

CHAPTER XXIX

THERMAL PROCESSES FOR THE REDUCTION OF MAGNESIUM

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THERMAL PROCESSES FOR THE REDUCTION OF MAGNESIUM

In view of the difficulty of producing anhydrous magnesium chloride and due to the high electrical-power consumption in its electrolysis, the cost of metallic magnesium is comparatively high. Therefore, scientific-technical thought has long been concerned with simpler and cheaper methods ~~possible~~ for obtaining this metal from abundant magnesium ores (magnesite and dolomite) by way of thermal reduction.

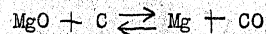
In the 1930's these efforts met with complete success and at the present time one may refer to the importance and industrial significance of producing magnesium by thermal reduction.

In 1942, approximately 30 percent of the magnesium produced in the United States of America was obtained by the thermal reduction process.

Reduction of magnesium oxide to the metal, may be achieved by two processes: Carbon and non-carbon, both methods having industrial application. (Metals and Alloys, Vol 15, 1942, No 3, 433)

108. Carbon Reduction of Magnesium Oxide

First effort to reduce magnesium oxide by carbon, even though unsuccessful, were made by Walter in 1884. Satisfactory production of metallic magnesium by carbon reduction of MgO was only recently possible and was based on an exact knowledge of the physico-chemical nature of this reaction. Numerous efforts during the previous 50 years to achieve this result had invariably led to negative results. The point is that the reaction



is normally reversible [right to left] and only with an increase in temperature moves from left to right. A temperature of over 2000 degrees [Centigrade] is required to shift the reaction completely to the right. Under

these temperature conditions, the products of reaction are CO and vaporized magnesium.

However, while cooling the products of reaction for the purpose of condensing the magnesium vapours, equilibrium is shifted back to the left - magnesium reacting with CO to return the MgO and carbon. This situation was long the main reason for failing to obtain metallic magnesium by carbon reduction of MgO.

Subsequent research showed that in order to prevent the back reaction of MgO \xrightarrow{Mg} and CO during the condensation of vaporized magnesium, the hot gas mixture must be shock-cooled (chemical chilling) to a temperature, at which the back reaction is suppressed. This may be achieved by spraying liquid hydrogen and mineral oil or hydrocarbons on the gaseous products of reaction (Report, Bureau of Mines No 3635, May 1942). As a result powdered magnesium (blue powder) with a small quantity of MgO is formed.

The above described process is the basis of the electro-thermal method of obtaining magnesium by carbon reduction of MgO, developed by the Austrian-American Corporation Magnesit. This process, tested in a pilot plant in Radenthein (Austria) is now used on an industrial scale in a number of countries (W.L. Landis, Met. Ind. (L), 1937, 51 No 17, p. 403).

A general flow-sheet of the process is illustrated in Figure 201.

Figure 201. TECHNOLOGICAL FLOW-SHEET OF THE PRODUCTION OF MAGNESIUM
BY REDUCTION OF MAGNESITE BY CARBON

- | | |
|---------------------|-------------------------|
| 1. Electric furnace | 5. Filter |
| 2. Cooler | 6. Cyclone |
| 3. Distilling Pipe | 7. Filter |
| 4. Oil | 8. High pressure washer |

Well-calcined magnesite, if possible free of impurities, is used as raw material. The magnesite is mixed with anthracite or ashfree coke (approximately 3 parts by weight of 92 percent magnesite and 1 part reducing agent) and the charge loaded between the electrodes of a hermetically

sealed three phase electric furnace (Figure 202). Pressure in the furnace reached approximately 100 millimeters of mercury.

The gaseous products of the reaction (CO, Mg vapors) on passing from the furnace to the condenser (Figure 203) are shock-cooled with a blast of liquid hydrogen.

As a result, the temperature of the gas mixture drops from 2200/2300 - 150/200 degrees [Centigrade] and the magnesium vapors condense into powder.

To achieve this 40-50 volumes of hydrogen are required for each volume of vaporized magnesium.

Figure 202. Electric Furnace For the Reduction of Magnesite at the Radenthein Works

Figure 203. Condenser for Magnesium Vapors at the Radenthein Works

Magnesium powder thus produced is continually removed from the condenser, while the separating gases (CO, CO₂, and H₂) are purified of all suspended particles by filtering. The magnesium powder consists of 60-70 percent pure magnesium and 15-22 percent MgO, the balance being impurities from the magnesite and the reducing agent which also volatilize during the high temperatures of the reduction process. The recovery of magnesium from the magnesite present in the magnesium powder is 80-90 percent.

In view of the fact that the latter is highly inflammable, it is mixed with oil before being transported, preparatory to distilling out the pure magnesium.

