

Technology of Processing of Navbakhore Dolomite on Magnesium Compounds

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ABSTRACT

The technology of production of hydroxide, oxide and carbonate of magnesium, as well as liquid complex nitrogen-calcium-magnesium fertilizers from dolomite of Krasnogorsk field Navbahor district of Navoi region of Uzbekistan is developed. Pilot samples of the products were obtained at JSC "Maxam-Chirchik". On the basis of material balance and optimization of processes' modes, a specification for industrial plant of dolomite processing was designed.

Keywords: Dolomite, Mineral, Magnesium, Processing.

INTRODUCTION

To further intensify the development of agricultural production in the country, a number of measures are needed, including the increase in the production of complex fertilizers. To promote the solution of this problem the development of technology of complex calcium – magnesium - nitrogen fertilizer should be organized. Existing mineral fertilizers do not contain magnesium. Meanwhile, magnesium is necessary for plants during the vegetation period: with its lack they have "magnesium starvation" - chlorosis and marbling of leaves, the root system suffers. The rate of plant nutrition is not less than 0.2%, in terms of dry weight. And if many greenhouse farms cover their need for it at the expense of imports, then the solution of the problem on the scale of the republic requires a different approach.

In nature there are 4 types of magnesium deposits.

- Fossil mineral deposits (magnesian and potassium-magnesian salts).
- Sea water.
- Brines (salt brine lakes)
- Natural carbonates (dolomite and magnesite).

The source of magnesium can be not only sea water, but also the water of salt lakes containing magnesium chloride. For example, in Russia there are such lakes: in the Crimea - Saki and

Sasyk-Sivash, in the Volga region - Lake Elton and others [1].

In the Republic of Uzbekistan, magnesium raw materials are the dolomites. They are an important magnesium feedstock. Deposits of dolomite are widely distributed in the world, their reserves are huge. We know about three dozen promising manifestations of dolomites with a magnesium oxide content of more than 18%. Deposits of dolomites that meet the raw material requirements are located in Dekhkanabad, Saukbulak (Almalyk), Muruntau, Fergana (Mamai), Navoi (Zimetdin-1), Bukhara regions. Another important type of magnesia raw material is magnesium hydroxide. It can be used for the production $MgCl_2 \cdot 6H_2O$, $MgSO_4 \cdot 7H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$. Magnesium hydroxide is also used: in flooring; in roofing materials; composite panels (copolymers of polyethylene); structural materials (polypropylene); electrical parts (polyamide 6.66); profiles and pipes (polypropylene); insulation, gaskets; and foamed insulation (polyolefins, PVC, etc.); -artificial leather (PVC), etc.

Magnesium oxide is also used in magnesia binders for the production of sulfur, glass-magnesium sheet (CML), foam magnesia, magnesian floors, building products and structures.

Magnesium carbonate is distributed as a separate type of raw material. It is applied as

filler in rubber compounds, for manufacturing heat-insulating materials, in the production of glass, cement, brick, in medicine, as a food additive, etc.

There are many ways to produce magnesium oxide and other forms of magnesia.

Their heavy forms are obtained during roasting of magnesite and dolomite, thermal decomposition of magnesium sulfate and hydrolysis of magnesium chloride.

Magnesia with different degrees of activity is obtained by precipitation from solutions of magnesium hydroxide and basic magnesium carbonates and their subsequent thermal treatment [2].

A method is known for the production of magnesium oxide from natural raw materials [3], which includes dissolving the raw material with hydrochloric acid, separating the insoluble residue from the magnesium chloride solution, purifying the latter from metal impurities upon heating, adding a granular serpentinite as a precipitant to 0-1mm granule, Precipitation of the magnesium-containing compound and its subsequent thermal decomposition to MgO and MgCl₂.

The use of this method for the production of MgO from dolomite is impossible due to the formation of a mixed solution of CaCl₂ and MgCl₂. Purification of the latter from CaCl₂ requires several additional operations. In addition, at the stage of thermal decomposition of MgCl₂, hydrogen chloride is formed, which requires the creation of treatment facilities to prevent environmental pollution.

In the method [4], hydrogen peroxide addition to sulfuric acid solution of serpentines natural raw material is proposed to transfer divalent ferrous ions to trivalent. The resulting solution should be cooled down to 5°C, crystallized, and the insoluble residue could be separated.

