote	Bulk truck	Bulk railcar
capacity, L	1,040	14,080	60,600
capacity, kg	1,560	21,100	90,700
$Mg(OH)_2$, kg	885	11,980	51,500

Table 13. **Properties of Magnesium Hydroxide Slurries**

Property	Normal grade[a]	Ultrastable grade[b]
	Slurry properties	
delivery/application	bulk	packaged
$Mg(OH)_2$, wt %	55–58	55–58
$Mg(OH)_2$, kg/L	0.799–0.844	0.799–0.844
bulk density, g/cm^3	1.451–1.499	1.451–1.499
viscosity, mPa(= cP)	100–300	200–400
heat capacity, J/g[c]	2.7	2.7
	Dry solids basis	
$Mg(OH)_2$, wt %	98.7	98.7
surface area, m^2/g	10–14	10–14
mean particle size, μm	1.5–3	1.0–3
	Particle size, cumulative wt %	
passing 325 mesh (−44 μm)	99.5	99.8

[a] Martin Marietta Magnesia Specialties, Inc. FloMag H.

[b] Martin Marietta Magnesia Specialties, Inc. FloMag HUS.

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

Table 14. **Properties of Commercial-Grade Magnesium Hydroxide Powders**

Property	Technical grade[a]	Controlled particle size (CPS)[b]	CPS-ultrafine (UF)[c]	USP[d]
		Powder properties		
$Mg(OH)_2$, wt %[e]	95.0	95.0	95.0	95.0–100[f]
Ca, wt %[g]	1.0	1.0	1.0	0.7
moisture at 105°C, wt %[g]	2.0	1.6	1.6	2.0
mean particle size, μm	35–50	15–25	10 ± 5	
surface area, m^2/g	50–80	60–80	60–80	
		Particle size, cumulative wt %		
passing 100 mesh (−149 μm)	100	100	100	
passing 325 mesh (−44 μm)			99	

[a] Barcroft Technical Grade.

[b] Barcroft CPS Grade.

[c] Barcroft CPS-UF Grade.

[d] Barcroft USP Grade.

[e] Minimum value.

[f] On dry basis.

[g] Maximum value.

Table 15. **Physical Properties of Magnesium Iodide and Hydrates**[a]

Property	MgI_2	$MgI_2 \cdot 6H_2O$	$MgI_2 \cdot 8H_2O$
mol wt	278.12	386.21	422.24
crystal system	hexagonal	monoclinic	orthorhombic
space group	$P\bar{3}m1$	C	Aca
lattice constants, nm			
a	0.4148	1.1159[b]	0.9948
b		0.7740	1.5652
c	0.6894	0.6323	0.8585
Z[c]	1	2	4
density, calculated, g/cm^3	4.496	2.353	2.098
mp, °C	637 dec		43.5
color	white	white	white
heat of formation, ΔH_{298}, kJ/mol[d]	−364.0		
free energy of formation, ΔG_{298}, kJ/mol[d]	−358.2		

[a] Refs. 26–28.

[b] The angle β is 93.12°.

[c] Number of formulas per unit cell.

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

Table 16. **Physical Properties of Magnesium Nitrates**[a]

Property	$Mg(NO_3)_2$	$Mg(NO_3)_2 \cdot 6H_2O$
mol wt	148.32	256.38
crystal system		monoclinic
space group		$P2_1/c$
mp, °C		89
heat of formation, ΔH_{298}, kJ/mol[b]	−790.7	−2613.3
free energy of formation, ΔG_{298}, kJ/mol[b]	−589.5	2080.7

[a] Refs. (1–3) and 34.

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

Table 17. **Physical Properties of Periclase**

Property	Value
mol wt	40.304
crystal form	fcc
lattice constant, nm	0.42
density,[a] g/cm^3	3.581
index of refraction	1.732
hardness, Mohs'	5.5–6.0
melting point, °C	2827 ± 30
thermal conductivity at 100°C, J/(s · cm · °C)[b]	0.360
electrical resistivity, Ω · cm	
at 27°C	1.3×10^{15}
727°C	2×10^{7}
1727°C	4×10^{2}
specific heat, kJ/(kg · K)[b]	
at 27°C	0.92885
227°C	1.1255
727°C	1.2719
1727°C	1.3389
2727°C	1.3598
heat of fusion at 2642°C kJ/mol[b]	77.4
heat of formation, ΔH_{298}, kJ/mol[b]	−601.7
free energy of formation, ΔG_{298}, kJ/mol[b]	−569.44
aqueous solubility, g/100 mL	
at 20°C	0.00062
30°C	0.0086

[a] Determined by x-ray.

