

MAGNESIUM OXIDE FROM SEA WATER
AND DOLOMITE

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A process has been developed in the Soviet Union for producing synthetic magnesium oxide from Si-vash brine diluted with Black Sea water to the salinity of ocean water, i.e., 3.5% [1, 2] and limestone, and from Black Sea water (salinity 1.8%) and dolomite.

In this article an analysis is given of the process of producing high-density sintered synthetic magnesium oxide from Black Sea water and dolomite.*

The magnesium oxide in the dolomite does not participate in the reaction of magnesium hydroxide precipitation from the sea water but is contained in the end product as additional yield.

The magnesium hydroxide was precipitated with dolomite milk from the dolomites of the Bosnin deposits. The dolomite was calcined at 1000-1050°C in a 22 mm long rotary furnace. The degree of calcination

*The chemical part of the technological process was developed by the Scientific and Technical Association "Iodobrom."

TABLE 1. Chemical Composition of Dolomite from the Bosnin Deposits, %

Dolomite	SiO ₂	R ₂ O ₃	CaO	CaO _{act}	MgO	CO ₂
Raw*	0,26—0,35	0,14—0,21	30,2—32,1	—	20,6—21,8	—
Calcined	0,28—0,38	0,32—0,34	—	55,5—58,7	35,5—40,5	0,11—0,49

*Loss to calcination was 46.1-47.6%.

TABLE 2. Chemical Composition of the Dried Magnesium Hydroxide Paste,* %

Material	SiO ₂	R ₂ O ₃	CaO	MgO	SO ₄ ^{''}	Cl'
Bone-dry magnesium hydroxide paste*	0,09—0,47	0,23—0,65	1,33—1,62	63,21—64,65	1,15—2,12	1,69—1,93
Ditto, in terms of calcined substance †	0,15—0,71	0,35—0,98	2,04—2,44	96,64—97,23	—	—

*According to data obtained by the section processing magnesium oxide from salt water.

†Calcination loss 30.6-33.0%.

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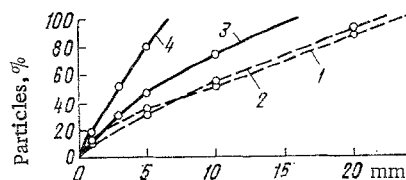


Fig. 1

Fig. 1. Grain size distribution of the briquette (---) and fired powder (—) from dried (2, 4) and dehydrated (1, 3) magnesium hydroxide paste.

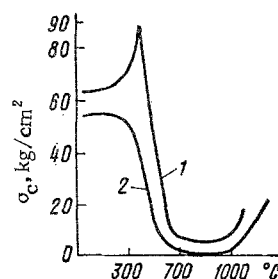


Fig. 2

Fig. 2. The ultimate compression strength σ_c of a specimen processed from salt water magnesium hydroxide: 1) with MgSO_4 added; 2) without additive.

TABLE 3. Chemical Composition of Dehydrated Paste of Magnesium Hydroxide Produced from Salt Water (in terms of calcined substance), %

Indices	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
Maximum	0.90	0.53	0.24	1.80	96.87
Minimum	0.81	0.46	0.22	1.56	96.69
Average	0.86	0.48	0.24	1.66	96.76

of the calcium component of the dolomite was 96-97%. The chemical composition of the dolomites is given in Table 1.

Consumption of calcined dolomite was 1.5 ton per ton MgO . The calcined dolomite was slaked with fresh water after which the dolomite milk was centrifuged. The impurities of the concentrated dolomite milk was 0.88-1.05%.

The chemical composition of the precipitated magnesium hydroxide after filtration prior to being charged into the furnace at a moisture content of 53-55% was as follows: calcination loss 13.8-15.5%, 0.04-0.22% SiO_2 , 0.11-0.31% R_2O_3 , 0.50-0.76% CaO , 28.5-30.4% MgO , 0.52-0.59% SO_4^{2-} , 0.76-0.91% Cl^- .

The magnesium hydroxide paste can be fired in one or two stages. In the former case the wet paste is charged into the firing kiln while in the two-stage process it is first dried to a residual moisture content of 20% or dehydrated, then briquetted and fired [3].

In the work reported here the writers produced sintered magnesite powders by the two-stage process.*

The progress of drying and dehydrating the magnesium hydroxide paste was studied with a 22 m long rotary kiln with an inside diameter of 1.14 m. The kiln was fired with petroleum residue by means of a centrifugal mechanically operated nozzle, the primary air being fed along the nozzle periphery.

For the drying process the kiln was modified to the straight-through principle of operation as in dryer drums. The charge rate of wet paste was 3.15 ton/h, the delivery of paste dried to a moisture content of 15-20% 1.56 ton/h, and the temperature of the waste gases about 250°C. The maximum evaporation rate was 64 kg/(m³·h), heat consumption 1050 kcal per kg moisture, and dust entrainment 10%. The chemical composition of the magnesium hydroxide paste is given in Table 2.