Neutralization of the solution with alkali at its concentration of 8 weight % to pH 5-7 leads to a solution of magnesium sulfate. It is dried in a spray dryer to give anhydrous crystalline magnesium sulfate. Heat treatment at 1100°C and washing of the heat-treated precursor produces a product containing 99 weight % of MgO.

A disadvantage of sulfuric acid leaching of magnesium from natural raw materials, followed by thermal decomposition of magnesium sulfate to MgO and SO₃ is the formation of sulfuric and sulfur dioxide gases.

The method [5] involves the preparation of magnesium hydroxide from magnesite-containing 97.6% MgSO₃ and 0.87% FeO, and from basic magnesium carbonate Mg₅(OH)₂(CO₃)₄·4H₂O, by treatment with solid sodium hydroxide, water, which forms magnesium hydroxide and anhydrous soda. The mixture is treated with water to dissolve the soda, magnesium hydroxide is separated by filtration. The magnesium hydroxide can be used to produce magnesium hydroxide.

However, when MgCO₃ and CaCO₃ are contained in the raw material, treatment with solid alkali and addition of a certain amount of water will not allow the separation of Mg²⁺ and Ca²⁺.

The method [6] of obtaining magnesium oxide from calcined dolomite, in combination with the production of soda, by treating dolomite milk with a distillation liquid of soda production, consists in separating the solid phase from the resulting suspension, washing the precipitate, repulping it in water, carbonizing the resulting suspension of magnesium hydroxide under pressure 1-6 atm. and decarbonization of the magnesium bicarbonate solution upon heating, precipitation of the precipitate of the basic magnesium carbonate, its calcination and sintering of magnesium oxide.

Carbonation of a suspension of magnesium hydroxide is carried out in the presence of sodium tripolyphosphate, taken in an amount (2-8)10⁻⁴ g per 1 kg of suspension).

The drawback of the method is the calcination of dolomite at a high temperature (1050°C) and the need to organize production in the composition of solo production.

The method [7] for obtaining magnesium oxide consists in the fact that the raw material - natural raw dolomite, consisting mainly of calcium and magnesium carbonates, is dissolved in nitric acid with a concentration of 28-30% by weight. The resulting solution is separated from the undissolved residue and out of it with the addition of ammonium sulfate; calcium is precipitated in the form of calcium sulphate. From the filtrate, after separation of the precipitate, impurity metals precipitate at pH (5-7), the magnesium-containing compound in the form of magnesium hydroxide is precipitated at the solution pH (10-11). The precipitation is carried out with an aqueous solution of ammonia. Magnesium hydroxide is separated and heat treated. Involvement in the processing

and production of fertilizers basing on flour of local natural magnesium-containing compounds is an actual issue.

Objective

Development of technology for processing dolomite for magnesium compounds and mineral fertilizers. Research's task are the following: selection of local magnesium-containing raw materials, development of regimes for obtaining magnesium compounds and complex nitrogen-magnesium fertilizer.

METHODS AND MATERIALS

The content of calcium and magnesium oxides was determined in accordance with State Standard GOST 23673.1-79 "Method for determination of the content of calcium and magnesium oxides".

Common sources of magnesium in nature are dolomite flour, its mixture with ammonium nitrate, serpentinite flour, vermiculite, burnt magnesite, epsolite, etc. It is found that the most suitable local magnesium raw material is the dolomite of the Krasnogorskoye field, Navbakhor district of the Navoi region, in which the MgO content is 19.0 wt. %, Which meets the requirement of State Standard GOST 23672-99, according to which dolomite should contain wt. %: MgO-19; CaO-34; FeO-0.05.

RESULTS AND DISCUSSION

The solution of the research task was the production of an experimental batch of hydroxide and magnesium carbonate from the dolomite. With the selected sample, tests were carried out at No.51 shop of JSC "Maxam-Chirchik". The preparation of magnesium hydroxide was carried out in the following stages:

- Dissolving ground dolomite in nitric acid (reactor volume 1.6m³, equipped with a stirrer, temperature 28-30°C, time 90-120 min). To the nitric acid (25%) ground dolomite was added. Dissolution was continued until carbon dioxide evolution ceased.
- Separation of the solution from the undissolved precipitate. The solution was filtered (vacuum pump), separating the precipitate.
- Treatment of the filtrate with ammonium sulfate. The filtrate solution of magnesium nitrate was heated in the reactor up to a temperature of 55-60°C and, with stirring,

ammonium sulfate was added up to fixation pH 3÷3.5.