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

Table 18. **Production Conditions and Resultant Magnesia Properties**

Magnesia	Calcination temperature, °C	Surface area,[a] m^2/g	Crystallite size, μm	Porosity, %
light-burned	< 950	$1 - 200^+$	< 0.5	70–80
hard-burned	1090–1650	0.1–1	1–20	40–50
dead-burned	> 1800	< 0.1	> 40	0–5

[a] Brunauer, Emmett, and Teller (BET) method.

Table 19. **Physical Properties of Magnesium Phosphates**[a]

Property	Farringtonite	Dittmarite	Struvite
CAS Registry number	[10043-83-1]	[16674-60-5]	[1309-48-4]
molecular formula	$Mg_3(PO_4)_2$	$NH_4MgPO_4 \cdot H_2O$	$NH_4MgPO_4 \cdot 6H_2O$
mol wt	262.85	155.33	245.40
crystal system	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	$Pmn2_1$	$Pm2_1n$
lattice constants, nm			
a	7.60	5.606	6.945
b	8.23	8.758	11.208
c	5.08	4.788	6.1355
Z[b]	2	2	2
density, calculated, g/cm^3	2.76	2.19	1.706
hardness, Mohs’		2	2
color	white to yellow	colorless	colorless to white
melting point, °C	1184		decrepitates
index of refraction	1.540, 1.544, 1.559	1.549, 1.569, 1.571	1.495, 1.496, 1.504

[a] Refs. 28,35 and 37.

[b] Number of formulas per unit cell.

Table 20. **Minerals Containing Magnesium Sulfate**

Mineral name	CAS Registry number	Formula
kieserite	[14168-73-1]	$MgSO_4 \cdot H_2O$
starkeyite	[24378-31-2]	$MgSO_4 \cdot 4H_2O$
pentahydrite	[15553-21-6]	$MgSO_4 \cdot 5H_2O$
hexahydrite	[13778-97-7]	$MgSO_4 \cdot 6H_2O$
epsomite	[10034-99-8]	$MgSO_4 \cdot 7H_2O$
vanthoffite	[15557-33-2]	$3Na_2SO_4 \cdot MgSO_4$
bloedite	[15083-77-9]	$Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$
langbeinite	[13826-56-7]	$K_2SO_4 \cdot 2MgSO_4$
leonite	[15226-80-9]	$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$
schoenite	[15491-86-8]	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$
kainite	[67145-93-1]	$4KCl \cdot 4MgSO_4 \cdot 11H_2O$
polyhalite	[15278-29-2]	$K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$

Table 21. **Physical Properties of Magnesium Sulfates and Magnesium Sulfate Hydrates**[a]

Property	$MgSO_4$	Kieserite	Epsomite			$MgSO_4 \cdot 3H_2O$	Starkeyite
	Pentahydrate	Hexahydrate					
mol wt	120.37	138.38	246.48	174.42	192.44	210.45	228.47
crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic	monoclinic	triclinic	monoclinic
space group	Cmcm	C_2/n	$P2_12_12_1$	PbCa	$P2_1/n$	$P\bar{1}$	A_2/a
lattice constants, nm							
a	0.5182	0.690	1.186	0.820	0.7902	0.6335	2.2442
b	0.7893	0.771	1.199	1.093	1.3594	1.055	0.7216
c	0.6506	0.754	0.6858	1.242	0.5920	0.6075	1.0119
angle, β degree		116.09			90.89	109.88	98.28
Z^b density, g/cm^3	4	4	4	8	4	2	8
calculated	2.908	2.571	1.678	2.082	2.009	1.904	1.718
observed	2.93		1.677			1.896	1.757
index of refraction	1.557, 1.582	1.520, 1.533, 1.584	1.4325, 1.4554, 1.4609	1.495, 1.497, 1.498	1.490, 1.491, 1.497	1.482, 1.492, 1.493	1.426, 1.453, 1.456
color	white	colorless	colorless		colorless	colorless	colorless
heat of formation, ΔH_{298}, kJ/mol[c]	−1284.9	−1602.1	−3388.6		−2496.6		−3087.0
free energy of formation, ΔG_{298}, kJ/mol[c]	−1170.7	−1428.8	−2871.9				−2632.2

[a] Refs. 3 and 35.