According to the production technology developed by the Ukrainian and All-Union Institutes of Refractories the magnesium hydroxide paste is dried with the heat of the dust-laden flue gas from the rotary kilns used for firing the magnesium oxide.

Dehydration of the magnesium hydroxide paste was conducted in a rotary kiln operating on the counterflow principle. According to preliminary experiments the optimum dehydration temperature is 800-1000°C.

The treatment temperature in a rotary kiln is difficult to monitor so that the quality of the experimental batches of dehydrated powder was controlled in terms of the hardening time of powder mixed with a solution of double-substituted phosphoric ammonium $(\text{NH}_4)_2\text{HPO}_4$ of density 1.11 g/cm³. The setting time for a good-quality heat-treated paste is 3-7 min, the bulk weight of the powder 0.5-0.7 g/cm³.

*N. A. Mast'ykina, G. T. Merkulov, V. F. Yudenko, and N. A. Nikiforova participated in the work.

TABLE 4. Process Characteristics of the Firing of the Magnesium Hydroxide Briquettes

Indices	Briquette from	
	dried paste	dehydrated paste
Duration of test, h	28	44
Maximum furnace temperature, °C	1750	1770
Temperature downstream from dust chamber, °C	640	720
Furnace speed, rpm	1.34	1.34
Fuel consumption, kg/h	275	275
Primary air flow (under normal conditions), m ³ /h	1800	1800
Coefficient of air consumption	1.08	1.06
Rate of briquette charge (in terms of calcined substance), kg/h	629	820
Rate of powder yield, kg/h	424	649
Dust entrainment, % (on the charge)	32.6	20.9
Specific furnace output, kg/(m ² · h)	5.5	8.5
Specific fuel consumption, kg/ton	894	585
Apparent density of the powder, g/cm ³ :		
fraction 1-3 mm	3.12	3.15
fraction >3 mm	3.09	3.12
Open porosity (%) of the powder		
fraction 1-3 mm	6.5	5.6
fraction >3 mm	7.6	6.6
Percent fraction finer than 1 mm in the powder	18.2	10.5

The average process indices for the dehydration of the magnesium hydroxide paste in the rotary kiln were as follows: charge rate of the paste 1500 kg/h, moisture content of the paste 54%, furnace speed 1.34 rpm, fuel oil consumption 165 kg/h, coefficient of air consumption 2.2, maximum furnace temperature along the flame cone 1320°C, temperature downstream from the dust chamber 225°C, furnace output 374 kg/h, product yield 4.6 kg/(m² · h), specific fuel oil consumption 608 kg/ton, removal of dust (calculated in the charge) 17.1%, bulk weight of the powder 0.57 g/cm³, setting time 4 min.

The practicable maximum rate of charging the paste was limited so that furnace output could not be increased.

The chemical composition of the dehydrated paste was determined in the chemical-analysis laboratory of the All-Union Institute for Refractories and is given in Table 3.

The experimental batches of dried and dehydrated magnesium hydroxide were shipped in polyethylene sacks to the experimental technological division of the All-Union Institute for Refractories for briquetting on a roller press with smooth rollers. The diameter of the rollers was 1 m, the tire width 175 mm, the speed 7 rpm, and the rolling pressure 800 kg/cm² approximately (data supplied by the All-Union Institute for Refractories).

The dried magnesium hydroxide was treated for 3-5 min in an edge-runner mixer to equalize the moisture content and reestablish it at 20%.

During the briquetting operation it was noticed that a decrease in the moisture content produced delamination and a friable component in the briquette while too high a moisture content reduced its apparent density. At a moisture content of 19-21% the thickness of the briquette varied 6-11 mm at an average of 9-10 mm for an average apparent density of 1.4 g/cm³.

The briquetted material contained 80-90% fractions coarser than 10 mm and 1-3% fractions finer than 2 mm.

The dehydrated magnesium hydroxide paste was briquetted at a moisture content of 17-20%. The paste was wetted with an aqueous solution of sulfite-liquor waste of density 1.03-1.04 g/cm³ for the purpose of increasing the strength of the briquette. The briquette was further solidified during the hydration of the causticized magnesium hydroxide which set in 3-4 h after briquetting and was accompanied by heat liberation. The thickness of the briquette varied 6-10 mm at a predominant thickness of 6-7 mm, and the apparent density of the dry briquette varied 1.9-2.15 g/cm³ giving a mean of 2.0 g/cm³. The briquetted material contained 65-85% fractions coarser than 10 mm and 5-10% fractions finer than 2 mm.

The briquetted material was shipped in polyethylene sacks for firing to the Saks experimental division for magnesium oxide from salt water. The briquettes were fired in the same rotary kiln which had been used for drying and dehydrating the paste.

