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PLASTIC MAGNESIA

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PLASTIC MAGNESIA

By O. C. Ralston, R. D. Pike, and L. H. Duschak

INTRODUCTION

Much detailed information on the production of plastic magnesia from magnesite mined near Chewelah, Wash., was accumulated during a cooperative investigation conducted by the Bureau of Mines and the Northwest Magnesite Co. at the laboratories of the University of California in 1919–1921. This bulletin gives mainly the results of the work done with Chewelah magnesite, supplemented by data on similar work with other magnesites, particularly those of California, in the endeavor to produce a plastic magnesia that would be satisfactory for making the so-called "Sorel" cement composition flooring, stucco, and plasters. As standardized methods for testing such compositions did not exist, it was necessary to examine carefully the various methods in use and choose those that seemed appropriate. In consequence, this report contains many tests made by the methods selected and can be used for reference by those who wish to adopt standard methods of testing.

ACKNOWLEDGMENTS

During the World War the Northwest Magnesite Co. worked a large magnesite mine at Valley, Wash., near Chewelah, the nearest railway point, and produced a refractory dead-burned magnesia that was used to supply the deficiency caused by the stopping of imports from Austria, but is now manufactured and sold in competition with the Austrian material. The Chewelah magnesite is crystalline, whereas most of the magnesite that has been burned to form plastic magnesia for composition cements has been "amorphous" or cryptocrystalline. There was, therefore, some question as to the suitability of the Chewelah magnesite for the manufacture of plastic magnesia, and since the investigation of this possibility was purely technical, arrangements were made with the Bureau of Mines to carry on an investigation in the laboratories of the Pacific experiment station of the bureau, under the joint supervision of its superintendent, L. H. Duschak, and of Robert D. Pike, chemical engineer, representing the Northwest Magnesite Co.

Wallace C. Riddell, chemical engineer for the Pacific experiment station of the bureau, gave technical aid throughout, and George H. West was in immediate charge of the laboratory after the first six months, succeeding R. L. Sebastian. Acknowledgments are also due E. H. Delius, R. Stewart, F. C. Henriques, H. H. Parker, L. P. Bradley, W. M. Schaufelberger, W. B. Lenhart, and M. Struve, who assisted in the laboratory. Most of the expense was borne by the Northwest Magnesite Co. The work was in progress from December 1, 1919, to April 1, 1921. Acknowledgment is also due the University of California in whose buildings the Pacific Experiment Station of the Bureau of Mines is housed, and especially to Dean F. H. Probert, Prof. W. S. Morley, and Prof. E. A. Hersam for assistance and criticism.

DEFINITION OF PLASTIC MAGNESIA

In plastic magnesia only a part of the carbon dioxide present in the original magnesium carbonate, or magnesite, has been expelled by burning because heating to a temperature high enough to liberate all the magnesium oxide in a reasonable length of time gives a "dead-burned" product that usually is unsuitable for making magnesian cements. As a matter of laboratory manipulation it may be possible to prepare plastic magnesia with no remaining carbon dioxide. Magnesium carbonate contains about 52.2 per cent carbon dioxide. A good commercial grade of plastic magnesia contains as much as 4 or 5 per cent of carbon dioxide, which means 7.7 to 9.6 per cent of $MgCO_3$; the remainder consists of magnesium oxide and any impurities in the original material. Chemically, such a product is often called "caustic magnesia," because of its similarity to caustic lime. Not all caustic magnesia, however, is plastic magnesia. The latter is a form of caustic magnesia that is adaptable to forming magnesium oxychloride cement (often called Sorel cement, after the original discoverer), when mixed with magnesium chloride solutions of proper consistence. The only way of determining whether a sample of burned magnesite is suitable for making this cement is to test it empirically.

Plastic magnesia has been variously known as "calcined magnesite," "caustic-burned magnesite," and "light-burned magnesite."

CONSTITUTION OF MAGNESIAN CEMENTS

How plastic magnesia combines with magnesium chloride in forming the magnesian cements discovered by Sorel[1] is not known; at

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[1] Sorel, Stanislaus, Caustic magnesia cement: Bureau of Standards Circular 135, 1922, p. 3; Compt. rend., t. 65, 1867, pp. 102, 103.

first it was thought that a series of magnesium oxychlorides was formed whose compositions depend on the proportions in which the magnesium oxide and chloride were mixed. The more modern view is that the oxide and chloride combine in a series of solid solutions whose components are not well known. It is certain that part of the magnesium oxide does not combine but is left free, particularly in the centers of the larger lumps. Preparations of magnesium oxychlorides in dilute solutions have shown such compounds as $3MgO.MgCl_2.7H_2O$ or $5MgO.MgCl_2.14H_2O$ or $10MgO.MgCl_2.14H_2O$, and it is even possible that some of these exist in the Sorel cements as prepared.

