

# THE CHEMISTRY AND TECHNOLOGY OF MAGNESIA

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**MARK A. SHAND**  
Premier Chemicals, LLC  
Findlay, Ohio

 **WILEY-  
INTERSCIENCE**

A JOHN WILEY & SONS, INC. PUBLICATION



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# PREFACE

This book attempts to encompass “all things magnesia.” Although the magnesia industry is similar in many respects to the much larger lime industry, there is to my knowledge no text concentrating solely on magnesia. There are, however, several excellent texts covering the lime industry. Unfortunately, in these books magnesia is practically a footnote. Although lime and limestone production far exceeds that of the magnesia industry (total lime production in the United States in 2004 was 20.4 million metric tonnes, compared with a total magnesia production of 280,000 metric tonnes), magnesia is still an important chemical and maintains many niche applications. By far, the largest consumer of magnesia worldwide is the refractory industry, which consumed about 56% of the magnesia in the United States in 2004, the remaining 44% being used in agricultural, chemical, construction, environmental, and other industrial applications.

This text starts with the geological occurrences of magnesite and brucite, followed by the processing of magnesite to the end product magnesium oxide. The production of magnesium hydroxide and magnesium oxide by precipitation from seawater and brine sources is also introduced, along with details on the wide range of applications in which magnesia is utilized. These applications span animal feed to wastewater treatment, catalyst support and fertilizers to the production of pulp and paper.

Like many industries, a certain amount of jargon arises as the industry matures, and the magnesia industry is no exception to this. However, there may be some confusion as to which compound *magnesia* really applies.

My definition is that the term *magnesia* is a generalization for magnesium oxide, whether it is derived from natural magnesite or extracted from seawater or brine. The term *magnesite*, in the strictest sense, refers to the mineral consisting of magnesium carbonate, but the same term is often used for the oxide, that is, *dead-burned magnesite*, the term even being used when the oxide has been produced from seawater or brine sources.

The major products produced by the magnesia industry are magnesium carbonate (magnesite); magnesium hydroxide, both natural (brucite) and that derived from seawater and brine; magnesium oxide, which in itself has a number of categories, namely, light-burned or caustic-calcined MgO, hard-burn MgO, and dead-burn MgO, or as it is otherwise known, periclase; and the last category, fused magnesia.

Light-burn or caustic-calcined MgO refers to a product that has been calcined at the lower end of the temperature spectrum, typically 1500–1700°F. This product typically has the highest reactivity and greatest specific surface area of the entire magnesium oxide category. Hard-burn MgO is calcined at a higher temperature, 2400–2800°F, and has a correspondingly lower reactivity and surface area. Dead-burn MgO, or periclase, is produced at temperatures above 2800°F, which having a very small surface area, makes it unreactive. Finally, fused magnesia, produced at temperatures above the fusion point of magnesium oxide (2800°C), is the least reactive.

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I also owe a debt of gratitude to John Gehret and the board of directors of Premier Chemicals, LLC for allowing me the opportunity to write the book. I would also like to especially thank my long-time friend and mentor, Dr. Ronald Wardle, along with John Noble of Vesuvius USA and Mark Wajer of Martin Marietta Magnesia Specialties for diligently correcting the text and providing helpful suggestions. I would also like to thank Lynden Johnson for increasing my knowledge of the process of mining magnesite.

Finally, I would like to thank Gerry Spoors, Dr. Theofilos Zampetakis, and John Turner for their affirmation that this book should be written, and to John Wiley & Sons for agreeing to publish said text.



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# 1

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## HISTORY OF MAGNESIA

### 1.1 HISTORY OF MAGNESIA

*Magnesia alba*, otherwise known to alchemists as white magnesia or mild magnesian earth, is known today as magnesite or magnesium carbonate,  $\text{MgCO}_3$ . *Magnesia nigra*, however, refers to black manganese oxide,  $\text{MnO}_2$ . Both of these names are derived from Magnesia, Μάγνησιá, which is a prefecture in Thessaly, Greece. Manganese and magnesium, as well as iron, are abundant in the form of oxides and carbonates in this region, and these minerals were referred to as “stones from Magnesia.” The iron oxides present in magnesia were in the form of magnetic magnetite or lodestone, and both *magnesia alba* and *magnesia nigra* contain large amounts of magnetite, thus making them magnetic. This explains why magnesium and magnet are both derived from the place name Magnesia.