[b] Number of formulas per unit cell.

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

Table 22. **Properties of Magnesium Sulfite Tri- and Hexahydrates**[a]

Property	$MgSO_3 \cdot 3H_2O$	$MgSO_3 \cdot 6H_2O$
CAS Registry number	[19086-20-5]	[13446-29-2]
mol wt	158.42	212.47
crystal system	orthorhombic	hexagonal
space group	$Pbn2_1$	R3
lattice constants, nm		
a	0.939	0.88385
b	0.9584	
c	0.5523	0.9080
Z[b]	4	3
calculated density, g/cm^3	2.117	1.723
mp, °C		200 dec
index of refraction	1.552, 1.555, 1.595	1.464, 1.511
color	colorless	white
heat of formation, ΔH_{298}, kJ/mol[c]	−1931.8	−2817.5

[a] Refs. 3,35.

[b] Number of formulas per unit cell.

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

Table 23. **Physical Properties of Magnesium Vanadates**[a]

Property	$Mg_{1.9}V_3O_8$	MgV_3O_8	$Mg_2V_2O_7$	$Mg_3V_2O_8$
CAS Registry number		[12181-49-6]	[13568-63-3]	[13568-68-8]
mol wt	327.01	305.12	262.50	302.79
crystal system	monoclinic	orthorhombic	triclinic	orthorhombic
space group	C2/Cm/C2/m	IC2a/Icma	$P\overline{1}$	Aba2
lattice constants, nm				
a	1.0293	1.428	1.3767	0.831
b	0.853	0.840	0.5414	1.142
c	0.7744	0.986	0.4912	0.606
angle, degree				
α			81.42	
β	119.5		106.82	
γ			130.33	
Z^b	2	4	2	4
density, g/cm^3				
calculated	3.41	3.42	3.26	3.473
observed	3.37	3.39	3.1	
heat of formation ΔH_{298}, kJ/mol[c]			−2835.9	
free energy of formation ΔG_{298}, kJ/mol[c]			−2645.3	

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[a] Refs. 26–28.

[b] Number of formulas per unit cell.

[c] To convert J to cal divide by 4.184.

Table 24. **U.S. Salient Statistics For Magnesium Compounds**[a,b]

Sector	1999	2000	2001	2002	2003[c]
production	395	370	388	312	285
imports for consumption	321	395	307	337	350
exports	52	56	62	66	50
consumption, apparent	664	709	634	583	585
stocks, producer, yearend[d]	NA	NA	NA	NA	NA
employment, plant number[c]	550	450	450	450	370
net import reliance[e] as a percentage of apparent consumption	41	48	39	46	51

[a] Ref. 44.

[b] Data in $\times 10^3$ t of magnesium content.

[c] Estimated.

[d] Not available.

[e] Defined as imports − exports + adjustments for government and industry stock changes.

Table 25. **U.S. Magnesium Compound Producers, by Raw Material Source, Location, and Production Capacity, in 2002**[a]

Raw material source	Producing company	Location	Capacity, t of MgO equivalent[b]	Products
brucite	Applied Chemical Magnesias Corp.	Van Horn, Texas, and Bullhead City, Ariz.	25,000	magnesium hydroxide
magnesite	Premier Chemicals LLC	Gabbs, Nev.	140,000	caustic-calcined and dead-burned magnesia
lake brines	Great Salt Lake Minerals Corp.	Ogden, Utah	106,000	magnesium chloride and magnesium chloride brines
	Reilly Industries Inc.	Wendover, Utah	45,000	magnesium chloride brines
well brines	The Dow Chemical Co.[c]	Ludington, Mich.	214,000	magnesium hydroxide
	Martin Marietta Magnesia Specialties LLC[d]	Manistee, Mich.	297,000	caustic-calcined and dead-burned magnesia
	Rohm and Haas Co.	Manistee Mich.	25,000	magnesium carbonate, magnesium hydroxide, and caustic-calcined magnesia
seawater	Premier Chemicals LLC	Port St. Joe, Fla.	75,000	caustic-calcined magnesia and magnesium hydroxide
	SPI Pharma Inc.	Lewes, Del.	5,000	magnesium hydroxide
	Western Salt Co.	Chula Vista, Calif.	3,000	magnesium chloride brines
	Total		*935,000*	

[a] From Ref. 119.

[b] Data are rounded to no more than three significant digits; may not add to total shown.