In practice a solution of magnesium chloride containing about 26 per cent $MgCl_2$ is mixed with finely ground plastic magnesia, and this mixture is used to fill the voids of an inert aggregate, in much the same way as Portland cement is used in making concrete. Under a microscope, the magnesian cement shows an amorphous mass that contains very few crystals and is apparently homogeneous except for grains of uncombined magnesia. Part of the magnesium chloride can be washed out of such a cement by soaking in water or in absolute alcohol. The cement probably consists of a solid solution in which are present free magnesium oxide, magnesium chloride, and at least one of the oxychlorides mentioned above. The cement can take up carbon dioxide; it also takes up water or gives off water according to the humidity of the surrounding atmosphere. The cement is not a material of constant composition and its mechanical properties depend upon the ratio and manner in which the various constituents have entered the complex.

TESTING

Since the only way of recognizing good plastic magnesia is by actual trial in making cement, all the work we did in producing it was checked by making test bars and blocks of magnesium oxychloride cements with suitable fillers. These methods of testing are described at length.

When we began our work the only existing specifications were certain requirements covering the percentages of magnesia and lime and the ignition loss. Recognizing that these chemical specifications meant little unless reinforced by physical tests, the obvious thing to do was to use the already developed methods of testing Portland cement so far as they would apply. We cooperated with the Dow Chemical Co., that was also interested in drawing up intelligent specifications for the purchase and sale of plastic magnesia. This company now has a series of bulletins describing its work.

METHODS OF CALCINING

If a sample of magnesite is to be used to make plastic magnesia the heat treatment which it receives is all important. Not only does one usually expect a certain amount of carbon dioxide to have been left in the commercial burned product, but the temperature of calcination should not have been too high. Magnesia produced at high temperatures is not caustic nor "plastic." That is why some carbon dioxide must be left in the commercial product, since its removal involves either a very long heating at low temperatures or quicker heating at higher temperatures. The work done during this investigation has covered mainly the temperature of burning as it affects the properties of the calcined magnesia. The time of burning has not been studied with as great care, although some data are available.

Careful consideration was given the kind of furnace that was best adapted to the heat treatment of magnesite in order to produce satisfactory plastic magnesia, and extensive tests in a small Herreshoff furnace gave favorable results.

The work has brought out clearly the fact that each magnesite must be studied separately and a specific temperature range and time of treatment determined experimentally in order to produce the best plastic magnesia. It has been demonstrated that the crystalline magnesites can be so treated as to give a good material for making cements.

FORMS OF MAGNESIA

Magnesia can exist in several allotropic forms or several different states of molecular aggregation. The alpha form is regarded as relatively active and soluble, but the beta form is crystalline, is identical with the mineral periclase, and is inactive and relatively insoluble. Plastic magnesia probably consists mostly of the alpha modification, which is converted into the beta form on heating. This fact explains why heating at too high a temperature is undesirable.

At the best, it is probable that a certain amount of the alpha form is altered to the beta, which seems to be the stable form, during calcining and plastic magnesia probably consists of an indefinite mixture of the two forms. Consequently plastic magnesia contains a certain amount of undecomposed magnesite, as well as silica and other impurities from the raw material, and a certain amount of the calcined magnesium oxide is inert. This fact helps to explain the differences in strength of cements made with different samples of plastic magnesia and also emphasizes the necessity of proper heat treatment of the magnesite.

If the alpha form is metastable, one can more easily understand why that form should be more active chemically than the crystalline beta form. Impurities, chiefly ferric oxide, hasten the transformation from the alpha to the beta form. Plants that produce dead-burned or refractory magnesia, which should be entirely of the beta form, utilize this fact by adding iron ore to the mix before burning. By this addition it is possible to effect the transformation rapidly and at temperatures that are practicable in fuel-fired rotary kilns. On the other hand, when it is desired to make none of the beta form of magnesia, as in the manufacture of plastic magnesia, the presence of as much as 2 per cent Fe_2O_3 in the crude rock necessitates calcining at a much lower temperature than if no iron were present.

