

PREPARATION OF "ACTIVE" MAGNESIUM CARBONATE FROM MAGNESITE.

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Magnesium carbonate, made by precipitation, will cause lime plaster to set quickly.¹ A quick setting plaster is highly desirable but the cost of manufactured magnesium carbonate is too great for commercial use. No mechanical method of grinding or treating the mineral magnesium carbonate or magnesite produces a material of sufficient activity to be valuable. The purpose of the research reported here was to study methods of obtaining, by chemical treatment, a suitable magnesium carbonate for this use with lime in plasters.

Outline of the Work. The mineral magnesium carbonate or magnesite was changed to magnesium oxide by heating or "burning." The oxide was then changed to the hydroxide by soaking in water. This hydroxide was changed to the carbonate by suitable treatment with carbon dioxide. Magnesium carbonate thus prepared, was found suitable for making a "quick set" lime plaster.

Review. Anderson² found that the temperature at which magnesium carbonate is burned affects the rate of solution in water. In general, the rate of solution increases to a maximum and then decreases again as the temperature and the time of burning are increased. Only samples of pure manufactured magnesium carbonate and not the mineral were used.

Campbell³ found that magnesium carbonate was completely decomposed at 600° C. Magnesium oxide produced by burning at 600 to 800° C. hydrated completely in three days. A reduced rate of hydration set in for magnesium oxide burned at 1000° to 1100° C. Magnesium oxide burned at 1450° C. (the temperature of the cement kiln) was only about 61 per cent hydrated after soaking in water for 18 months. Samples burned at 1000° C. hydrated completely in three months. After six years, samples burned at 1300° C. were only 85 per cent hydrated, samples at 1400° C. were 81 per cent hydrated and samples at 1450° C. were only 70.3 per cent hydrated.

Jesser⁴ prepared the most active magnesium oxide by burning at a temperature just sufficient to liberate the carbon dioxide.

Grunwald⁵ separated the light calcined magnesium oxide from the

¹ U. S. Pat. No. 1,604,575 and 1,607,473.

² J. Chem. Soc., 87, 257 (1905).

³ J. Ind. Eng. Chem., 1, 665 (1909); 10, 595 (1918).

⁴ U. S. Pat. No. 1238147; Chem. Abst., 11, 3102 (1917).

⁵ U. S. Pat. No. 1285683, 1361324 and 1361866; Chem. Abst., 13, 251 (1919) and 15, 579 (1921).

"Proc. Ind. Acad. Sci., vol. 38, 1928 (1929)."

dead burned by sedimentation in water. The magnesium hydroxide, thus prepared, was then treated with carbon dioxide to make "light" magnesium carbonate.

Schurecht⁶ found that the tendency of dead burned magnesium oxide to hydrate decreased as the temperature of burning increased.

Monhaupt⁷ obtained 9.7 to 11.3 per cent of magnesium oxide in solution as the bicarbonate by passing carbon dioxide through a suspension of magnesium hydroxide.

Berkurts⁸ made "magnesia alba" (basic magnesium carbonate) by treating slightly burned dolomite under 5 to 6 atmospheres pressure of carbon dioxide. The solution of magnesium bicarbonate was filtered from the insoluble calcium carbonate. Magnesia alba was precipitated from the filtrate by boiling. The magnesium carbonate from unignited dolomite will not readily dissolve in an aqueous solution of carbon dioxide.

The Austro-American Magnesite Co.⁹ found that high reactivity towards magnesium chloride was obtained by burning above the lower limit for caustic magnesia with increased steam in the burning atmosphere.

Sisson¹⁰ treated light calcined dolomite with sea water until all the calcium oxide was dissolved as calcium chloride by the magnesium chloride with simultaneous precipitation of an equivalent amount of magnesium hydroxide. This residue of magnesium hydroxide was finally carbonated.

Simon¹¹ treated burned dolomite with carbon dioxide and obtained magnesium bicarbonate in solution. Magnesium carbonate was obtained from this solution by boiling.

Materials Used. The sources of the magnesite used in these experiments were unknown. Two different samples were used. Duplicate experiments using the two different samples showed no noticeable differences in final results.

The calcination or the burning of the magnesite was done in an accurately controlled Hoskins furnace for all moderate temperatures. The calcination was done in a platinum crucible with a Meker burner for the temperature of 1000° C.

Experimental. The first experiments were made to determine the influence of the following conditions upon the completeness with which the magnesium oxide would hydrate with water: the fineness of grinding of the original magnesite; the temperature and the time of burning; and the time of soaking the magnesium oxide in water.

⁶ J. Am. Ceram. Soc., 4, 127 (1921).

⁷ Chem. Ztg., 28, 868 (1904). J. Chem. Soc. (Abst.) 86, 731 (1904).