- Separation and washing of gypsum. The precipitated gypsum was transferred to a nutch filter and washed with water, dried in air. Wash water was combined with the filtrate.
- An 18% solution of soda ash was added to the basic filtrate with continuous stirring to pH 10.5÷11. At the same time, magnesium carbonate precipitated in the tank and was settled.
- Separation and washing of magnesium carbonate. The precipitate was transferred to a suction filter and washed from the residues of nitrate ions, and dried in air.

Heat treatment of magnesium carbonate at 50 °C and at 800°C (Table 1).

As it follows from Table. 1, the precipitation of magnesium in the form of MgCO₃ with the use of soda occurs most fully, in comparison with ammonia and the ammonium salt. The yield of MgO = 67.73%, which corresponds to caustic magnesite in accordance with State Standard GOST 1216-87.

The next stage was the production of a pilot batch of MgCO₃, MgO from dolomite at the installation of the JSC "Maxam-Chirchik." The material balance of obtaining magnesium carbonate from dolomite is made; the data for designing and creation of industrial productions are received. Data are given for the launch of a pilot plant for the production of magnesium oxide: the year of commissioning -; Production capacity - 200 tons per year; Number of technological lines - 1; Method of production - processing of dolomite by decomposition with nitric acid; Production mode - periodic; The organization that carries out the working project - the design department of JSC "Maxam-Chirchik". Product characteristics: - magnesium oxide, in accordance with State Standard GOST 1216-87, as caustic magnesite.

The technological process should be carried out according to the scheme (Fig. 1).

An explanation of the scheme in Fig. 1. Nitric acid with a concentration of 28-30%, at a temperature of 25-30 °C, from the bone (pos. 8) through the flow meter (pos. 6a) by means of a pump enters the reactor (pos. 7) in the amount of 4.35 m³. The crushed dolomite with the size dcp.- 20 mm in the amount of 0.115 t / h through the mash (pos.6) is fed in portions to the reactor (pos. 7) from the upper part of it.

Table1. The result of the test of the process for the preparation of magnesium hydroxide

No	Result	Experiences		
		1	2	3
1	Concentration of nitric acid solution, wt. %	28	26	25.8
2.	Consumption of dolomite, per volume of nitric acid solution	785	350	300
3.	Concentration of salts in a solution of dolomite, g / 1 $Mg(NO_3)_2$	1.8	1.0	0.9
		218.5	160.4	237.8
4.	Ammonium sulfate consumption for precipitation of $CaSO_4$	325	200	140
5.	Solution after precipitation of $CaSO_4$, g/l			
	$Mg(NO_3)_2$	177.7	123.4	182.6
	$Ca(NO_3)_2$	8.2	27.1	16.4
Magnesium precipitation: I-ammonia, II-carboammonium salt, III-soda				
6	CaO	1.37	6.11	7.55
	MgO	32.73	24.11	67.73
	n.n.n. (wt. %)	65.88	69.77	24.38

Table2. The material balance of the process of obtaining MgO from dolomite and HNO_3

No	Articles name	Expenditure, kg	No	Articles name	receipts, kg
1	Dolomite	1000	1	Gypsum	874.3
2	Nitric acid	1435.5	2	$MgCO_3$	420
3	Ammonium sulphate	707	3	Ammonium nitrate	857
4	Calcined soda	530	4	Sodium nitrate	850
			5	Carbon dioxide gas	456