FREE LIME

One of the most uncertain points in the use of plastic magnesia for cements has been the effect of free lime. Almost every magnesite deposit contains more or less calcium carbonate, probably in the form of dolomite, and during the calcination of the magnesite some of this calcium carbonate is decomposed into calcium oxide and carbon dioxide. Fortunately magnesium carbonate decomposes at a much lower temperature than does calcium carbonate, as will be discussed later, and under the conditions that usually prevail during the calcination of plastic magnesite only a part of the calcium carbonate is calcined to free lime.[1a]

We have not obtained enough data to establish any definite relation between the free-lime content and the properties of the plastic magnesia cements. All that can be said is that "too much" free lime is definitely detrimental. In several tests the deliberate addition of 2 or 3 per cent of free lime to the batch under test showed no effect at all or even a slight improvement. Just how much free lime could be tolerated was not determined.

RECARBONATION OF FREE LIME

During the research it was found that if calcined magnesia containing free lime (CaO) were brought into contact with CO_2 gas at temperatures slightly above the dissociation temperature of magnesium carbonate but below that of calcium carbonate, all of the free lime was rapidly converted to calcium carbonate with a rather large liberation of heat, while the magnesia remained unaffected. This reaction, which was termed recarbonation, was of such a quantitative nature and seemingly of such potential importance that much

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[1a] This statement is not entirely consistent with the facts, because if the content of lime and other impurities is small, no attention is paid to the calcination of the lime; and in practice as much as 4 per cent free lime can be tolerated.

experimental work was done on it. Although the results of recarbonation of low-lime magnesites were not immediately visible, the effects on the products containing higher amounts of lime were very pronounced; even calcined dolomite gave a satisfactory product after it had been recarbonated in order to render the lime inert. Of course, this would make the dolomite consist of about 70 per cent inert material, but since most of the cement mixtures used call for the addition of a rather large amount of inert material and an excellent cement can be made with 12 per cent MgO, this matter is not important. For flooring about 40 per cent MgO is used, consequently dolomite would not serve unless the usual mix were changed.

The research, therefore, arrived at a more or less unexpected conclusion. Originally undertaken to develop methods of making satisfactory plastic magnesia from the various magnesite deposits in the Western States, it attained this object, but it also revealed that plastic magnesia of fair quality could be produced from dolomite, a material cheaply obtainable in the Eastern States, where the market for plastic magnesia is largest. If large-scale development of the process for treating dolomite proves successful, the deposits of magnesite in the Western States will become less important, as far as the supplying of plastic magnesia is concerned.

STORAGE

Accelerated weathering tests of samples of plastic magnesia prepared for this work showed that plastic magnesia took up both moisture and carbon dioxide and that the physical properties of the resulting cements were somewhat changed—notably the setting time was lengthened.

Other variables might have been investigated, particularly the size of the material calcined or the size of the material used in making oxychloride cements and the proper strength of magnesium chloride solution to use with each kind of magnesia produced, but time did not permit these points to be investigated, and after 18 months of intensive research enough data for satisfactory commercial operation had been obtained by the Northwest Magnesite Co., so no more money was appropriated for research. This bulletin therefore reports such work as was done, and presents some discussion of plastic magnesia.

CONTEMPORARY WORK

The Dow Chemical Co., of Midland, Mich., was actively investigating magnesium oxychloride cements at the same time that the work described herein was carried out, and operated a magnesia cement laboratory under the direction of Max. Y. Seaton. The Dow company wished to gain information which would allow it intelligently to market magnesium chloride, a by-product of its salt and bromine industry. Acknowledgment is due the company and Mr. Seaton for information on testing methods and for their willingness to test the materials used in our investigation and thus check the work done.

The United States Bureau of Standards has also been interested in preparing standard specifications for plastic magnesia for various purposes. P. H. Bates, of that bureau, has consequently kept in close touch with our work and has assisted by suggestions.

Mr. William Baumbach, president of the National Association of Composition Flooring Manufacturers, has also assisted and has contributed to the final conclusion that crystalline Washington magnesite can be made into a satisfactory strong and dense oxychloride cement.

USES OF MAGNESIAN CEMENTS

The first commercial use of magnesian cements was in Germany. Their use in the United States was just being established at the beginning of the World War, but is gaining rapidly at present.

