Magnesium—Its Sources, Methods of Reduction, and Commercial Applications;

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Magnesium is an exceedingly strategic material but the importance of its production at the time this war started was not realized. Our Government then suddenly became much alive to the need of a tremendous increase in magnesium output, and became a participant in the industry. In this paper an attempt will be made to give an over-all picture of the industry as it has been, and is being, developed.

The present war is giving a great acceleration to the use of lighter metals. Development of facilities for production of great tonnages of aluminum and magnesium is bound to bring about some interesting changes in later peace times because costs will be low and production capacities high. As our knowledge of the metallurgy of magnesium alloys increases, this metal will become of vital peace-time importance and will be used in ways we do not now imagine. Household refrigerators, furniture, automobiles, even houses will all be lightened through the use of magnesium.

Higher taxes on gasoline to help meet government debts will emphasize the necessity of getting increased automobile mileage from gasoline and this necessity will bring about the development of automobiles much lighter in weight. We may still have our roomy and comfortable motor cars but with higher gasoline mileage due partly to the greatly decreased weight.

Magnesium is the sixth most plentiful element in the earth’s crust and the fourth most plentiful metal. That it has not been as important as copper and nickel is due partly to its great reactivity with other elements, thus making it difficult to produce the metal in the pure state. It is never found in nature as a metal but always combined with oxygen or chlorine, or as a carbonate, sulphate, or silicate. The most common forms in which it has been stored by nature together with the average magnesium contents of these several minerals are shown in the accompanying table.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Composition</th>
<th>Approximate Per Cent Magnesium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite</td>
<td>MgCO₃-CaCO₃</td>
<td>13</td>
</tr>
<tr>
<td>Serpentine</td>
<td>3Mg₂SiO₃·2H₂O</td>
<td>25</td>
</tr>
<tr>
<td>Olivine</td>
<td>Mg(OH)₂</td>
<td>28</td>
</tr>
<tr>
<td>Magnesite</td>
<td>MgCO₃</td>
<td>28</td>
</tr>
<tr>
<td>Brucite</td>
<td>Mg(OH)</td>
<td>41</td>
</tr>
<tr>
<td>Hydromagnesite</td>
<td>3MgCO₃·Mg(OH)₃·3H₂O</td>
<td>26</td>
</tr>
<tr>
<td>Kieserite</td>
<td>MgSO₄·H₂O</td>
<td>13</td>
</tr>
<tr>
<td>Kainite</td>
<td>MgSO₄·KCl·3H₂O</td>
<td>9</td>
</tr>
<tr>
<td>Langbeinite</td>
<td>2MgSO₄·K₂SO₄</td>
<td>11</td>
</tr>
<tr>
<td>Talc</td>
<td>Na₂Mg₅(SO₄)₃·5H₂O</td>
<td>20.7-26.9</td>
</tr>
<tr>
<td>Sea Water</td>
<td>K₂SO₄·H₂O</td>
<td>.13</td>
</tr>
<tr>
<td>Brines</td>
<td></td>
<td>Variable</td>
</tr>
</tbody>
</table>

Practically unlimited quantities of dolomite, serpentine, and olivine exist in the United States and sea water of course is unlimited. Apparently unlimited quantities of magnesium-bearing brines also are present in certain parts of the United States. Brucite, magnesite, and hydromagnesite are found in limited amounts. One deposit of langbeinite, near Carlsbad, N. Mex., is being operated by the International Minerals & Chemical Corp. and the part this is to play in the production of magnesium will be described later.

Sea water is the greatest reservoir of raw material but its concentration of magnesium is small, amounting to about 0.13 per cent, or 0.01105 lb. of metal per gallon. In other words, it requires about 200,000 gallons of sea water to produce a ton of magnesium metal if all of it could be recovered. Magnesium is contained in sea water as the chloride and sulphate. Although sea water is free, production of magnesium from other sources can still compete with that from sea water because of other factors including materials, plant locations, and power costs.

Magnesium metal is silvery white, malleable, and ductile. It weighs only 109 lb. per cu. ft. On a volume basis, it is two thirds the weight of aluminum. One fifth the weight of copper. It can be cast, extruded, rolled, welded, and easily machined.

Alloyed with aluminum, zinc, and manganese, it forms light alloys of high strength. One alloy of magnesium and aluminum is as strong as three times its weight in ordinary steel though on an equal volume basis, the strengths of its alloys have not yet been developed to equal that of steel. Plenty of competition will be ahead for any alloys that will be developed, for no doubt new alloys of steel will be made, reducing the weight of metal required per unit of strength. It will therefore become a race between the cost of magnesium and steel alloys, and also a race to increase the strengths of these alloys per unit of cross section. This much is certain, the entire field of materials of construction is undergoing a great change and new alloys will be available for both new and old uses after this war.