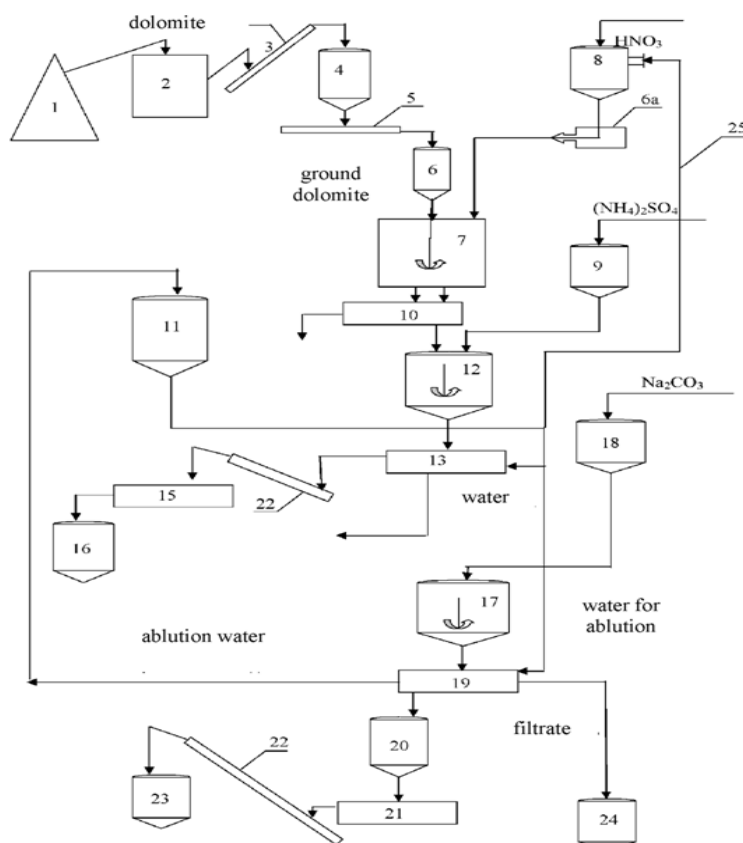


Fig1. Principal technological scheme of production of MgO based on dolomite and nitric acid.

Designation: 1-dolomite warehouse, 2-crusher, 3,5,14,22-conveyor, 4-bunker, 6-hopper, 6a-flow meter, 7-reactor, 8-capacity for 28-30% HNO_3 , 9 -dispenser capacity for $(NH_4)_2SO_4$, 10-filter for insoluble precipitate, 11-capacity for H_2O , 12-reactor for precipitation of gypsum, 13-filter for gypsum filtration, 15-gypsum drier, 16-storage for $CaSO_4 \cdot 2H_2O$, 17-reactor for precipitation of $MgCO_3$, 18-capacity for Na_2CO_3 , 19-filter for separation of $MgCO_3$, 20-container for storage of $MgCO_3$, 21-furnace for firing $NaNO_3$, NH_4OH , 23-storage tank, 24- 25 - washing water.

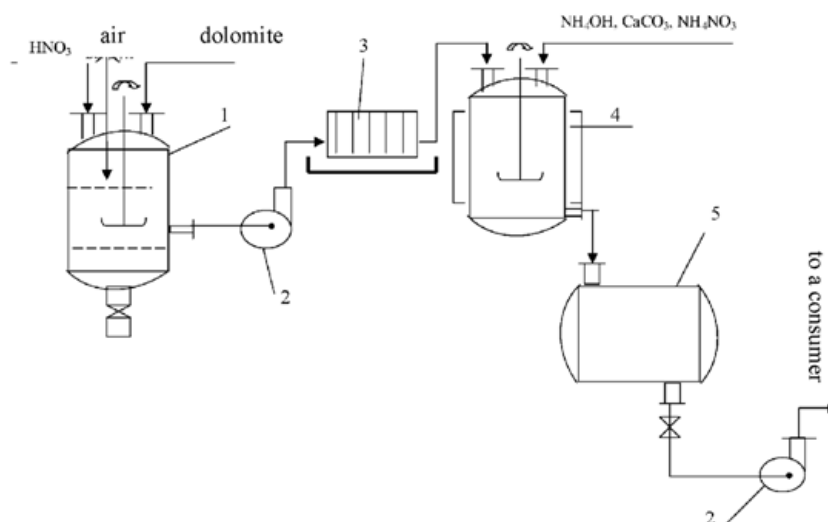
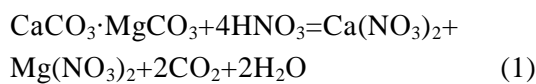


Fig2. Schematic diagram of obtaining a liquid Mg-containing fertilizer.

Designations: 1 - reactor for dissolving dolomite; 2 - centrifugal pumps; 3 - the filter press; 4 - reactor for neutralization and dissolution of ammonium nitrate; 5 - container for the end product.

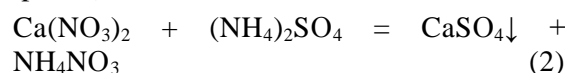
Dissolution is carried out by rotating the agitator for 90 minutes until the gas evolution ceases from the mixture, at a temperature of 28-30°C. In the reactor, a decomposition reaction of dolomite occurs:



The solution is filtered with a nutch filter (pos. 10) to separate the residue.