[c] Most of Dow's production was shipped to ANH Refractories Co. in Ludington, Mich. where it was converted to dead-burned magnesia at a 200,000 t/yr. capacity plant.

[d] In addition to its Michigan plant, Martin Marietta owned a 15,000 t/yr capacity magnesium hydroxide plant in Lenoir City, Tenn. which used imported magnesite as a raw material.

Table 26. **U.S. Exports of Magnesium Compounds**[a,b]

Material	2001		2002		Principal destinations, 2002
	Quantity, t	Value × 10^3 $	Quantity, t	Value × 10^3 $	
magnesium chloride, anhydrous and other	3,630	5,080	4,580	2,340	Canada, 90%
magnesium hydroxide and peroxide	20,800	9,630	14,500	11,000	Canada, 61%; Germany, 14%
magnesium sulfate, natural kieserite and epsom salts	406	223	3,350	449	Canada, 81%; Panama, 16%
magnesium sulfate, other	6,360	3,860	7,450	3,610	Canada, 82%

[a] Ref. 119.

[b] Data are rounded to no more than three significant digits.

Table 27. **U.S. Imports for Consumption of Magnesium Compounds**[a,b]

	2001		2002		
	Quantity, t	Value × 10^3 $	Quantity, t	Value × 10^3 $	Principal sources, 2002
magnesium chloride, anhydrous and other	62,000	8,840	20,100	4,930	Israel, 90%
magnesium hydroxide and peroxide	6,930	10,500	3,930	6,000	Netherlands, 30%; Austria, 20%
magnesium sulfate, natural epsom salts	77	20	65	29	Germany, 56%; China, 28%
magnesium sulfate, natural kieserite	22,500	640	13,300	815	Germany, 100%
magnesium sulfate, other	36,900	8,430	30,900	5,830	Germany, 53%; Canada, 40%

[a] Ref. 119.

[b] Data are rounded to no more than three significant digits.

Table 28. **U.S. Magnesium Compounds Shipped and Used**[a,b]

	2001		2002	
	Quantity, t	Value × 10^3 $	Quantity, t	Value × 10^3 $
caustic-calcined and specified (USP and technical) magnesias[c]	136,000	43,300	127,000	38,100
magnesium hydroxide [100% $Mg(OH)_2$][b]	268,000	100,000	218,000	86,900
magnesium sulfate, anhydrous and hydrous	38,100	12,000	38,000	12,400
precipitated magnesium carbonate[c]	1,750	4,170	1,710	4,130
refractory magnesia	213,000	71,300	123,000	37,800

[a] Ref. 119.

[b] Data are rounded to no more than three significant digits.

[c] Excludes material produced as an intermediate step in the manufacture of other magnesium compounds.

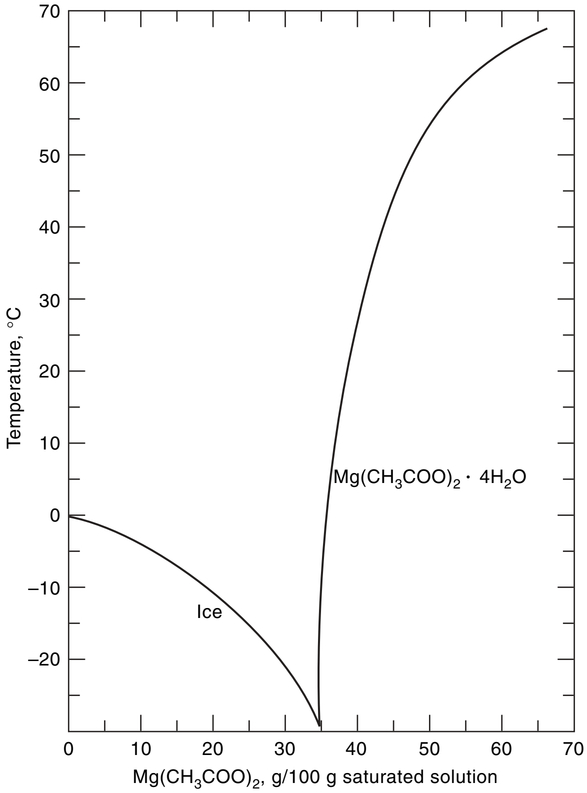

Fig. 1. The $Mg(CH_3COO)_2 \cdot H_2O$ system.