⁸ Arch. Pharm. (3) 18, 429, and 19, 13. J. Chem. Soc. (Abst.) 42, 13 (1882).

⁹ Ger. Pat. No. 291686 (1913).

¹⁰ Brit. Pat. No. 24134 (1906). Chem. Abst., 2, 1758 (1908), Fr. Pat. No. 383407 (1907). Chem. Abst. 3, 2358 (1909).

¹¹ Brit. Pat. No. 176785 (1922). Chem. Abst. 16, 176 (1922).

TABLE I. Relation of Time of Calcination (at 700° C.) and of Hydration to Degree of Hydration. (The temperature of calcination was 700° C. and the magnesite was ground to 100 mesh.)

Time of Calcination	Time of hydration or soaking of the oxide	Completeness of hydration
1 Hr.	24 Hrs.	94.8%
1 Hr.	48 Hrs.	94.9%
1 Hr.	72 Hrs.	95.4%
1 Hr.	96 Hrs.	95.4%
2 Hrs.	24 Hrs.	94.0%
2 Hrs.	48 Hrs.	94.9%
2 Hrs.	96 Hrs.	95.3%
2 Hrs.	120 Hrs.	94.3%
3 Hrs.	24 Hrs.	94.6%
3 Hrs.	48 Hrs.	99.5%
3 Hrs.	92 Hrs.	95.3%
3 Hrs.	114 Hrs.	95.5%
4 Hrs.	24 Hrs.	95.6%
4 Hrs.	48 Hrs.	95.8%
4 Hrs.	72 Hrs.	95.9%
4 Hrs.	96 Hrs.	96.1%

This table shows that the degree of hydration is above 94.8 per cent for all samples whether burned one hour or four hours. The degree of hydration was as high after 24 hours soaking as after 96 hours. It should be noted that burning for four hours gave just as active an oxide as did burning for only one hour.

TABLE II. Relation of Time of Calcination (at 1000° C.) and of Hydration to Degree of Hydration.

The conditions were the same as for Table I except that the temperature of calcination was 1000° C., in platinum crucibles with a Meker burner.

Time of Calcination	Time of hydration or soaking of the oxide	Completeness of hydration
0.5 Hr.	24 Hrs.	88.0%
0.5 Hr.	48 Hrs.	93.1%
0.5 Hr.	72 Hrs.	93.5%
0.5 Hr.	96 Hrs.	94.3%
1 Hr.	24 Hrs.	95.6%
1 Hr.	48 Hrs.	94.8%
1 Hr.	72 Hrs.	91.2%
1 Hr.	91 Hrs.	92.0%
2 Hrs.	24 Hrs.	92.8%
2 Hrs.	48 Hrs.	88.8%
2 Hrs.	68 Hrs.	90.0%
2 Hrs.	115 Hrs.	90.5%
3 Hrs.	24 Hrs.	83.8%
3 Hrs.	48 Hrs.	88.3%
3 Hrs.	72 Hrs.	91.4%
3 Hrs.	96 Hrs.	91.2%

This table shows that calcination at 1000° C. gave somewhat less active magnesium oxide than did the calcination at 700° C. The most

active magnesium oxide was made by calcination at 1000° C. for only one-half or one hour. Also this magnesium oxide became more than 91.2 per cent hydrated by soaking for 24 hours except in one case which was evidently experimental error. Increase in the time of burning to two and to three hours decreased the activity of the oxide until the percentage of hydration by soaking was from 83 per cent up. It therefore seems that 1000° C. for one-half to one hour is an entirely satisfactory condition for making an active magnesium oxide as tested by its activity towards water.

TABLE III. Relation of Time of Calcination (at 1000° C., with Meker Burner) and of Hydration to Degree of Hydration, using Magnesite of 10 mesh size.

Time of Calcination	Time of hydration or soaking of the oxide	Completeness of hydration
0.5 Hr.	24 Hrs.	94.9%
0.5 Hr.	48 Hrs.	95.6%
0.5 Hr.	96 Hrs.	97.0%
1 Hr.	24 Hrs.	94.2%
1 Hr.	48 Hrs.	93.6%
1 Hr.	72 Hrs.	95.0%
1 Hr.	96 Hrs.	94.9%
2 Hr.	24 Hrs.	92.5%
2 Hrs.	48 Hrs.	92.4%
2 Hrs.	72 Hrs.	92.5%
2 Hrs.	115 Hrs.	93.6%

This table shows that the magnesium oxide made at 1000° C. for two to four hours was a little more active than was the magnesium oxide of 100 mesh prepared under the same conditions.

TABLE IV. Relation of Time of Calcination (at 700° C.) and of Hydration to Degree of Hydration, using Magnesite of 10 mesh size.