Most of the plastic magnesia now made from domestic magnesite comes from California producers, who ship about 40,000 tons a year. Of this total, 30,000 tons is probably used for making outside stucco and the remainder for composition flooring.

One square yard of stucco in place weighs about 32 pounds and contains about 4.6 pounds of plastic magnesia; hence 30,000 tons would cover 13,000,000 square yards of surface, and if the average house receives 300 square yards of stucco surface the yearly output would cover 43,400 houses.

Magnesia stucco has gained headway in competition with cement stucco largely because it makes a stronger, harder, and more elastic cement which adheres more firmly to wood surfaces and takes and securely holds dashes of ornamental colored pebbles. This stucco gives a house a more finished appearance, probably due to the colored pebbles, but it has one disadvantage—it is not as weatherproof as cement stucco. Weatherproofing compounds are therefore being tried. The structural firmness and density of the stucco are the qualities that best insure protection, and these qualities largely depend on the quality of the plastic magnesia used, which in turn—the use of proper crude material being granted—depends mainly on selecting and accurately controlling the proper calcining temperature. Judged from the cumulative experience of the industry, properly made magnesian stuccos are resistant enough to weathering to be considered entirely satisfactory.

FLOORING

As a square foot of composition flooring contains about 1 pound of plastic magnesia, 10,000 tons would correspond to 20,000,000 square feet of flooring laid annually. Composition floors if properly laid are superior to any others of like cost; they are permanent, warm to the touch, elastic, fireproof and fairly ornamental, and can be laid over old or new wooden floors. Bathroom floors and walls are now quite commonly covered with composition flooring, and bathtubs are frequently encased in it. Slabs of the same material, often appropriately tinted, are used for drainboards in kitchen sinks and for similar purposes.

OTHER USES

Interior plaster offers a field as yet little exploited, although such plaster is much stronger and better than either lime or gypsum plasters. Other uses will doubtless develop. At present manufacturers of composition flooring and of stucco buy plastic magnesia and prepare mixtures that are ready to be moistened with magnesium chloride solution at the point of application. Many manufacturers are inadequately financed because the necessary capital seems small. Moreover, the supply of plastic magnesia was for a while variable and occasionally bad, but this condition is now rapidly improving.

MISCELLANEOUS FACTS ABOUT MAGNESIAN CEMENTS

Finely ground magnesium oxide will set into a cement only when mixed with a rather strong brine of magnesium chloride—dilute solutions are valueless. Properly made magnesium cements do not shrink perceptibly, but usually expand during setting so that reproductions of fine lines and corners in molds can be obtained, whereas plaster of Paris shrinks too much for such fine work. In fact, mixes of magnesian cements will sometimes be found which expand enough to burst molds. Such cements adhere tenaciously to wood, so glass or stoneware molds are better. Waxed paper is frequently used to line molds of other materials. Molded forms of this type of cement tend to warp and twist after being removed from the mold. It is said that this difficulty can be avoided by mixing barium carbonate or monobasic potassium phosphate in the cement, but neither of these reagents seems thoroughly reliable.

DESCRIPTION OF RAW MATERIALS

Various grades of magnesite and dolomite were obtained from the mines of the Northwest Magnesite Co. in Chewelah, Wash., and several rather large shipments became necessary as the scale of operations increased. All of this magnesite was the crystalline variety, which had previously been supposed to be ill adapted to the preparation of plastic magnesia. Numerous samples from various deposits of magnesite in California, all of which were of the cryptocrystalline or "amorphous" variety, were likewise obtained, as well as several samples of dolomite and calcite from well-known quarries in California. Table 1 contains a list of the important samples of magnesite, dolomite, and limestone tested, also their sources and quantities. Table 2 gives analyses of these samples. Prof. W. S. Morley, of the school of mines of the University of California, analyzed a number of samples and parallel analyses by Messrs. Morley, Riddell, and Sebastian made of sample M-1 in order to ascertain the degree of variation that might be expected from different analysts. Very satisfactory checks were obtained.