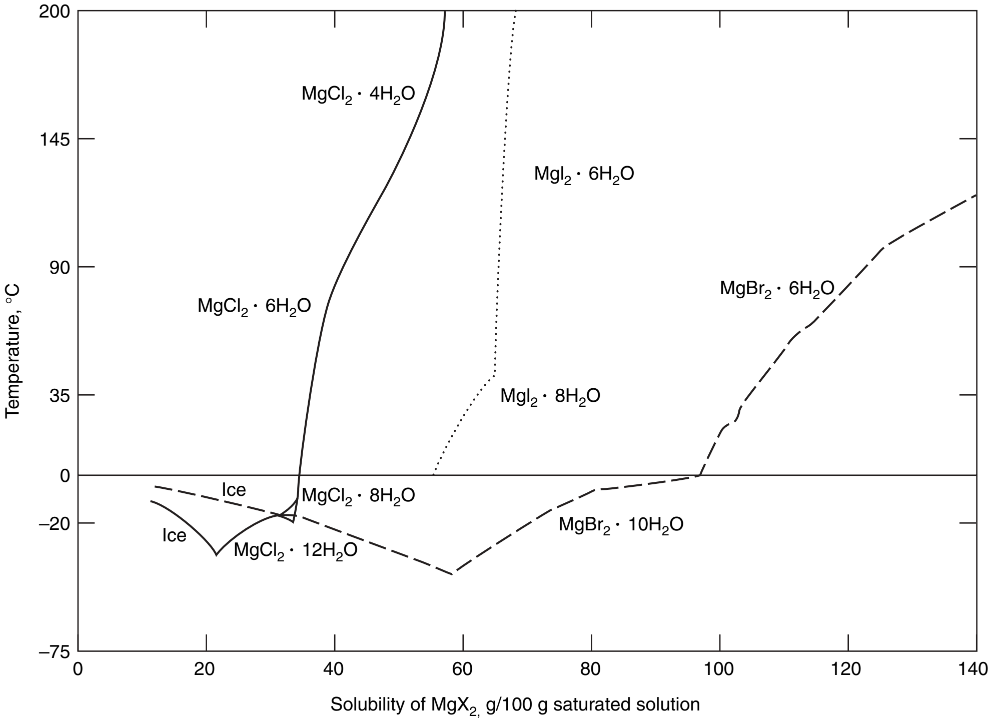

Fig. 2. The solubility of (—) $MgCl_2$, (–) $MgBr_2$, and (·····) MgI_2 in water.

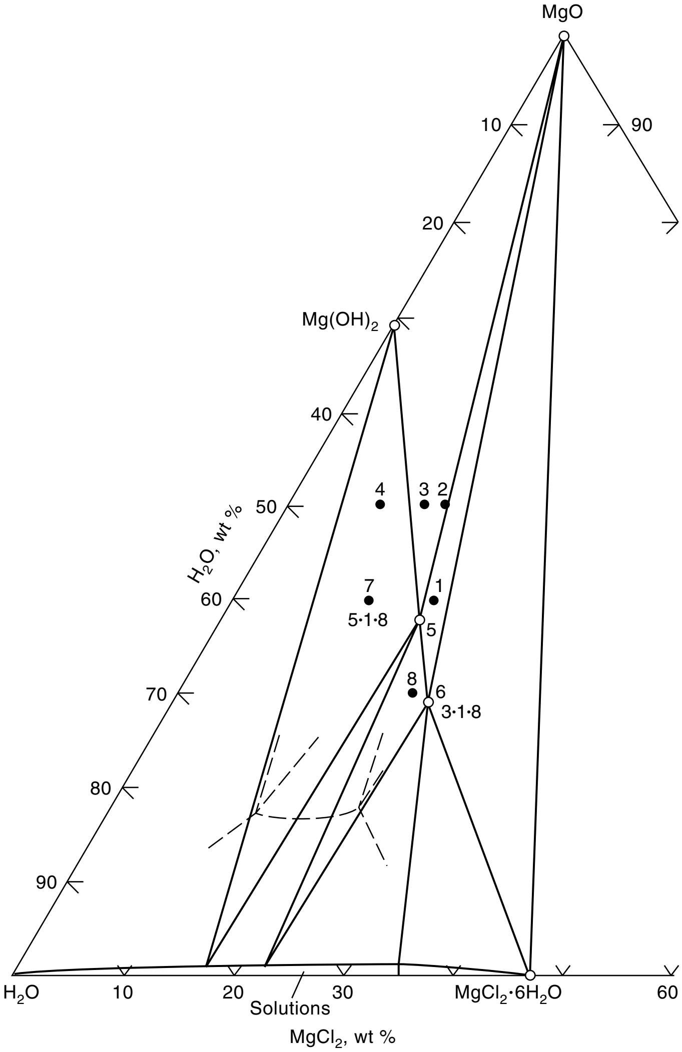

Fig. 3. Isothermal section at 23 ± 3°C of the system $MgO \cdot MgCl_2 \cdot H_2O$ showing phases in equilibrium with vapor phases in sealed containers.