The filtrate is transferred via a pump to the next reactor (pos. 12), and the precipitate is washed with water and the washings are collected in a container (pos. 11) for further use. The filtered solution is heated to 60 °C, crystalline ammonium sulfate is added in an amount of 707 kg. The mixture is stirred for 1 hour to precipitate calcium as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

(pos.12), in the reaction:



The gypsum is filtered with a nutch filter, at 20 °C (pos.13), washed and submitted for drying (pos. 15), stored in a container (pos. 16). The filtrate is pumped to the reactor (pos.17) and heated to a temperature of 80-90°C. 18% aqueous solution of soda ash is supplied to the reactor (pos. 17) by means of a pump from the tank (pos. 18) to the pH of 10.5÷11.0. The reactor precipitates magnesium carbonate. The precipitate is filtered off in a suction filter (pos. 19) and washed; the washings are pumped into a collection (pos.11)



Table3. The results of obtaining a liquid nitrogen-calcium-magnesium fertilizer

No Experience	Name of sample	Volume and density	pH	Mass fraction of solution components, %			
				MgO	CaO	NaNO ₃	NaNH ₄
0	The initial nitric acid solution of dolomite	V=100 cm ³ P=1.334 g/cm ³	2.8	4.3	5.5	5.8	-
1	Nitric acid solution after neutralization with a slurry of calcium carbonate	V=100 cm ³ P=1.337 g/cm ³	6.2	4.3	5.5	5.5	-
	Nitric acid solution after neutralization with a slurry of calcium carbonate	V=50cm ³ P=1.365 g/cm ³	-	3.2	4.6	10.99	4.90
2	Nitric acid solution after neutralization with 25 % NH ₄ OH	V=100cm ³ P=1.325 g/cm ³	6.4	4.3	5.9	5.9	0.23
	The solution after addition of ammonium nitrate	V=50 cm ³ P=1.372 g/cm ³	-	3.9	5.2	10.76	5.45

It is filtered through a nutch filter (pos.19) and washed until the NO_3^- ion disappears with water, collected in a container (pos. 20), dried and calcined in a furnace (pos. 21) at 750-800°C for 40 min. Washing water is pumped into the collection (pos. 11). The gypsum precipitate is dried in a dryer (pos. 15) at a temperature of 200-250°C to produce a semi-aquatic gypsum as an astringent material. Magnesium carbonate is calcined in an oven at a temperature of 750-800°C to produce magnesium oxide. The fired magnesium oxide along the conveyor (pos. 22) is fed into the hopper (pos. 23) for storage. The flow rate of dolomite and ammonium sulphate is controlled by a weight proportional. The material balance of the process is compiled (Table 2), the norms of the technological regime, specific consumption of raw materials and materials per 1 tone of product are calculated.

An economic calculation of the cost of production of 1 t MgO from dolomite was made, the cost of dolomite is 91,000 Uzbek soums (USD 11.2) per t; Nitric acid (56%) - 95,750 soums per t; Ammonium sulfate - 191,760 soums per t; Soda - 412,000 sum per t; MgO - 6000,000 soum per t; Electricity - 23 kW / h; Fuel - 342 m³; Technical water - 65.1 m³; Drinking water - 4,4 m³; Polypropylene bags - 66 pcs.

The next task of the study was the development of a technology for producing liquid Mg-containing fertilizers. Table 3 shows the data of the realization of the process schematic diagram (Fig. 2). In particular, it is seen that the acid solution of dolomite after neutralization with ammonia water has a pH of 6.4 and a density of 1.325 g / cm³. It contains Mg (NO₃)₂ in terms of MgO - 4.3%. It dissolves ammonium nitrate, and with its addition it is possible to increase the content of total nitrogen to 16% or more.

CONCLUSION

In order to develop the technology of magnesium compounds and mineral fertilizers based on them, a suitable magnesium-containing mineral source of raw materials - dolomite of Krasnogorskoye field, Navbahoro

district of Navoi region (MgO 19.0 wt.%) was chosen first. At the JSC "Maxam-Chirchik" carbonate and magnesium oxide were obtained from it, gypsum and a solution of magnesium compounds as by-products. The process regulations have been developed and the production of pilot-industrial lots of magnesium hydroxide and magnesium carbonate from dolomite is provided on its basis. It is shown that the precipitation of magnesium with soda gives the greatest yield of the product - 67.73 wt.%. The product obtained in JSC "Maxam-Chirchik", in terms of MgO content, is close to the requirements of State Standard GOST 1216-87. The terms of reference for the design of the magnesium compound production plant have been drawn up. The technology of obtaining liquid Mg-containing fertilizers has been developed.

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