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MODERN METHODS OF PROCESSING DOLOMITE INTO MAGNESIUM AND CALCIUM COMPOUNDS WITH MINERAL ACIDS

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Abstract: Optimal conditions for obtaining granular and liquid nitrogen calcium and magnesium fertilizers, as well as Mg(OH)2 and MgO, by decomposing dolomite raw material with nitric acid to form a solution of $Ca(NO_3)_2$ and $Mg(NO_3)_2$ and ammonizing this solution with ammonia were studied.

Keywords: “Kaiser Refractories”, “magnetic” fire magnesite with large periclase grains, filter liquor, sea water and brines, carnallite, magnesite, dolomite, serpentinite, magnesium chloride, hydroxide and oxide, sodium sulfate and sodium chloride.

Dolomite flour is a raw material consisting mainly of $CaCO_3{\cdot}MgCO_3$, containing approximately 20% MgO and 28% CaO. The residue remaining on a 0.25 mm sieve of class A dolomite flour should not exceed 32%, and in class B - not more than 60%. The content of the sum of calcium and magnesium carbonate salts is not less than 65%. Bulk density - 1.5 g/cm3. The fertilizer is used for liming acidic soils at a rate of 1.5-3 t/ha. At the same time, the soil is enriched with magnesium in sufficient quantities to feed plants during one or two rotations. Dolomite flour is transported in bulk by all types of transport [1].

Magnesia with varying degrees of activity is obtained by precipitation of magnesium hydroxide and basic magnesium carbonates from solutions and subsequent heat treatment. By burning magnesite at relatively low temperatures (~ 700 °C) at high temperatures, heavy forms of magnesia are obtained from magnesite and dolomite, which contain all the impurities present in magnesite. Such magnesias, called "caustic magnesite", are used in the production of cement and building materials. When magnesite is burned at high temperatures (1500-1800 °C), an inactive form of magnesium oxide is formed, the general product of magnesium oxide processing is "magnetic" fire magnesite, consisting of large periclase grains, which is used for the production of metallurgical powder and refractory materials and products.

According to statistics from 2010, 53% of magnesium crystals in the United States were used for the production of fire-resistant products, and the remaining 47% were used in agriculture, the chemical industry, construction, and environmental protection [2].

There are various methods for removing silicate compounds from dolomite and obtaining magnesium oxides. Thus, it was proposed to burn dolomite in a mixture of silicate and a small amount of iron oxide, which improves the synthesis of the raw material. After that, the boiled material is treated with water, and the main part of the CaO formed during the burning, which is not part of the ferrite, is wetted and washed. The latter is purified by separation of magnesium oxide and magnetite, then treated with hydrochloric acid to free it from $Ca(OH)_2$ residues and thoroughly washed with water [3]. Also, at the Kaiser Refractories plant (USA), crushed dolomite is separated from sand impurities in a separator filled with a crushed mixture of ferrosilicon and magnetite, through which compressed air is blown. The density of the mixture is 2.72-2.76 g/cm³, and the density of dolomite is 2.85 g/cm3; therefore, it sinks to the bottom and is removed, while sand and other lighter impurities remain on the surface of the material filling the separator. Dolomite is cleaned and washed from ferrosilicon and magnetite particles trapped in vibrating chambers. It is then fired in 91-meter-long rotary drum kilns, calcined to 1800 °C with the addition of 5% iron oxide to obtain high-density "burnt dolomite"; it is crushed and treated with petroleum bitumen at 80 °C to prevent hydration. This material is used as a metallurgical flux. Dolomite intended for the production of magnesium oxide is fired at a temperature not exceeding 1100 °C.

After the products obtained by burning magnesite and dolomite raw materials, it is possible to obtain light forms of magnesia from them by chemical processing of the residues. One of such processing methods uses the stages of transferring low-active magnesium oxide into a solution in the form of magnesium bicarbonate, followed by precipitation of active magnesium from it. The magnesium oxide obtained as a result of burning magnesite is crushed and quenched with water. The resulting suspension - milk of magnesia - is carbonized with carbon dioxide in autoclaves under a pressure of more than 5 atm. This is the process of producing a magnesium bicarbonate solution.