In alchemical terms, magnesia meant “a stone shining like silver” and was purported to be an ingredient of the philosopher’s stone. In the more modern sense of the word, it is thought to have originated from *magnes carneus*, which means flesh magnet from the way it stuck strongly to the lips. Bergman’s essay (Bergman et al. 1784–1791) “De Magnesia” claimed that the Roman Count di Palma prepared a white powder that he claimed was a panacea for all diseases. The white powder was called “*magnesia alba*,” or Count Palma’s powder, and its origin was a closely guarded secret.

In 1701 M.B. Valentini (Valentini, 1707) prepared *magnesia alba* by the calcination of the residue remaining after evaporating the mother liquor to dryness from the preparation of niter or potassium nitrate. To add even more to the confusion, it is apparent that at least three minerals of different chemical composition were called magnesia: (1) *magnesium lapis*, which referred to magnetic magnetite, (2) *magnesia nigra*, which refers to pyrolusite ( $\text{MnO}_2$ ), and (3) a silver-white mineral that was probably steatite or talc.

At the beginning of the eighteenth century the term *manganee* was employed for the manganese mineral and *magnesia* for the white mineral. However, the difference between *magnesia nigra* and *magnesium lapis* was not demonstrated until the middle of the eighteenth century. Hoffman (Hoffman, 1729) was the first to recognize the differences between magnesia and lime. He stated that an alkaline earth prepared by the reaction of a bitter salt (Epsom salts) with a fixed alkali differed from lime. Whereas lime gave a sparingly soluble salt with sulfuric acid that was nearly without taste, *magnesia alba* gave a bitter soluble salt.

However, it was not until 1754 that magnesia was finally distinguished from lime by Joseph Black. Black was the first person to recognize that magnesium was an element. Black, a prominent professor of anatomy and chemistry at Edinburgh, showed that *magnesia alba* (magnesium carbonate), when heated, evolved "fixed air" (carbon dioxide). The residue from this heating, calcined magnesia (magnesium oxide), was lighter and more alkaline than the basic carbonate. Limestone (calcium carbonate) was found to behave in the same manner. Black also demonstrated that *magnesia alba* produced a soluble sulfate in contrast to lime. He gave the alkaline earth the name *magnesia*. Black's thesis (Black, 1777) presented in June 1754, "On the Acid Humour Arising from Food and Magnesia Alba" dealt primarily with the value of magnesia as an antacid.

In 1808 Humphrey Davy (Davy, 1808) proved definitively that magnesia is the oxide of a metal, which he named magnium. At this juncture, the term *magnesium* was being used by some to define metallic manganese. Davy's technique involved mixing moistened alkaline-earth oxide with mercuric sulfide (cinnabar) and placing the paste onto a platinum plate. A drop of mercury was dropped into a depression made in the paste and the whole covered with naphtha. The platinum plate and drop of mercury were then connected to the poles of a voltaic pile. The resultant amalgam that formed on the mercury pole was then transferred to a glass tube and the mercury distilled off. Davy described the characteristics of magnesium as follows (Davy, 1808)

The metal from magnesia appears to react with the glass, especially before all the mercury has distilled off. In one experiment, in which I interrupted the distillation before the mercury had been completely removed, the metal appeared

as a solid body, which exhibited the same white color and the same luster as the other metals of the alkalide-earths. It immediately sank to the bottom of the water although surrounded by gas bubbles, formed magnesia. It changed quickly in the atmosphere, a white crust forming, and finally it disintegrated into a white powder, which proved to be magnesia.

Eventually, much to the consternation of Davy, the name magnesium was adopted for the metal in *magnesia alba* and manganese for the metal in pyrolusite. Michael Faraday produced magnesium metal in 1833 by the electrolysis of fused anhydrous magnesium chloride.