Besides its importance as a metal of construction where lightness is of great value, as in the fabrication of both airplane and engine parts, magnesium is used as a deoxidizer in the production of nickel and certain of its alloys because of its great affinity for both oxygen and nitrogen. However, this is not relatively so important as its use in the making of incendiary bombs and flares. Large parachute flares for illumination of war operations are produced from mixtures of which magnesium powder is the major constituent. Aerial reconnaissance now requires large flash bombs for instantaneous illumination of a terrain being photographed by a camera carried in an airplane thousands of feet above the ground. Such illumination is made possible by magnesium.

Because of these uses, one might think that magnesium metal is a high fire hazard. It is not, when its properties are well understood, for it must be heated to about 1200°F. to ignite it in...
air. Once ignited, it burns avidly and is best extinguished by smothering with a mist of water.

One use of considerable potential importance to petroleum refiners at such time as magnesium powder becomes available for purposes other than war, is the possibility of using it on a large scale in the production of organo-magnesium halides in organic synthesis—such compounds being known to chemists as Grignard's reagents.

Magnesium was first made in 1808 by Sir Humphrey Davy, using magnesium oxide and potassium vapor, though this was only as an experiment and of value only from a scientific standpoint. About 1857, commercial production of the metal in a small way was begun in France, and in 1864, small-scale production was started in England. Some was produced in the United States as early as 1865, for flash-light purposes, but this was discontinued in 1892. These operations were of no great importance, however, and the industry remained relatively undeveloped until about 1896, when the Germans began making the metal on a larger scale by passing an electric current through molten magnesium chloride which was obtained as a by-product from their operation of the Stassfurt potash deposits.

A part of the Kaiser magnesium plant in California using the Hunsfig process.

Dr. Dow Starts Magnesium Production in U. S.

PRACTICALLY the entire credit for the development of the industry in the United States is due to Herbert H. Dow and the organization he started. Dr. Dow lived in Midland, Mich., and noting that certain saline brines produced from deep wells near-by contained magnesium chloride, he began research and development work on the production of magnesium from these brines. The story of the industry that has been built up from this start is one of the most interesting in the entire history of American enterprise. Within a relatively short period of time, The Dow Chemical Co., founded in 1890, became one of the major chemical organizations in the United States, with net sales of $46,907,850 in 1941, and a net income of $7,750,547. All of this grew from the experimental work done on those Michigan brines.

In 1915, magnesium metal sold for $5 per pound and three years later a total of 142 tons was produced in the United States. In 1925, production was 122 tons and the price was $1 per pound. From that time on a marked increase has taken place in annual tonnage, at a constant decrease in price. In 1941, the U. S. production exceeded 8500 tons. Production may exceed 350,000 tons annually in 1943 when all plants now being built are brought to capacity. This represents an increase of over 200 times the production in 1935.

As stated previously, the intense chemical reactivity of magnesium makes its reduction difficult. It can be freed as a metal by heating the oxide with some substance more avid for oxygen than is magnesium. This reaction is now being practiced in several new plants using a compound of silicon and iron as the reducing agent. A new plant installed by the Ford Motor Co., in Michigan has been recently brought into operation. In this process, dolomite is calcined to produce "dolime" and is ground to a powder with crushed 75 per cent ferrosilicon mixed with a binder. The proportion of dolomite to ferrosilicon is between five and six parts to one. The mixture is then briquetted.

Finished briquets are charged into horizontal retorts, 10 in. in diameter and 22 ft. long, made of chrome-nickel steel, set in multiple in a furnace. After charging each retort, the condenser-cover is put in place. A high-vacuum pump is started to maintain the charge in the retort under as high a vacuum as possible, and the heat is turned on around the retort. This heat causes the reaction to take place between the ferrosilicon and the calcined dolomite. Magnesium vapor is liberated and is deposited on a condenser-head which extends into the end of the retort and which is cooled by water passing through its inner chamber. The magnesium is deposited on sleeves at the end of the retort. Approximately eight hours is required for the completion of the reaction and about 70 lb. of magnesium per retort should result.

A second process, depending for its operation on the reduction of magnesium oxide by carbon, was developed by Fritz Hunsfig in Austria several years ago. This process was operated in a small plant in Austria until an explosion destroyed the enterprise. A similar installation, on a larger scale, was made first in England by two of Dr. Hunsfig's associates and later in Korea by Dr. Hunsfig himself. In 1941, the Permanente Metals Co. at Permanente, near Los Alisos, Cali., built, under the supervision of Dr. Hunsfig, a plant for the production of magnesium metal, which utilized a modification of the original Hunsfig process.

In the Hunsfig process, magnesium oxide, produced as pure as possible, is mixed with carbon such as a petroleum coke. This mixture, made into briquets, is then charged continuously into an electric furnace, the magnesium oxide then reacting with carbon to produce carbon monoxide and magnesium metal. However, in spite of the fact that the reaction is simple, it is reversible—that is, the reaction tends to reverse so that carbon monoxide and magnesium produce magnesium oxide and carbon. The reaction goes in favor of producing magnesium metal at a temperature above 2000°C. Magnesium boils under a atmospheric pressure at 1107°C. The equilibrium point of the reaction is reached at atmospheric pressure and stoichiometric proportions at about 1800°C. The essential point in this process is, therefore, the removal of the magnesium before it can react with the carbon monoxide to form carbon and magnesium oxide.