$Mg(OH)_2 + 2CO_2 = Mg(HCO_3)_2,$

After the magnesium bicarbonate solution is separated from the solid impurities, it is hydrolytically decomposed by boiling in the next step:

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

The resulting basic magnesium carbonate precipitate is separated and, after drying, is obtained in the form of a very fine powder - alba magnesia. Magnesia is also obtained from dolomite in a similar way. During calcination, the dissociation of dolomite occurs in two stages:

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

The decomposition of $MgCO_3$ in dolomite occurs at ~730 °C, i.e., $MgCO_3$ is ~80 °C higher than the decomposition of magnesite. This is due to the thermal effect of the formation of $CaMg(CO_3)_2$. It has been experimentally established that there is no initial decomposition stage in the carbonates that form dolomite. At a temperature of 730 °C, dolomite decomposes, forming a solid solution of carbonates reduced to MgO and magnesium carbonate:

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

In this process, further dissociation of the solid solution is achieved by increasing the temperature to 910 °C:

$MgCO_3 \cdot nCaCO_3 = MgO + nCaO + (n + 1)CO_2.$

The degree of dissociation of dolomite is less than that of magnesite; it increases in the presence of 1% fluorine or sodium chloride [4]. Dolomite raw materials are fired at temperatures of 700-800 °C or 1100-1250 °C, depending on the mesh of the product to be formed. If the firing process is not complete, only $MgCO_3$ decomposes and half-burnt dolomite is obtained. It can be obtained, in particular, by rapidly heating dolomite in a closed zone of a rotary kiln to 750-800 °C in the presence of atmospheric CO_2 for 15 minutes and cooling to 500 °C for 30 minutes. When completely burned dolomite is quenched with water, a suspension of magnesium and calcium hydroxides is formed:

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

The rate of MgO hydration decreases sharply with increasing firing temperature, especially above 1300 °C; it also decreases in the presence of impurities of CaO, SiO_2, Al_2O_3 and other components and depends on the size of the magnesium oxide particles. When the suspension settles, magnesium hydroxide forms in the upper layer, which allows it to be separated from other solid components. The addition of small amounts of $MgCl_2$ accelerates its hydration, but can also accelerate the formation of oxychlorides.

To obtain a relatively large amount of $Mg(OH)_2$ crystals in the suspension, the quenching process of the suspension is carried out at 95-100 °C, the slurry containing ~ 17% of the solid phase is heated with hot steam and, to separate magnesium and calcium hydroxides from it, it is diluted by adding 11% of the solid phase to the slurry, cooled to 60 °C and carbonated. In this process, $Ca(OH)_2$ is converted to $CaCO_3$, and $Mg(OH)_2$ remains unchanged:

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

Also, in the temperature range of 40-60 ° C, the carbonation of calcium hydroxide occurs at maximum speed. The process of precipitation of $CaCO_3$ is carried out in steel apparatuses under high atmospheric pressure, in incinerators with a CO_2 content of up to 40% using turbo-gas blowers. The completion of the carbonization process of calcium hydroxide is determined by the electrical conductivity of the slurry - after the carbonization of $Ca(OH)_2$ is completed, the electrical conductivity increases sharply due to the beginning of the carbonization of $Mg(OH)_2$ [5]. The resulting slurry is sent for the next carbonization process, and a magnesium bicarbonate solution is formed in it. In order to prevent the precipitation of magnesium carbonate during the preparation of magnesium bicarbonate, the temperature does not exceed 26 ° C. The bicarbonate solution ($CaCO_3$, SiO_2, etc.) separated from the sludge is decomposed by stirring and heating to a temperature of 45-50 ° C. This process mainly produces magnesium carbonate crystals $3MgCO_3$ and $Mg(OH)_2$, which are dried and extracted as light magnesia.

It can also be used to separate suspensions containing carbonized $Mg(OH)_2$, decompose $Mg(HCO_3)_2$ and purify technical magnesium oxide or hydroxide; in this case, after separating impurities from the $Mg(HCO_3)_2$ solution, it is dried and calcined, or the magnesium extracted from it is also calcined.

In Paynesville (Ohio, USA), the process for producing magnesium oxide in large quantities from dolomite containing 20% MgO is combined with the soda ash production process. The gas obtained by burning dolomite in mine furnaces and containing up to 40% CO_2 is used in the production of soda ash and in the processing stages of magnesium hydroxide. The dolomite milk is sent to the distillation station of the soda ash plant, where it interacts with an ammonium chloride solution (filter liquid). With a sufficient amount of dolomite milk, which provides an equivalent ratio between CaO and NH_4Cl, magnesium hydroxide does not react, remains unchanged, and decomposes into $Ca(OH)_2$ and converts to $CaCl_2$ as a result of a chemical reaction:

$Mg(OH)_2 + Ca(OH)_2 + 2NH_4Cl = Mg(OH)_2 + CaCl_2 + 2NH_3 + 2H_2O$.