The mineralogical term *magnesite* was first applied to a series of magnesium salts (carbonate, sulfate, nitrate, and chloride) by J.C. Delaméthrie (Delaméthrie, 1795) in 1795. The same term was also being applied to magnesium carbonates and silicates by A. Brongniart (Brongniart, 1807). Deposits of natural magnesium carbonate were discovered at Hrubschütz in Moravia, which is now Hrubšice in the Czech Republic, and named *Kohlensaurer Talkerde* by W.A. Lampadius in 1800 (Lampadius, 1800). C.F. Ludwig described these minerals as *talcum carbonatum* in 1803. The use of the term magnesite was first restricted to the carbonate minerals by D.L.G. Karsten in 1808 (Karsten, 1808). The name magnesite gradually grew in acceptance.

Deposits of magnesite were found in Austria and Greece during the later half of the nineteenth century, and around the same time magnesite mines were opened in Canada. In 1886 magnesite was discovered in California and commercial mining commenced around 1900, and in 1913 production of magnesia commenced in Pennsylvania. The development of the magnesite industry was accelerated in 1914 by the outbreak of World War I as supplies from Austria and Greece were cut-off by the blockade of central European powers. Magnesite was found in Stevens County, Washington, in 1916 and mining started in 1917. During World War I, California magnesite came from small deposits in the Porterville district, which were operated in a crude fashion by small owners or contractors. The deposits situated at Magnesite, California, which is a short distance from Portersville, were developed in a more systematic manner, and after the war formed the nucleus of a sound mining and production operation. However, much of the early magnesite technology was developed in the Portersville district, such as the mechanical beneficiation of magnesite and the calcining of magnesite to develop a product with specific and controllable characteristics. It was also at Portersville that the first high-purity crystalline magnesium oxide was produced in a rotary kiln. Commercial production of refractory-grade magnesia was also in operation in the Livermore district of California by Western Mine and the Bald Eagle mine operation by Westvaco Chlorine products in Stanislaus County, California.

An immense deposit of medium- to low-quality magnesite exists in Steven County, Washington, which was exploited by the Northwest Magnesite Company during World War I. Operations were centered on the towns of Chewelah and Valley. It was here that the first use of froth flotation to beneficiate magnesite was employed to reduce silica and lime content.

A very large deposit of dolomite, magnesite, and brucite in the Paradise Range, Nye County, Nevada, has been known since about 1927 when brucite was discovered by Harry Springer. Drilling by U.S. Brucite in 1930 and 1931 revealed the presence of considerable quantities of magnesite adjacent to the brucite. From 1931 to 1933, the U.S. Geological Survey mapped the deposit and estimated that there were 71 million tons of magnesite and brucite bearing rock. Both magnesite and brucite were mined by Basic Ores, Inc., and the Sierra Magnesite Company. Currently, the only magnesite deposit being exploited in the United States is the one at Gabbs, Nevada.

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# 2

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## FORMATION AND OCCURRENCE OF MAGNESITE AND BRUCITE

### 2.1 INTRODUCTION

Magnesium is the eighth most abundant element in the solar system and constitutes about 2% of Earth's crust. It is also the third most abundant element in solution in seawater, with a concentration of about 1300 ppm. The element magnesium is composed of three stable isotopes:  $^{24}\text{Mg}$  (78.6%),  $^{25}\text{Mg}$  (10.1%), and  $^{26}\text{Mg}$  (11.3%), with an average atomic weight of 24.31. More than 60 magnesium-containing minerals are known. The most important rock-forming minerals containing magnesium are the chlorites, the pyroxene and amphibole group minerals, dolomite, and magnesium calcite (calcite with some of the Ca replaced by Mg). Magnesium is also present in magnesite ( $\text{MgCO}_3$ ), and the hydrated carbonates such as nesquehonite ( $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ ) and lansfordite ( $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ ) as well in brucite [ $\text{Mg}(\text{OH})_2$ ]. In addition there is a series of basic magnesium carbonates having the empirical formula  $x\text{MgCO}_3 \cdot y\text{Mg}(\text{OH})_2 \cdot z\text{H}_2\text{O}$ . These include hydromagnesite [ $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ] and artinite [ $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ ]. Magnesium also occurs in salt deposits such as carnallite ( $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ ), epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), and kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ).