TABLE 1.—*List of samples used for plastic magnesia investigation*

No.	Material	Source	Quantity	Date received	Remarks
M-1	Magnesite (crude)	Chewelah, Wash	900 pounds	Sept. 1, 1919	
M-2	Magnesium chloride.	Whitney Chemical Co., San Francisco, Calif.	1 pound	Nov. 2, 1919	
M-3	do	do	80 pounds	Sept. 15, 1919	
M-4	Magnesite (calcined).	Hoff Manufacturing Co., Oakland, Calif.	1 barrel	do	
M-5	Asbestos	Williams-Wendt Co., Chicago.	200 pounds (2 sacks).	Dec. 1, 1919	
M-6	Wood fiber		1 sack	Nov. 1, 1919	
M-7	Standard sand (Ottawa).	Fairbanks, Morse Co	200 pounds (2 sacks).	Oct. 12, 1919	
M-8	Silica, 200 mesh	Braun Knecht, Heimann Co., San Francisco, Calif.	135 pounds (1 sack).	Nov. 5, 1919	
M-9	Magnesite (crude)	Red Mountain, Calif	2 pounds	Dec. 1, 1919	
M-10	do	White Rock mines, Rutherford, Calif.	200 pounds (2 sacks).	Dec. 8, 1919	
M-11	do	Porterville Magnesite Co., Porterville, Calif.	200 pounds (2 sacks.)	do	
M-12	do	Tulare Mining Co., Porterville, Calif.	200 pounds (2 sacks).	Dec. 12, 1919	
M-13	do	Western Magnesite Development Co., Livermore, Calif.	100 pounds (1 sack).	Dec. 8, 1919	
M-14	do	Northwest Magnesite Co., Chewelah, Wash.	2,700 pounds (27 sacks).	Dec. 22, 1919	
M-15	Dolomite (crude)	Chewelah, Wash	100 pounds (1 sack).	Dec. 12, 1919	
M-16	Magnesite (crude)	do	300 pounds (3 sacks).	do	
M-18	do	Tulare Mining Co., Porterville, Calif.	100 pounds	Sept. 27, 1919	Selected
M-19	Crushed magnesite, before Fe_3O_4 added.	Chewelah, Wash	5 pounds	do	
M-20	Magnesite (crude)	Tulare Mining Co., Porterville, Calif.	100 pounds	do	Mine run.
M-21	do	C. S. Maltby, Porterville, Calif.	20 pounds	Jan. 9, 1920	Selected.
M-22	Magnesite (calcined).	National Kellastone Co., Porterville, Calif.	75 pounds	Jan. 8, 1920	
M-23	Limestone	Santa Cruz Portland Cement Co., Santa Cruz, Calif.	20 pounds	Jan. 25, 1920	
M-24	Magnesite	C. S. Maltby, Livermore, Calif.	16 pounds	Jan. 15, 1920	
M-25	do	Northwest Magnesite Co., Chewelah, Wash.	100 pounds	Feb. 9, 1920	
M-26	Limestone	Pacific Portland Cement Co., Auburn, Calif.	25 pounds	Feb. 6, 1920	
M-27	Magnesium chloride, c. p.	Baker Chemical Co	5 pounds	Mar. 8, 1920	
M-28	Magnesite (calcined).	C. S. Maltby, Livermore, Calif.	1,000 pounds	Apr. 2, 1920	Lump calcine.

TABLE 1.—*List of samples used for plastic magnesia investigation*—Continued

No.	Material	Source	Quantity	Date received	Remarks
M-29	Magnesite (crude)	Northwest Magnesite Co., Chewelah, Wash.	2,700 pounds	Feb. 20, 1920	Low lime, selected.
M-30	Magnesite (calcined).	Tulare Mining Co., Porterville, Calif.	1,050 pounds	Apr. 7, 1920	Ground calcine.
M-31	Magnesium chloride.	Dow Chemical Co., Midland, Mich.	30 pounds	Apr. 26, 1920	
M-32	do	do	200 pounds	May 2, 1920	
M-33	Magnesite (crude)	Northwest Magnesite Co., Chewelah, Wash.	19,000 pounds		
M-37	Caustic magnesia (commercial).	National Kellastone Co., Porterville, Calif.	1,050 pounds	Aug. 3, 1920	
M-41	Sampson magnesite (calcined).	C. S. Maltby, Sampson Peak, San Benito County, Calif.	14 pounds	Aug. 10, 1920	
M-42	Porterville high lime.	C. S. Maltby, Porterville, Calif.	5 pounds	do	
M-44	Magnesite	do	2,400 pounds	Aug. 28, 1920	
M-45	do	Northwest Magnesite Co., Chewelah, Wash.	½ car	Sept. 10, 1920	Fine.
M-46	do	do	do	do	Coarse.
M-48	Dolomite	California Alkali Co., Cartago, Calif.	4,000 pounds	Sept. 15, 1920	
M-49	Magnesite	Cliffside Magnesite Co., Cliffside, Calif.	2,000 pounds 200 pounds	Oct. 12, 1920 Sept. 20, 1920	
M-50	do	do	3,360 pounds	Nov. 24, 1920	
M-51	Calcined magnesite.	C. S. Maltby, Livermore, Calif.	150 pounds	Sept. 22, 1920	Calcined Scott furnace.
M-52	do	Livermore, Calif	do	do	Calcined stack furnace.
M-53	Brucite	Keystone quarry, Chewelah Wash.	50 pounds	Oct. 4, 1920	
M-57	Magnesite	Nevada Magnesite Co., St. Thomas, Nev.	4,000 pounds	Oct. 28, 1920	
M-60	do	C. S. Maltby, Porterville, Calif.	200 pounds	Dec. 30, 1920	
M-61	do	do	1,000 pounds	Jan. 10, 1921	