After distillation of NH_3, the suspension of $Mg(OH)_2$ in the $CaCl_2$ solution is concentrated, the magnesium hydroxide is filtered, washed, and calcined to convert it to magnesium oxide.

According to another option, the distillation liquid obtained by treating the filtered liquid with milk of dolomite undergoes carbonation, as a result of which $CaCO_3$ precipitates and $Mg(OH)_2$ is converted to $MgCl_2$:

$Mg(OH)_2 + Ca(OH)_2 + 2NH_4Cl + CO_2 = MgCl_2 + CaCO_3 + 2NH_3 + 3H_2O$.

The resulting magnesium chloride solution is then processed into magnesia.

Magnesium hydroxide can be obtained by treating a solution of $MgSO_4$ with ammonia and carbon dioxide simultaneously with ammonium sulfate.

The lime method for the production of magnesia involves the precipitation of magnesium hydroxide from solutions of magnesium chloride with lime (milk of lime). Since the solubility of Mg(OH)2 is significantly lower than that of $Ca(OH)_2$ (1.6 g/l at 25 °C), the reaction proceeds towards the formation of $Mg(OH)_2$.

$MgCl_2 + Ca(OH)_2 = CaCl_2 + Mg(OH)_2$.

Magnesium hydroxide is filtered, washed thoroughly with water and calcined at low temperatures. Depending on the methods of precipitation and calcination, various types of magnesia can be obtained.

In a number of countries (USA, Netherlands, Japan, Mexico, Israel, Ireland, Jordan), magnesium oxide is obtained from seawater by mixing it with calcined dolomite or limestone:

$CaO/MgO + MgCl_2 + 2H_2O \rightarrow 2Mg(OH)_2\downarrow + CaCl_2$.

First, magnesium hydroxide is precipitated, and then the magnesium hydroxide precipitate is calcined until magnesium oxide is formed. To justify the economic feasibility of this method, for example, in the United States, although there are industrial deposits of magnesite, the majority of the magnesium oxide in this country is obtained from seawater and groundwater.

According to the United States Geological Survey, Japan, the Netherlands, and the United States currently account for 56% of the production of magnesium powder from seawater [6].

There is a known method for obtaining magnesium hydroxide from bischofite, which involves filtering the bischofite solution, precipitating magnesium hydroxide from the solution by treating the filtrate with ammonia, and further precipitating magnesium from a basic magnesium solution with a pH of 10-10.5 by raising the pH to 11.0-11.5 using ammonium carbonate solution. To obtain magnesium oxide from the precipitated magnesium hydroxide, the precipitate is heat-treated at 500-700 °C for 1-2 hours.

Magnesium oxide is also obtained from bischofite in crystalline form. To do this, bischofite undergoes thermal hydrolysis at low atmospheric pressure in three stages: the first stage is the formation of liquid-phase bischofite at a temperature of 107-117°C, the second stage is the formation of magnesium hydroxide at a temperature of 20-30-290°C, and the third stage is the formation of magnesium oxide at a temperature of 410-490°C.

Magnesium oxide is also obtained by grinding the raw material containing magnesium to a fraction smaller than 0.5 mm and treating it with sulfuric acid at a temperature of 60-70 ° C, cleaning the suspension from metal impurities, and purifying the remaining raw material and silica gel from additives in it by precipitation. To the total composition of 20-30% milk of lime or soda solution, 2-8% magnesium sulfate solution and calcined magnesium are added, and the filtrate obtained after separation of magnesium hydroxide from magnesium oxide is sent to precipitate to obtain magnesium hydroxide. [7]. The Na_2O in the precipitate is washed three times until the sodium oxide content in the precipitate drops to 0.43%, dried at 350 ° C to 1.5% moisture, and heat-treated at 850 ° C and cooled.

Another method of obtaining magnesium oxide from magnesium-containing raw materials is to treat serpentine with 10-15% concentrated sulfuric acid at a temperature of 90-100 °C, purify the resulting magnesium sulfate solution from metal impurities by precipitation with caustic soda to pH 8-8.5, separate the precipitate of the formed metal hydroxides, carbonize the solution at pH 10-12, separate magnesium carbonate, wash, dry, and heat treat at 900 °C in stages [8].