It has been estimated that the total mass of the sedimentary layer in Earth's crust is  $1.4 \times 10^{18}$  tonnes (Wedephol, 1968). Magnesium is present in the sediment mainly in dolomite and phyllosilicates, such as chlorite and

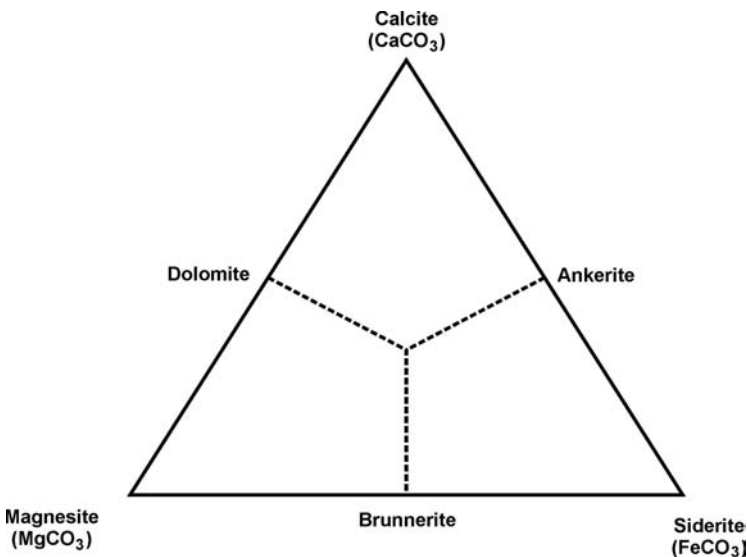
glaucanite. Carbonate rocks constitute about 8 wt % of the total sediments (Goldschmidt, 1954). Dolomite makes up about 30 wt % of the carbonates in the sedimentary layer and contains  $4.6 \times 10^{15}$  tonnes Mg.

Magnesite is the magnesium end member of an isomorphous series of carbonates. An increase in calcium content results first in dolomite and then calcite as the Ca end member. Since the difference between the ionic diameters of  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  ( $\text{Mg}^{2+} = 0.65 \text{ \AA}$ ,  $\text{Fe}^{2+} = 0.79 \text{ \AA}$ ), is not as great as that between  $\text{Ca}^{2+}$  ( $0.99 \text{ \AA}$ ) and  $\text{Mg}^{2+}$ , Fe and Mg substitute for each other and form the isomorphous series from magnesite through brunnerite (5–30%  $\text{FeCO}_3$ ) to siderite ( $\text{FeCO}_3$ ), and from dolomite to  $\text{CaCO}_3 \cdot \text{FeCO}_3$ ; see Figure 2.1.

This isomorphous miscibility results in the presence of both calcite and dolomite in magnesite deposits as mechanical admixtures. However, iron is bound within the magnesite crystal lattice. Pure magnesite is rarely found, and the natural mineral tends to occur part way along an isomorphous series.

Four main types of magnesite deposits have been described to date:

1. Magnesite as a sedimentary rock
2. Magnesite as an alteration of serpentine
3. Magnesite as a vein filling
4. Magnesite as a replacement of limestone and dolomite



**Figure 2.1** Isomorphous series substitution of Fe for Mg to form brunnerite.

There are two physical forms of magnesite: cryptocrystalline or amorphous magnesite and crystalline, macrocrystalline, or bone magnesite.