Magnesium powder is then briquetted under a hydrogen atmosphere and the briquettes are automatically transferred to the distilling furnace.

The distilling furnace is a hermetically sealed installation with a residual pressure of 20 millimeters of mercury. The furnace is heated by internal electric resistance up to a temperature of 750-950 degrees [Centigrade].

From the distilling furnace the vaporized magnesium is fed into the condenser, where the magnesium vapors condense as spherical drops varying in

size from small pellets to balls over 1 centimeter in diameter. Drops of condensed magnesium fall into an oil filled collector. Magnesium is then filtered from the oil, melted in an electric furnace and poured into ingots. The oil is returned to the collector.

Non-volatile residue after the distillation of magnesium, mostly MgO , is removed from the distillery furnace by mechanical means and returned for reduction.

Magnesium recovery of magnesium in the powder after the second distillation reaches 98 percent so that total recovery of magnesium from calcined magnesite is over 80 percent.

The metal obtained after additional distilling and remelting is of a very high purity.

Electrical energy consumed in individual stages of the reduction by the electro-thermal process per 1 kilogram of metal in ingots is broken down as follows:

KILOWATT HOURS

Reduction	14.5
Distilling	2.5
Remelting	0.5
Auxiliary Operations	<u>0.5</u>
	18.0

Hydrogen used for each 1 kilogram of magnesium is about 0.25 cubic meters and may be returned into the process after removal of CO . To this end, the gas mixture, remaining after separation from the magnesium powder, is treated by steam in a contact chamber where CO is converted into CO_2 . The CO_2 is then absorbed by the water and the pure hydrogen returned into the process.

109. Reduction of Magnesium Oxide by Non-carbon Reducing Agents

Reduction of magnesium oxide by non-carbon reducing agents is simpler than by carbon. In this case solid rather than gaseous products result from

oxidation-reduction and this makes it possible to produce commercial metal in one operation.

As reducing agents for non-carbon reduction of MgO one could use for example, aluminium, silicon, silico-aluminium and ferrosilicon.

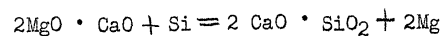
Reduction of MgO by non-carbon reducing agents goes virtually to completion and is comparatively simple in its technical aspect.

The drawback of this process is however the comparatively high cost of the reducing agents, which clinker completely.

Of special interest are methods for the reduction of magnesite or dolomite with the aid of silicon, usually used in the form of ferrosilicon.

This process (in a furnace with carbon electrodes) was first introduced by Blecker and Morrison in 1915. At the present time, technical methods have been developed for the reduction of magnesite (dolomite) by silicon (ferrosilicon), which are the basis for a number of operating industrial installations.

The reaction in the reduction of calcined dolomite with silicon follows the equation:



Thus, calcium oxide present in calcined dolomite is changed into calcium orthosilicate; magnesium oxide from the calcined dolomite is reduced practically completely to a metal.

Besides, this process does not require temperatures as high as those for the reaction in the reduction of MgO by carbon (above 2000 degrees), but is conducted at a satisfactory rate at 1200/1400 degrees. As an example of how the technological problem of reducing dolomite by ferrosilicon is solved let us examine the process of producing magnesium at the H. Ford plant (G.E. Stedman. Chem.-a. Met. Eng. September 1942, 134-137).

The technological flow chart is represented by Figure 204.

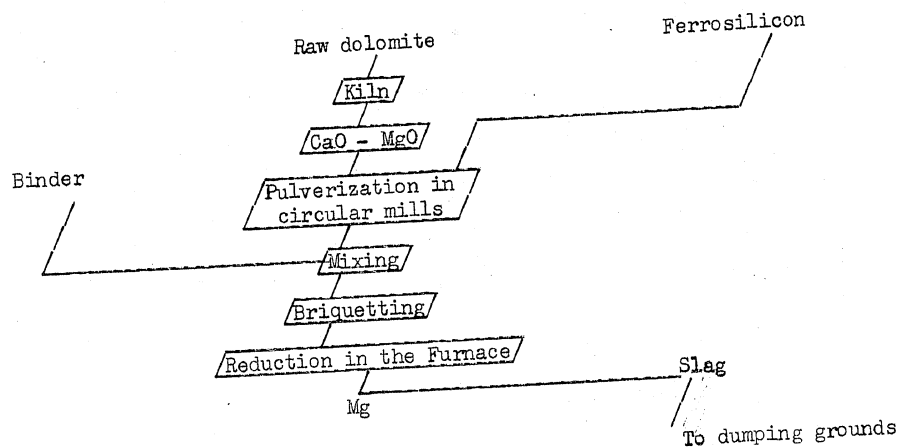


Figure 204. Technological Flow Chart - for producing magnesium through the reduction of dolomite by ferrosilicon at the H. Ford Plant

The process consists of 2 basic stages: Conditioning the dolomite, and the process of reduction (smelting). Raw dolomite from Michigan quarries is delivered to the plant, where it undergoes calcination (roasting) and grinding. As a result of calcination, the dolomite loses, in the form of carbon dioxide, approximately 50 percent of its original weight.

