INTERNATIONAL MULTI DISCIPLINARY JOURNAL FOR RESEARCH & DEVELOPMENT
eISSN 2394-6334 Impact factor: 8.854 Volume 13, issue 02 (2026)

# PHYSICOCHEMICAL SYSTEMS OF MAGNESIUM CHLORIDE PRODUCTION STUDIED

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**Abstract**

The physicochemical processes of bishofete production, which is currently in high demand for agriculture and the cotton industry, have been studied by complex treatment of sodium chloride raw materials and dolomite ores with hydrochloric acid.

**Keywords**

"Kaiser Refractories", "magnetic" fire magnesite with large periclase grains, filter fluid, seawater and brines, hydrochloric acid, magnesite, dolomite, magnesium chloride, hydroxide and oxide, sodium sulfate and sodium chloride.

There are many methods for producing magnesium oxide and other forms of magnesia. The heavier forms are obtained by thermal decomposition of magnetic sulfate and hydrolysis of magnetic chloride, and by calcination of magnesite and dolomite [1]. Magnesia of various activity levels is obtained by precipitation of $Mg(OH)_2$ solution and basic magnesium carbonates, followed by thermal treatment.

High-quality heavy forms of magnesia are obtained from magnesite and dolomite at relatively low temperatures (700 °C). Magnesia, called "caustic magnesite", is used in the manufacture of cement and building materials. Inactive forms of magnesium oxide are obtained by calcining magnesite at high temperatures (1500-1800 °C). It is called metallurgical powder and is used in the production of refractory materials. The roasting process is carried out in shafts, rotary kilns, and also in suspended layer furnaces. To obtain metallurgical powder, it is recommended to roast magnesian materials - brucite, dolomite or magnesite mixtures (MgO or CaO) in rotary kilns at a temperature of 1500-1800 ° C.

At the plant of the company "Kaiser Refactories" (USA), granular dolomite is cleaned of sand impurities in a separator, the density of which is filled with crushed ferrosilicate and magnesite is 2.72-2.76 g / cm³, and that of dolomite is 2.85 g / cm³, therefore it falls to the bottom of the vessel and is separated, sand and other light impurities remain in the upper part of the material, filling the separator. Ferrosilicate and magnesite are cleaned and washed from the particles retained in the vibrating chamber. It is then burned in 91m long rotating drums.

By burning at 1800 °C with the addition of 5% iron oxide, a high-density "burnt dolomite" is obtained, which is ground and treated with petroleum bitumen at 80 °C to stop the hydration process. This material is used as a metallurgical flux. Dolomite intended for the production of magnesium oxide is burned at a temperature not exceeding 1100 °C. Dolomite contaminated with silicate and crinite is also calcined in a fluidized bed and simultaneously separated. The resulting magnesium oxide powder has a size of 0.25 mm and is sprayed into the collector by a gas stream, while larger impurities settle to the bottom of the vessel and are removed from the burning zone [2].

In the production of caustic magnesite, the separation of $SO_2$ from the mixture is also carried out during the roasting process.

By rapidly heating the magnesite mixture to 600-800 °C, at 575 °C the p-modification of quartz is converted to the a-modification, which is in the form of a fine powder and is easily removed from the furnaces with gas [3].

Continuing the chemical processing of magnesite and dolomite products, it is possible to obtain light forms of magnesia from them. One of such methods is to obtain a solution of magnesium bicarbonate, which is less active magnesium oxide. The magnesium oxide obtained as a result of roasting magnesite is ground and quenched with water. The resulting suspension is carbonated with carbon dioxide in an autoclave under 5 atm of magnesia water. The result is a solution of magnesium bicarbonate:

$Mg(OH)_2 + 2C\ O_2 = Mg(HCO_3)_2$

It is solid, after it is purified from impurities, it is hydrolytically decomposed by boiling:

$2Mg(HCO_3)_2 = MgCO_3 + Mg\ (OH)_2 + 3CO_2 + H_2O$

The resulting precipitate is separated and dried to obtain alpha magnesia in the form of a fine powder. Magnesia is obtained from dolomite in a similar way. During calcination, dolomite dissociates in two stages:

$MgCO_3 \cdot CaCO_3 = MgO + CaO + 2CO_2 - 74$ ккаl

The decomposition of $MgCO_3$ occurs at 730 °C, i.e. 80 °C higher than the decomposition of dolomitic magnesite. This is due to the thermal effect of the formation of $CaMg(CO_3)$. The earlier decomposition of dolomite has been experimentally demonstrated [4]. At 730 °C, dolomite decomposes, forming MgO and a solid carbonate solution (38):

$nCaMg\ (CO_3)_2 = (n-1)MgO + MgCO_3 \cdot nCaCO_3 + (n-1)CO_2$

when the temperature reaches 910 °C, solid, solution dissociation continues:

$Mg\ CO_3 \cdot nCaCO3 = MgO + nCaO + (n+1)CO_2$

The dissociation rate of dolomite is lower than that of magnesite; it is accelerated in the presence of 1% fluoride or sodium chloride [38, 39, 40]. Dolomite is calcined at 700-800 °C or 110-1250 °C, depending on the intended use of the product.

If dolomite is not completely calcined, only $MgCO_3$ decomposes and underburnt dolomite is formed. It is partially obtained by rapid calcination of dolomite, i.e. in a closed rotary kiln at 750-800 °C, cooled in the atmosphere for 15 minutes and then cooled to 500 °C within 30 minutes [5].

Fully calcined dolomite is quenched with water to form a suspension of magnesium and calcium hydroxide:

$$(C+CaO)+2H_2O= Mg(OH)_2 + Ca(OH)_2$$

The hydration rate of MgO decreases with increasing firing temperature, especially above 1300 °C; it may also decrease depending on the presence of CaO, $SiO_2$, $A1_2O_3$ impurities and the size of the magnesium oxide particles [42]. When the suspension settles, magnesium hydroxide is in the upper layer, which facilitates its separation from coarse impurities.

Even a small amount of $MgC1_2$ is added to accelerate the hydration process, but this may contain chlorine oxides [6].

To obtain relatively large $Mg(OH)_2$ crystals in the suspension, it is quenched with water by heating the pulp containing 17% solids to 95-100 °C, boiling, and steaming. To separate magnesium and calcium hydroxides, the pulp is added until the solids are 11%, cooled to 60 °C and carbonated.

In this case, it turns into $Ca(OH)_2$, while $Mg(OH)_2$ remains unchanged:

$$Ca(OH)_2 + Mg(OH)_2+ CO_2= CaCO_3 + Mg(OH)_2+ H_2O$$

At a temperature of 40-60 ° C, the carbonation of calcium hydroxide proceeds at maximum speed. The precipitation of CaCO3 occurs in steel apparatuses, to which gas from combustion furnaces containing up to 40% CO2 is supplied through turbogas injectors. The completion of the carbonization process can be determined by the electrical conductivity of the pulp. When the carbonization of Ca(OH)2 is completed, the electrical conductivity increases rapidly. The resulting pulp is sent for carbonization again, and a magnesium bicarbonate solution is formed.

To prevent magnesium bicarbonate from precipitated as a result of carbonization, the temperature is not raised above 26 ° C.

The bicarbonate solution separated from the sludge (CaCO3, SiO2, etc.) is heated at 45-50 ° C and decomposed. This forms the main magnesium carbonate MgSO3· Mg(OH)2, which is dried and sold as light magnesia.

The solution is purified from iron and manganese compounds by adding hydrated magnesium carbonate to it [7]. The solubility rate of Mg(OH)2 in the carbonation of an aqueous suspension is determined by the rate of solubility processes and the rate of CO2 hydration. In practice, the carbonation rate of magnesium hydroxide depends on the partial pressure of CO2 in the gas and the intensity of suspension mixing. The optimum pressure of CO2 is 2.5-3 atm. At this pressure, 80-90% of Mg(OH)2 dissolves and the saturated bicarbonate increases in stability. The average solubility rate of magnesium hydroxide decreases with increasing concentration.