In the original Hunsfig plant, built in Austria in 1929, this was accomplished by mixing the magnesium vapor and carbon monoxide, as it left the electric furnace, with a large quantity of refrigerated hydrogen gas. This accomplished what is termed shock-cooling of the vapor and the magnesium metal condensed as an impalpable powder. Some impurities were carried over with the vapor and since the melting of a metallic powder of this fineness is extremely difficult, the next step was to form the powder into small briquets or pellets and charge them into a retort.
from which the metal was distilled under a high vacuum to be condensed as pure and crystallized magnesium.

Metalllic magnesium resulting from the shock-cooling part of the process is extremely pyrophoric; upon exposure to air, it will instantly catch fire. Therefore, it is necessary to store the powder and handle it under an inner atmosphere such as hydrogen or methane. The handling of the vapor and of this highly inflammable magnesium powder are the sources of the principal hazards and troubles which have dogged this process since its development. Numerous fires have occurred in plants using the process and the Austrian plant finally blew up and was completely destroyed. In the modification of the Hansging process in use at Permeante, shock-cooling is not accomplished by the use of refrigerated hydrogen but by natural gas. After the removal of the magnesium dust from the resulting mixture of natural gas and carbon monoxide from the cooler, it passes into cement kilns wherein it is used as a fuel.

Considerable difficulty has been experienced in this process owing primarily to the necessity of working under gastight conditions and also because of the high temperatures required in operation.

Sea water has been used as a source of magnesium salts and magnesium metal for several years. Magnesium oxide, hydrogen oxide, and carbonates have been manufactured for a number of years on a large scale on the Pacific Coast. However, this material was not used for the production of metallic magnesium except as a laboratory experiment. Several years ago, H. H. Chesney, working with an English organization, developed a process for the production of magnesium oxide from dolomite and sea water. This process was utilized and is still being operated to produce large amounts of magnesium oxide and this oxide was and is being used as a raw material in the manufacture of magnesium metal.

RECENTLY, the Dow Chemical Co. began operating a large plant in Texas for the production of magnesium metal from sea water, the first one in the world using this raw material for this purpose. In this process, the sea water is first treated with lime produced by calcining oyster shells and hydrating the lime so produced. This sea-water treatment results in the precipitation of magnesium hydrate which is settled in large Dorr thickeners and then further dewatered by filtration. The magnesium hydrate cake from the filters is then reacted with hydrochloric acid and the magnesium chloride thus formed is concentrated, purified, and dried after which it is used as a feed to the magnesium-producing cells. In the magnesium cells, electrolysis of the magnesium chloride results in the formation of magnesium metal and a mixture of air, chlorine, and hydrochloric acid in low concentrations. This acid and chlorine are used in the production of hydrochloric acid which is then used to neutralize additional magnesium hydroxide.

This process is a modification of the process originally developed by Dr. Dow and his associates and practiced so successfully at Midland, Mich. There, the raw material is a natural brine pumped from deep wells, which contains calcium chloride, magnesium chloride, and sodium chloride as well as a small amount of bromine. The bromine is removed and the brine concentrated to produce a double salt of calcium and magnesium chlorides called tachydrite. This is filtered off, the calcium chloride removed, the magnesium chloride concentrated and dried, and the latter fed to the electrolytic cells.

A process originally developed in Germany and later modified and used in England utilizes the electrolysis of magnesium chloride in a somewhat different way. In this process, it is necessary that the magnesium chloride be absolutely anhydrous and it is produced by reacting calcined magnesite with carbon monoxide and chlorine to form magnesium chloride and carbon dioxide. In carrying out this process, the calcined magnesite is ground to a fine powder and mixed with lime and magnesium chloride to contain other agents such as peat moss to make the mass porous. The mixture is then briquetted and fed into the top of a vertical chlorination furnace. The lower part of each furnace or tower is packed with coke or other carbonaceous material so that when the mass is heated and chlorine is passed in the above reaction takes place. Magnesium chloride runs from the bottom of the furnace as a molten anhydrous liquid. This process is essentially the one which has been installed in Nevada by Basic Magnesium, Inc.

IN addition to the plants which the Dow Chemical Co. is building and already has in operation, two other manufacturers in this country are utilizing the Dow electrolytic cells for the production of magnesium metal. One of them is the Diamond Alkali Co., operating in Ohio, and the other is the International Minerals & Chemical Corp., whose plant is in Texas. In each of these plants the magnesium chloride feed for the cells is made by a different process—each process having been developed by the respective organization. At the plant being operated by International, a part of the magnesium chloride is produced as a by-product from the manufacture of potassium sulphate, utilizing langbeinite and muriate of potash, both of which are produced at the company's mines near Carlsbad, N. M.

The Mathieson Alkali Works is now building a magnesium metal plant in Louisiana. Working with Consolidated Mining and Smelting Co. of Canada, they have developed a new type of electric cell which uses fused magnesium chloride as a feed. Chlorine is produced by this cell in a concentrated condition.

Cell houses for the electrolysis of magnesium chloride extracted from sea water. 348