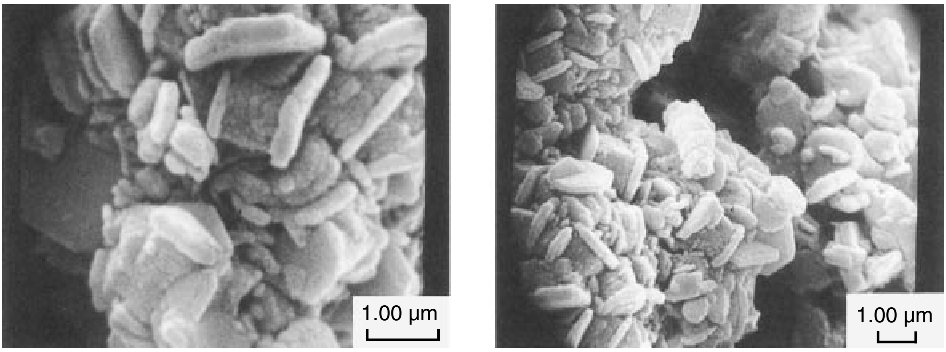

Fig. 4. Magnesium hydroxide. (**a**) ×20, 000; (**b**) ×10, 000. Courtesy of Martin Marietta Magnesia Specialties, Inc.

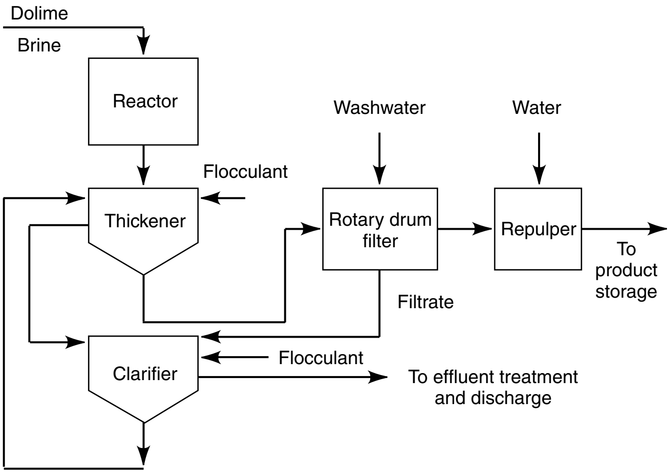

Fig. 5. Brine–dolime production of $Mg(OH)_2$.

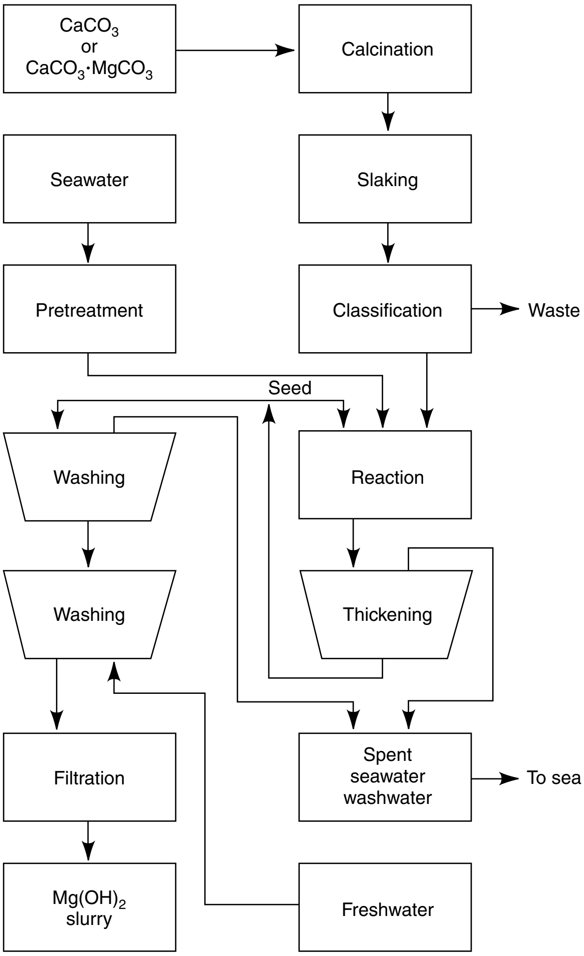

Fig. 6. Magnesia recovery from seawater.