It has been established [3, 4] that to produce a high-density sintered powder of magnesium oxide precipitated from salt water the briquette should be fired at 1700-1900°C but it is difficult to produce a temperature of above 1700°C in small kilns with a secondary air supply of inadequate temperature.

Both types of briquette were fired at 1750-1770°C under conditions in which fuel combustion was complete and the temperature of the secondary air about 100°C. The fuel was fine-grain grade 100 petroleum residue with a combustion heat of 9650 kcal/kg and heated to 125°C.

TABLE 5. Chemical Composition of the Briquette (in terms of calcined substance) and Fired Powder*

Paste	Briquette					Fired powder							
	content, %												
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	l. o. i.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	B ₂ O ₃	
Dried	0,95	0,85	0,45	1,28	96,16	0,34	1,65	0,66	0,42	1,25	95,70	0,15	
Dehydrated	0,87	0,70	0,33	0,96	97,14	0,27	1,21	0,60	0,29	1,30	96,36	0,13	

* Mean data.

High temperatures were produced by increasing the proportion of primary air by 62% on the theoretically necessary proportion because with a low-temperature secondary air an increase in the proportion of primary air gives a higher combustion temperature [5], by intensifying the mixing of the fuel and air by means of a mixer unit, and by utilizing the full effective fuel pressure (25 atm).

The mean indices of the firing process are given in Table 4.

The grain size distribution of the green briquette and fired magnesite powders is plotted in Fig. 1. Prior to firing the grain size distribution of the briquettes of dried and dehydrated magnesium hydroxide were almost the same with a rather high proportion of fine fractions produced during the long journey but after firing they differed considerably. The percent fraction finer than 1 mm in the powder from the dehydrated paste is half of that in the powder from the dried paste. This is caused by the fact that the briquette from the dried magnesium hydroxide rapidly loses its mechanical strength over the temperature range of Mg(OH)₂ dehydration (Fig. 2) and is pulverized in the furnace to a slightly greater degree than the briquette from dehydrated paste. The briquette strength over the temperature range 700-1000°C can be increased with an additive in the form of magnesium chloride or magnesium sulfate.

In the technology developed by the All-Union and Ukrainian Institutes for Refractories the strength of the briquette from dried magnesium hydroxide is increased with 15-20% active magnesite dust recovered from the flue gases of the firing kilns — an effective means of making use of this dust.

The investigation was carried out over a relatively short furnace time (only about 70 tons of briquette from dried and about 40 tons of briquette from dehydrated paste were fired) so that it was not possible to elucidate the advantages of one type of briquette over the other.

The magnesite powders produced from the two briquette types had a mean open porosity of 6.5-7.6 and 5.6-6.6% and an apparent density of 3.09-3.12 and 3.12-3.15 g/cm³ for the briquettes from dried and dehydrated pastes respectively, i. e., they were high-density sintered powders.

The powder from the briquette from the dehydrated paste was coarser so that dust entrainment was lower, the yield per m² furnace area greater, i. e., 8.5 in place of 5.5 kg/(m²·h), and the charge larger, i. e., 820 in place of 629 kg/h, but total fuel consumption for the heat treatment and firing was higher since for drying the magnesium hydroxide paste use is made of the heat of the flue gases from the rotary kilns.

In the kilning process the briquettes became slightly contaminated with silica and calcium oxide. The powders from the dehydrated paste were least contaminated since the corresponding briquettes were fired after those from the dried paste (Table 5).

CONCLUSIONS

The technological process of producing synthetic magnesium oxide by the hydration method from Black Sea water and Bosnin dolomite gives a product containing 96.7% MgO.

The two-stage treatment of the magnesium hydroxide paste processed from salt water and dolomite either in a drying-briquetting-firing cycle or in a dehydration-briquetting-firing cycle yields high-density powders for the production of refractories.

LITERATURE CITED

1. B. A. Shoikhet, É. M. Karasik, I. G. Lyutkevich, et al., in: Problems in the Efficient Utilization of the Natural Wealth of the Sivash [in Russian], Naukova Dumka, Kiev (1969), pp. 69-82.

2. E. V. Ivanov, G. Z. Dolgina, V. P. Bunina, et al., in: Problems in the Efficient Utilization of the Natural Wealth of the Sivash [in Russian], Naukova Dumka, Kiev (1969), pp. 83-95.
3. E. V. Ivanov, G. Z. Dolgina, and V. P. Bunina, Trans. Ukrainian Scientific Research Institute for Refractories, Vol. 14 [in Russian], Metallurgiya, Moscow (1971), pp. 5-9.
4. Ya. A. Orlovskii, Byul. In-ta Chermetinformatsiya, No. 22 (666), 24-29 (1971).
5. G. Seidel, Silikattechnik, No. 1, 1-5 (1968).