The degree of saturation of the solution is strongly influenced by the size of the magnesium hydroxide particles formed depending on the conditions of burning the magnesium raw material. During the carbonation of semi-burnt dolomites, the solubility of magnesium bicarbonate is observed, but as the process progresses, its amount in the solution decreases, and the precipitate is formed as Mg(OH)2 salt mixed with insoluble components of dolomite [48]. During the treatment of CO2 under pressure, the double salt 2Mg(HCO3)2 MgCO3 is formed in the fired dolomite suspension; at a pressure of 16 atm, it is in the solid phase $MgCO_3 3\ H_2O$, and in the solution it is 2Mg(HCO3)2, which precipitates at a pressure of 60 atm, and the magnesium content in the solution is 24 g/l (relative to $MgCO_3 3\ H_2O$) [8].

In the production of basic magnesium carbonate, the process of decarbonation of magnesium bicarbonate solution is accelerated by passing air through it. However, this leads to a decrease in its concentration during the airing process, which makes it difficult to return it to carbonation. Therefore, the decomposition of the solution is carried out by mechanical stirring, using the gas formed. After reducing the concentration of Mg(OH)2 to 4 g/l, air is sprayed through the solution, and the formed gas is released into the atmosphere. In the production of basic magnesium carbonate, the decomposition of the bicarbonate solution is carried out at temperatures above 45 °C, which is why at 25 °C, not the basic salt, but MgCO3·3H2O (rhombic crystal system) is separated from the saturated metastable solution; at 10 °C, MgCO3·5H2O (crystals of the monoclinic system); The conversion of MgCO3·3H2O to MgCO3·3H2O occurs at 13.9 °C [9]. The decomposition of the bicarbonate solution is carried out “instantaneously” by heating it to 100 °C. In this case, an injection steam stream is supplied to the reaction chamber, and 4Mg(OH)2· MgCO3 particles with a size of 2 μm are formed in small solution droplets [50].

In addition, it is proposed to treat the Mg(HCO3)2 solution with 2-5% alkali or rosin soap at 80-90 °C. As a result, a precipitate of the main salt MgCO3 · Mg(OH)2 is formed, the grains are covered with soap, and it is recommended to use it as a filler for rubber mixtures.

Carbonation of the suspension containing Mg(OH)2 and subsequent decomposition of Mg(HCO3)2 can be used in the purification of technical magnesium oxide and hydroxides.

In such cases, Mg(HCO3)2 is separated from the impurities in the solution, dried and calcined, and magnesias are obtained from it. Magnesium carbonate can be obtained by thoroughly mixing a magnesium bicarbonate solution with an aqueous suspension of magnesium hydroxide at a temperature below 50 °C:

$$Mg(HCO_3) + Mg\ (OH)_2 = 2MgCO_3 + 2H_2O$$

To increase the activity, it is recommended to keep it at a temperature below 27 °C (55).

Ammoniacal methods of magnesia extraction. A large plant in Paceville (Ohio, USA) produces magnesium oxide from dolomite containing 20% MgO, combined with the production of soda ash. The dolomite is burned in mine furnaces, and the gas containing 40% $CO_2$ is used to produce soda ash and to process magnesium hydroxide. The dolomitic water is sent to the distillation station of the soda ash plant, where it reacts with ammonium chloride solution (with the filtered liquid). A sufficient amount of dolomitic water provides an equivalent ratio of CaO and NH4Cl, magnesium hydroxide does not react and remains unchanged, and $Ca(OH)_2$ is converted to $CaC1_2$:

$$Mg\ (OH)_2 + Ca(OH)_2 + 2\ NH_4\ Cl = Mg\ (OH)_2 + CaC1_2 + NH_3 + 2H_2O$$

After removal from the suspension, the Mg $(OH)_2$ and $CaC1_2$ in the solution are condensed, the magnesium hydroxide is filtered, washed, and calcined to convert to magnesium oxide.

The 2nd grade metallurgical powder of magnesium oxide obtained in this way meets the requirements of the standard [10].

According to another option, the obtained distillate liquid, i.e. the filtered liquid of dolomite water, is carbonated, as a result of which $CaCO_3$ precipitates, and $Mg(OH)_2$ is converted to $MgC1_2$.

Then the obtained magnesium chloride solution is recycled to obtain magnesia. It is also possible to simultaneously treat the $MgCO_4$ solution with ammonia to obtain ammonium sulfate.

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