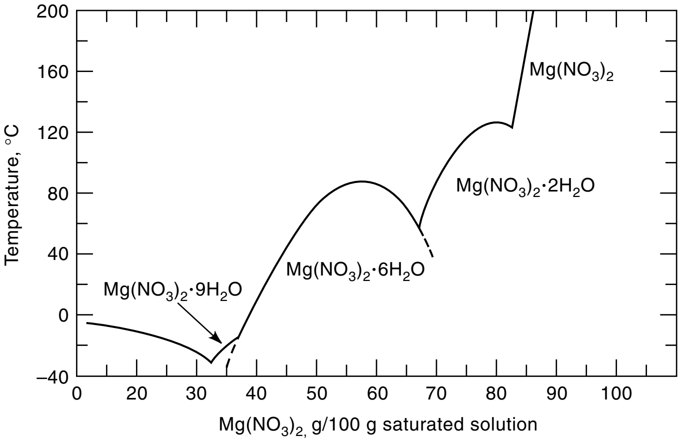

Fig. 7. The system $Mg(NO_3)_2 \cdot H_2O$.

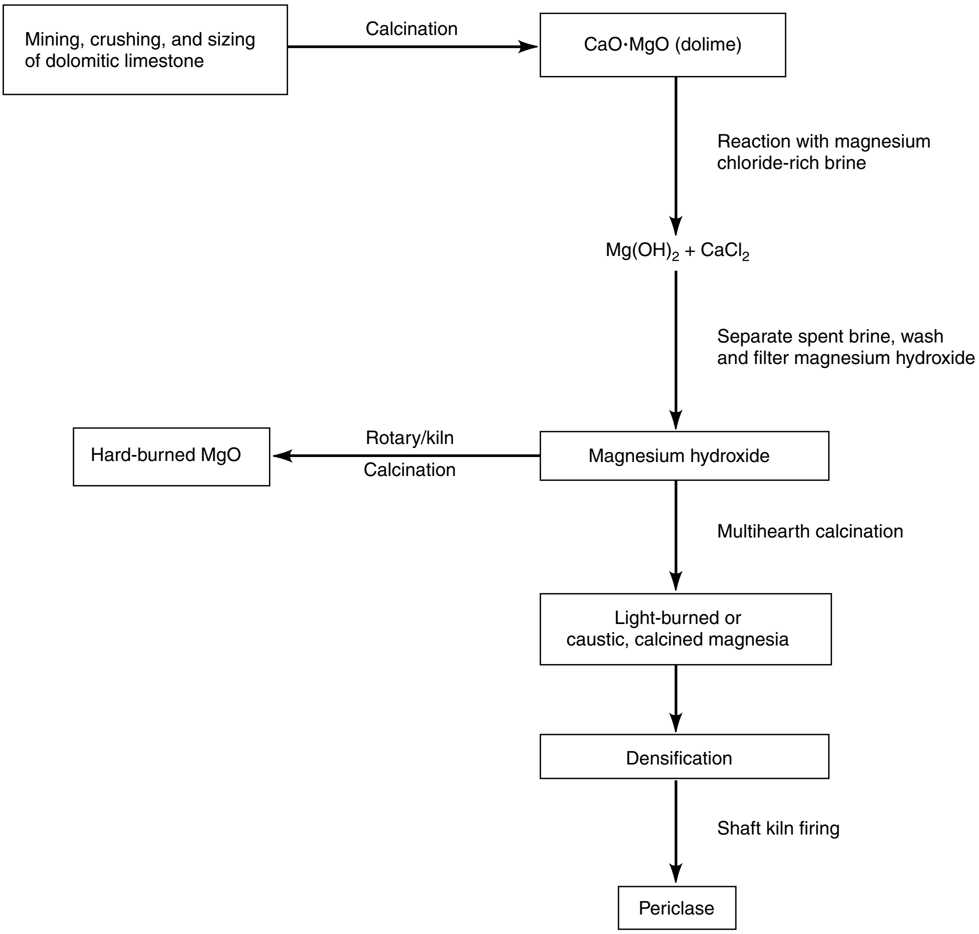

Fig. 8. Magnesia manufacturing process, Martin Marietta Magnesia Specialties, Inc.