Time of Calcination	Time of hydration or soaking of the oxide	Completeness of hydration
1 Hr.	24 Hrs.	94.8%
1 Hr.	48 Hrs.	94.4%
1 Hr.	72 Hrs.	95.7%
2 Hrs.	24 Hrs.	92.9%
2 Hrs.	48 Hrs.	94.4%
2 Hrs.	72 Hrs.	94.9%
3 Hrs.	24 Hrs.	92.0%
3 Hrs.	48 Hrs.	93.2%
3 Hrs.	72 Hrs.	94.0%
3 Hrs.	115 Hrs.	93.7%

There was no noticeable effect due to the increase in size from 100 mesh to 10 mesh when the burning temperature was 700° C.

TABLE V. Relation of Time of Calcination (at 1000° C., with a Meker burner) and of Hydration to Degree of Hydration, using pieces of Magnesite of 1-2 cm. Diameter.

Time of Calcination	Time of hydration or soaking of the oxide	Completeness of hydration
0.5 Hr.	23 Hrs.	96.8%
0.5 Hr.	68 Hrs.	95.0%
0.5 Hr.	115 Hrs.	97.3%
0.5 Hr.	139 Hrs.	97.5%
1 Hr.	20 Hrs.	94.62%
1 Hr.	68 Hrs.	93.8%
1 Hr.	115 Hrs.	94.7%
1 Hr.	139 Hrs.	95.6%
2 Hrs.	24 Hrs.	93.0%
2 Hrs.	48 Hrs.	92.6%
2 Hrs.	72 Hrs.	91.4%

The activity of the oxide is greater for the shorter periods of calcination and is appreciably greater than for the smaller sizes under the same conditions. The maximum percentage of hydration was 97.3.

TABLE VI. Relation of Time of Calcination (at 1000° C., with a Meker burner) and of Hydration to Degree of Hydration, using pieces of Magnesite 4-5 cm. Diameter.

Time of Calcination	Time of hydration or soaking of the oxide	Completeness of hydration
0.5 Hr.	24 Hrs.	91.9%
0.5 Hr.	60 Hrs.	92.1%
0.5 Hr.	96 Hrs.	92.3%
1 Hr.	24 Hrs.	97.6%
1 Hr.	48 Hrs.	97.8%
1 Hr.	96 Hrs.	98.0%

One hour of calcination gave magnesium oxide which showed above 97.6 per cent of hydration. With 0.5 hour calcination, the results were lower, evidently due to incomplete burning.

Addition of sodium chloride to the crucibles during the burning of the magnesite did not change the activity of the magnesium oxide.

A summary of the above tables shows that perhaps the most satisfactory conditions were lumps 4-5 cm. in diameter burned at 1000° C. for one hour. The completeness of hydration of the oxide thus formed was 97.6 per cent, or more.

Carbonation of the Hydrated Magnesia. The magnesium hydroxide, prepared as shown in the foregoing experiments, was treated in an aqueous suspension with carbon dioxide. The degree of carbonation was determined by measuring the carbon dioxide evolved from the dried, (100° C.) carbonated material in a gas evolution apparatus. It is likely that 27 per cent carbon dioxide would represent as complete carbonation as could be expected judging from the fact that the magnesium carbonate, in the store room, showed this per cent of carbon dioxide.

Preliminary experiments soon showed that only very slight carbonation was obtained when carbon dioxide, under slight pressure, acted upon an aqueous suspension, if the containing vessel or flask was not shaken. The pressure of the carbon dioxide in these experiments was equal to the height of 74 cm. of 1:1 water and hydrochloric acid in the carbon dioxide generator. The most important factor in securing rapid carbonation was found to be agitation or rapid shaking of the flask while the carbon dioxide was being introduced. The method of agitation or of shaking was as follows: The flask with the rubber tube conveying the carbon dioxide attached, was clamped rigidly into a box. A wooden tongue attached this wooden box to an eccentric on a water motor. The box itself was suspended from a cross bar by two parallel wires in such a way that the box would be swung back and forth by the water motor about 60 times per minute. This agitation on one sample gave 34.8 per cent of carbon dioxide as compared to 7 per cent for a duplicate, minus the agitation.

TABLE VII. Effect of Time on Degree of Carbonation.

(Ten mesh particles of magnesite were calcined with a Meker burner at 1000° C. for one hour. These samples were hydrated by soaking in water for 24 hours. This magnesium hydroxide was treated with carbon dioxide with agitation.)

Time of carbonation	Carbon dioxide in the final dried material
24 Hrs.	23.65%
48 Hrs.	30.75%
72 Hrs.	34.87%

These results show that quite long periods of carbonation are necessary and that the percentage of carbon dioxide in the carbonated material increases as the time of carbonation increases. The sample carbonated for only 24 hours contained tiny grains of hard material which appeared to be the uncarbonated centers of the small lumps. The material carbonated for 48 hours contained fewer of these hard particles and the 72 hour material apparently contained none. It is likely that the agitation rubbed the magnesium carbonate from the surfaces of the magnesium hydroxide particles as fast as formed, thereby exposing fresh magnesium hydroxide to the carbon dioxide. This explains why the percentage of carbon dioxide was so small in the case of the unagitated material.