Calcined dolomite and ground 75 percent ferrosilicon (in the proportion 6:1) is measured out directly into large circular mills, which perform simultaneously the functions of grinding and mixing the materials.

A mixture of calcined dolomite and ferrosilicon flows into bunkers, from where, as necessity arises it is transported to the reduction department. Here the furnace charge is briquetted before going into the furnace.

Furnaces for the reduction of dolomite (Figure 205) are arranged in several rows. Each furnace is 5.7 meters high, 4.8 meters wide and 5.4 meters long.

Eleven pipes of chrom-nickel steel, in two horizontal rows - six in the lower and five in the upper row - are laid in the middle of each furnace. The reduction process takes place in these retorts.

Each retort has the following dimensions: Diameter 0.25 or 0.30 meters; Overall Length 6.6 meters of which 3.9 meters are actually in the heat

zone and 0.7 meters extend outside the walls on each side of the furnace. The retorts rest on a crown of refractory brick in the center of the furnace.

Cylinders of sheet steel are inserted into the protruding ends of each retort and serve for the condensation and crystallization of magnesium (Figure 206).

Figure 205. General View of Furnaces for the Reduction of Dolomite

The process of reduction is conducted in a vacuum. For this purpose, each retort is connected at both ends to a vacuum line by means of a 1.5 inch pipe. Each furnace is served by four vacuum pumps of 2800 liters per minute capacity. To obtain a high vacuum the retorts are sealed on both sides by tight fitting covers.

Before being loaded into the retorts, the briquettes are heated in the upper part of the furnace by exhaust gases directed into the pipe. A single charge for each retort is approximately 175 kilograms of briquettes. After charging with the briquettes, condensing cylinders are inserted, the covers securely screwed on and the vacuum pumps turned on.

Each furnace is equipped with several generator gas burners in order to maintain the required internal temperature.

The process of reduction for each charge of dolomite continues for eight hours. Magnesium vapors (under influence of reduced pressure) flow towards the ends of the retort, where magnesium solidifies on the inner surface of the steel cylinders. After several experiments with water cooling, it was determined that the natural contact of cool air with the flanges of the retorts was sufficient for the normal solidification of magnesium.

After eight hours of heating, the cylinders with the deposited magnesium are removed from the retort, the two halves opened and druses of crystallized magnesium removed from the surface.

Theoretically the recovery of metallic magnesium should represent 20 percent of the weight of the briquettes. This represents approximately 35 kilograms of metal for each retort.

After removing the cylinders containing the condensed magnesium, the retorts are scraped free of slag formed during the process. This slag, having a high lime content, may be used in agriculture.

At another magnesium plant in the province of Ontario (Canada), also using the ferrosilicon process of dolomite reduction operating since 1942, the retorts are heated electrically by means of sillimaniterous (Engineer and Mining Jour. 1943, Vol 144, No 5, 56-61). The latter are grouped, strictly in accordance with their power of resistance. Inasmuch as the resistance of the sillimanite rods varies with wear, a system of transformers, regulating the voltage, is provided to compensate for the changing resistance of the bars. This makes it possible to maintain a constant temperature.

At the magnesium producing plants in Murex (?) Great Britian and Broken Hill, Australia, metallic magnesium is obtained by reducing calcined magnesite by calcium carbide (Canter A A Electrometallurgy Eng. Min. J. 1942, Vol 143, No 2, 13). To this end finely crushed magnesite is briquetted with crushed CaC_2 ; the briquettes are heated in steel retorts at a temperature of 1100-1200 degrees. The reduction process is conducted in a vacuum, and magnesium solidifies in the upper regions of the retort on the surface of the condensers, is cooled by water, and forms a solid ring of crystalline metal of high purity (99.85 percent Mg). The heating cycle takes 24-36 hours depending on the size of the retort. During the reduction process, the briquettes should not be subject to melting. A solid residue of a mixture of lime and coal remains after the process.

Production of metallic magnesium by the thermal reduction process, during the past years, particularly over the war period, has become highly developed in various countries.

There is reason to believe that ultimately, due to the simple technological technique, safety, compact installation and lower power consumption, production by this process will exceed that by the electrolytic process.

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