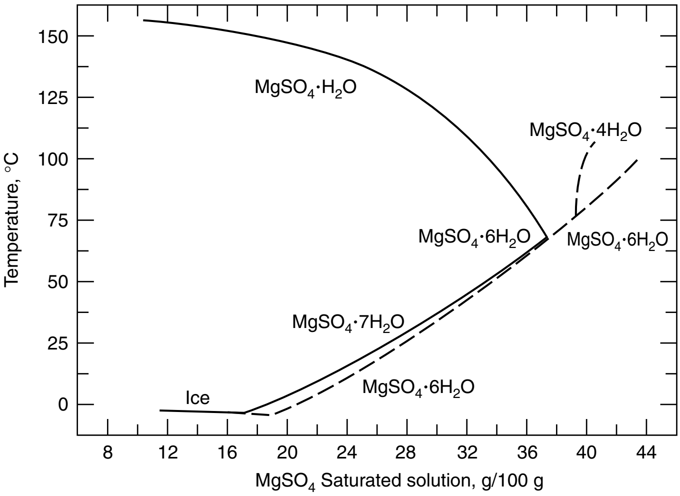

Fig. 9. The $MgSO_4 \cdot H_2O$ system where the dashed lines represent metastable phases.

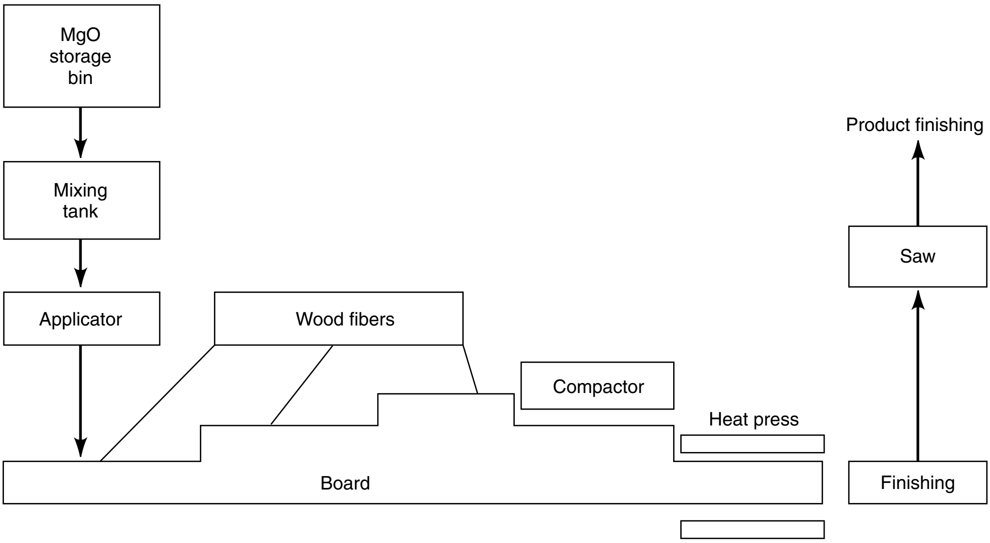

Fig. 10. Manufacturing of oxysulfate cement boards.

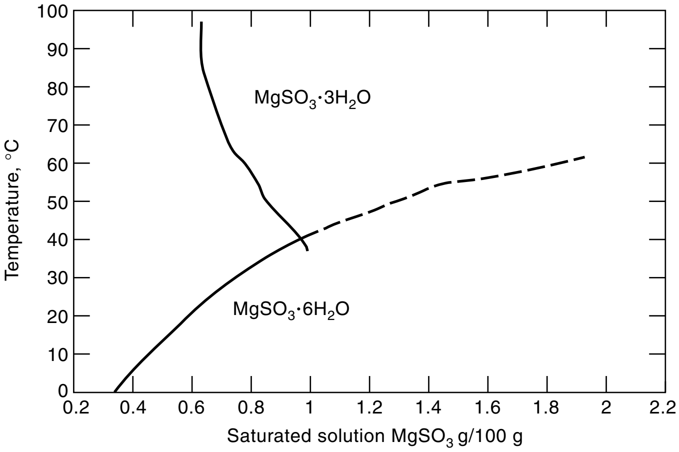

Fig. 11. The $MgSO_3 \cdot H_2O$ system (86).