Methods for obtaining MgO from natural brines are characterized by precipitation of magnesium hydroxide by treating limestone with thermally calcined milk of lime, thickening of the slurry with calcium chloride and magnesium hydroxide precipitate in the presence of polyacrylamide, filtration, washing of the final precipitate, bicarbonate solution, carbonization of the slurry to obtain magnesium and solid precipitate crystals, separation, heating of the magnesium bicarbonate solution with magnesium carbonate precipitate to boiling point and calcination at high temperatures. Highly mineralized brine is used with a content of 60-350 g/l and is cooled to a temperature of +18 to -25 °C.

Thus, by decomposing dolomite raw materials with nitric acid, a solution of $Ca(NO_3)_2$ and $Mg(NO_3)_2$ is formed, and by ammonizing this solution with ammonia, granular and liquid nitrogen calcium and magnesium fertilizers, as well as $Mg(OH)_2$ and MgO, are obtained.

In addition, there are certain methods for obtaining $Mg(OH)_2$ and MgO from dolomite raw materials, and scientific research has been carried out on the extraction of magnesium hydroxide and oxides from magnesium silicates contaminated with silicon oxide and oxides of some metals [9].

Another method of obtaining magnesium oxide is to treat natural dolomite with sulfuric acid or its mixtures with hydrochloric acid in a molar ratio of 1:2. After cleaning the magnesium chloride solution from gypsum precipitate, magnesium hydroxide is precipitated from it under the influence of an alkaline reagent providing pH=10.6-12.0, then the precipitate is separated and heat-treated at 760-1200 °C to obtain refractory magnesium oxide.

Another method of processing dolomite with mineral acids involves crushing the raw material and washing it several times with an acidic solution at a temperature of 60-90 °C to obtain a magnesium chloride solution, and treating the solution with salts containing calcium and magnesium chlorides. Mixing a mixture of synthetic carnallite of the same composition with naturally enriched carnallite, two-stage dehydration to produce anhydrous carnallite, electrolysis to produce magnesium chloride and spent electrolytes, recycling part of the chlorine for dehydration and mixing with waste electrolytes, while using an acid-salt solution from titanium production waste for washing in a chloride ion and water ratio of 1: (2-9) by mass, and pre-concentrating the acid-salt solution by circulating it. The waste solution of titanium chlorates or the waste gases of titanium chlorates are used as aqueous wastes of titanium production, which ensures the reduction of magnesium costs and gas emissions into the atmosphere.

Unlike previous methods, this method uses methods of processing the electrolyte used for the synthesis of carnallite and chlorine, using methods of evaporation of the purified $MgCl_2$ solution, carnallite synthesis, dehydration with HCl, and electrolysis to obtain ready-made magnesium. In the following processes, the solid phase of the hydrochloric acid extract is washed. In this case, the ore is washed until the residual hydrochloric acid content is no more than 1.0 - 1.5% HCl, the washed solid phase is used in the production of liquid glass.

The method of obtaining pure magnesium oxide involves dissolving the starting materials made from magnesium silicates and hydrosilicates, such as olivine, serpentine, garnierite, in hydrochloric acid, separating the insoluble residue from the suspension, precipitating additional compounds contained in the thickened slurry, as well as impurities of hydroxide and other contaminants. Thus, to obtain magnesium oxide from a magnesium chloride solution, it is thermally decomposed by calcination. In this method, 1.5-2.5 times more serpentine is added than the norm according to the chemical stoichiometric reaction equation to precipitate magnesium. Purification of the slurry from additional compounds and heating and mixing with chlorine or peroxide using oxidizing air at a temperature above 80 ° C is carried out. In this case, in order to increase the purity of the slurry, magnesia or its powder obtained by calcining magnesite at a high temperature is additionally added.

This description is related to the method of obtaining magnesium compounds from magnesium-bearing ores, which involves washing serpentinite residues with dilute HCl to dissolve other elements such as magnesium, iron, and nickel. The silica remaining in the serpentinite residue is removed and further neutralized to separate the nickel from the enriched solution. Magnesium chloride reacts with sulfuric acid to form magnesium sulfate and hydrochloric acid. Magnesium sulfate can be decomposed by calcination into magnesium oxide and sulfur dioxide. The sulfur dioxide can then be converted to sulfuric acid.

The nitric acid method for processing magnesium silicates is considered the most promising in terms of low corrosion of steel equipment. At the same time, the technological cycle for expensive reagents is closed, which ensures the environmental safety of production [10-11].

Thus, the products of processing natural resources are seawater and brines, carnallite, magnesite, dolomite, serpentinite, magnesium chloride, hydroxide, and oxide. When processing brackish and saline waters, additional sodium sulfate and sodium chloride are obtained.

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