TABLE VIII. Effect of Time on Degree of Carbonation.

(Magnesite pieces 1-2 cm. in diameter were burned at 1000° C. for one hour with a Meker burner and then hydrated for 24 hours.)

Time of carbonation	Carbon dioxide in the final dried material
24 Hrs.	36.72%
48 Hrs.	27.07%
72 Hrs.	33.59%
96 Hrs.	24.75%

These results are somewhat difficult to explain but the variations are thought to be due to inability to get average samples. The highest percentage of carbon dioxide was in the material carbonated for only 24 hours. In this material, the uncarbonated cores or centers were large enough that they could be picked out completely whereby only the fine, completely carbonated particles were actually analyzed. These uncarbonated centers were rounded like pebbles in running streams. As the time of carbonation increased, these lumps became smaller and hence were more difficult to pick out. Low results on per cent of carbon dioxide are therefore attributed to incomplete separation of the unhydrated portions.

A sample of very fine magnesium hydroxide was made by grinding some of the magnesium oxide, burned at 1000° C. with a Meker burner, until the particles floated in water. These fine particles, carbonated for 15 minutes, contained 22.7 per cent of carbon dioxide and after 30 minutes of carbonation the per cent of carbon dioxide was 30.9. Increased time of carbonation to 24 hours did not change the value from this beyond experimental error. Also decrease in time of burning to one-half hour and increase in the time of hydration to 48 hours were without effect.

TABLE IX. Effect of Time of Calcination, Hydration and Carbonation on Degree of Carbonation.

Time of calcination	Time of hydration	Time of carbonation	Carbon dioxide in final dried material
1 Hr.	24 Hrs.	0.25 Hr.	22.76%
1 Hr.	24 Hrs.	0.5 Hr.	30.91%
1 Hr.	24 Hrs.	0.75 Hr.	31.84%
1 Hr.	24 Hrs.	1.5 Hr.	32.04%
1 Hr.	24 Hrs.	3 Hrs.	32.37%
1 Hr.	24 Hrs.	12 Hrs.	31.37%
0.5 Hr.	48 Hrs.	24 Hrs.	29.45%
1 Hr.	48 Hrs.	24 Hrs.	31.64%

Carbonation was also tried by bubbling the carbon dioxide through the aqueous suspension of the floated magnesium hydroxide in an open beaker. The magnesium hydroxide had been previously hydrated for 24 hours. The contents of the beaker were stirred continuously with a glass stirrer. After 24 hours the percentage of carbon dioxide was only 25. Another sample of the floated magnesium hydroxide was carbonated under pressure for three hours but the flask was shaken only at intervals. The percentage of carbon dioxide was only eight. This clearly shows the necessity for continuous and vigorous shaking. An attempt at carbonation in a ball mill during grinding by bubbling the carbon dioxide through the wet mix gave only 19.5 per cent. A sample of floated magnesium hydroxide was carbonated under pressure at 80° C. for 45 minutes. The result was only 19.8 per cent carbon dioxide. This was not as good as results at room temperature.

Activity of the Magnesium Carbonate in Promoting Quick Setting of Lime Plaster. The magnesium carbonate used contained 34.6 per cent

of carbon dioxide. The plasters as tested contained 33.3 per cent hydrated lime, 66.6 per cent sand, and 1.6 per cent of the magnesium carbonate.

A blank was made as above except without magnesium carbonate. Magnesium carbonate (Merck) from the storeroom was also tried. The blank was mixed with 34 ml. of water and the others with 36 ml. of water for each 100 grams of the plaster.

The magnesium carbonate made in this research produced a hardening in 45 minutes and a set in three hours (Gilmore needle). In three hours the Merck's magnesium carbonate had only started the hardening. The blank never set.

SUMMARY.

"Active" magnesium carbonate can be easily formed as follows: 1. Burn magnesite at 1000° C. for one-half hour if the pieces are 100 mesh, or for two hours if the pieces are 4-5 cm. in diameter. 2. Hydrate this oxide by soaking for 24 hours in water. 3. Carbonate this hydroxide by treating with carbon dioxide under slight pressure but the material being carbonated must be vigorously shaken or agitated during the time of carbonation. 4. The length of time of carbonation depends upon the size of the pieces of the magnesium hydroxide. If the magnesium hydroxide pieces are 4-5 cm. in diameter perhaps 72 hours will be required. If the particles of the magnesium hydroxide are fine enough to float in water, carbonation is fairly complete in one-half hour.

Calcium hydroxide containing 4 per cent of its weight of this magnesium carbonate produces a plaster that will set in three hours.