## 2.2 SEDIMENTARY MAGNESITE—BASIS FOR CARBONATE DEPOSITION

Carbonate compounds are relatively insoluble, and Table 2.1 lists the solubility constants for a number of geologically important carbonates. Since these minerals are relatively insoluble, carbonates are precipitated at relatively low carbonate and counterion concentrations. As an example, a solution containing  $10^{-4}$  M  $\text{Ca}^{2+}$  will be precipitated by a concentration of  $\text{CO}_3^{2-}$  in excess of  $10^{-4.32}$  M. This occurs because the product of the two ionic concentrations exceeds the solubility constant for calcium carbonate; see Equation (2.1):

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = K_{\text{sp}} = 10^{-8.32} \quad (2.1)$$

Since the solubility of calcium carbonate is considerably less than that of magnesium carbonate, evaporation and concentration of salt lakes and lagoons must have produced calcium carbonate deposits initially. The brine would gradually be depleted of calcium ion and enriched with magnesium. Eventually, a condition would be reached where the brine concentration of the magnesium ion and carbonate exceeds the solubility constant of magnesite, and precipitation would proceed; see Equation (2.2):

$$[\text{Mg}^{2+}][\text{CO}_3^{2-}] = K_{\text{sp}} = 10^{-5} \quad (2.2)$$

Sedimentary deposits of cryptocrystalline magnesite occur either in lagoons, salt lakes, or freshwater lakes (lacustrine). The genesis of magnesite in saltwater requires specific conditions for it to occur: a reducing alkaline environment, a high concentration of magnesium sulfate, and a concentration

**TABLE 2.1 Solubility Constants of Geologically Important Carbonates**

Compound	( $K_{\text{sp}}$ )	Ref.
$\text{CaCO}_3$	$10^{-8.32}$	Latimer and Hildebrand (1942)
$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	$10^{-5}$	Latimer and Hildebrand (1942)
$\text{MgCO}_3$	$10^{-4.59}$	Weast and Astle (1982)
$\text{CaMg}(\text{CO}_3)_2$	$10^{-16.7}$	Stumm and Morgan (1981)

Source: Adapted from H. L. Lutz, *Geomicrobiology*, Marcel Dekker, New York, 2002, p. 191.

of  $\text{CO}_2$  above 380 mg/L, a low Ca content (below 50 mg/L), and the presence of  $\text{H}_2\text{S}$ , ammonia, or organic salts, along with an elevated temperature. It is thought that magnesium precipitates as the hydroxide first [ $\text{Mg}(\text{OH})_2$ ], which is subsequently altered by reaction with carbonate ion to form  $\text{MgCO}_3 \cdot x\text{H}_2\text{O}$ . Dehydration then follows to form  $\text{MgCO}_3$ . Massive magnesite formation in freshwater lacustrine environments proceeds from magnesium derived from either hot solutions emanating from magma or from weathering of ultrabasic rock or serpentinites.

### 2.2.1 Secondary Nodular Magnesite

A variation of the sedimentary process occurs when the host ultrabasic rock is weathered by water, the eroded material being transported and deposited in a distant lacustrine environment. Here, magnesite was precipitated as concretions along with impurities in a mud matrix. The recrystallization of the magnesite would then have occurred through additional uptake of carbon dioxide from the atmosphere. Wave movement on the lake during crystallization carried away noncrystallized impurities such as  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{CaO}$  from the newly formed magnesite nodules. These impurities are then deposited on the exterior and in the pores of the magnesite nodule. The resultant sand-clay matrix with embedded magnesite nodules is covered with soil and compacted, and over time a silica-rich encrustation forms over the nodule. The percolation of bicarbonate-rich subsurface waters through the deposit results in raising the magnesite density (Schmid, 1987).

### 2.2.2 Biogenic Carbonate

A significant portion of the insoluble carbonate deposits at Earth's surface is of biogenic origin, while the remainder is the result of magmatic and metamorphic activity. The biological fixation of carbon as carbonate involves bacteria, fungi, and algae, and the carbonate can be deposited both extra- and intracellular. A part of magnesium present in the oceans is withdrawn by marine  $\text{CaCO}_3$ -secreting organisms, and this Mg replaces a part of the Ca in the hard parts of the organism. The quantity of Ca replaced depends upon the phylogenetic position of the organism. Algae have the highest (5 wt %) and barnacles the lowest Mg concentration (0.9 wt %) (Chave, 1954).

Sedimentary deposits of magnesite have been described as having either a biogenic origin or a chemical route via direct precipitation. These deposits are cryptocrystalline in form. *Actinomyces* bacteria, which belong to the genus *Streptomyces*, are thought to have played a role in the formation of