TABLE 2.—*Analyses of raw materials—magnesite, calcite, and dolomite*

Mark	Date analyzed	Analyst	Insoluble	SiO_2	Al_2O_3	Fe_2O_3	CaO	Ignition loss	MgO, by difference	Remarks
M-1	1919 Aug. 15	Riddell, Morley, and Sebastian.	4.63	------	1.23	0.93	2.78	48.48	41.92	
M-4	1920 Jan. 19	Morley	2.34	1.70	.12	.33	4.26	5.70	87.34	H_2O, 0.96.
M-10	do	do	4.81	4.47	.29	2.23	.10	48.68	43.88	H_2O, 0.70.
M-11	do	do	1.61	1.16	.19	.29	.73	50.00	47.17	H_2O, 0.20.
M-12	do	do	.94	.93	.16	.14	.18	50.56	48.01	H_2O, 0.25.
M-13	do	do	1.40	1.22	.01	.43	.72	50.40	46.61	H_2O, 0.21
M-15	do	do	2.76	1.47	.36	1.17	25.26	45.9	24.50	H_2O, 0.10.
M-16	do	do	3.01	1.21	.38	.83	.10	50.15	45.53	H_2O, 0.08.
M-18	do	do	1.64	1.36	.06	.14	.61	50.16	47.39	H_2O, 0.26.
M-19	Aug. 20	Henriques	.80	------	.3	Trace	.9	51.1	46.9	
M-20	do	do	6.29	4.87	.52	.70	2.04	47.01	43.44	
M-21	do	do	.4	------	.3	Trace	1.0	51.2	47.1	
M-22	Mar. 3	Delius	8.50	------	.38	.51	3.67	4.30	82.65	
M-23	Jan. 22	Santa Cruz Portland Cement Co.	------	.06	Trace	.17	54.90	43.96	1.29	SO_3, trace.
M-24	Aug. 20	Henriques	.8	-----	.4	Trace	.8	51.1	46.9	
M-25	Feb. 10	Delius	2.06	------	.15	.68	.59	50.88	45.63	
M-26		Pacific Portland Cement Co.	------	.12	[1] .10	------	55.10	43.74	.76	
M-28	Apr. 7	Delius	1.05	------	.35	.30	2.42	5.86	90.03	
M-29	Sept. 18	Delius and Henriques.	3.84	------	.34	.36	.19	49.34	45.92	
M-30	Apr. 9	Delius	4.24	------	.24	.41	1.39	3.51	90.21	
M-33	July 6	Delius	4.63	------	.41	.94	2.09	47.72	44.21	
M-37	Aug. 20	Henriques	.6	------	.3	.2	2.3	9.4	87.2	
M-41	Aug. 21	Delius	1.18	------	.28	.72	.82	7.43	89.57	
M-42	do	do	5.50	------	.22	.14	8.23	19.23	66.68	
M-44	Oct. 21	Henriques	3.48	------	.37	.10	1.89	47.92	45.24	
M-45	do	do	4.44	------	.79	.92	1.77	42.50	49.49	

[1] R_2O_3.

TABLE 2.—*Analyses of raw materials—magnesite, calcite, and dolomite*—Con.

Mark	Date analyzed	Analyst	Insoluble	SiO_2	Al_2O_3	Fe_2O_3	CaO	Ignition loss	MgO, by difference	Remarks
M-46			4.44		0.79	0.92	1.77	42.50	49.49	
M-48	Oct. 21	Henriques	.55		.15	Trace	30.4	46.04	22.86	
M-49	do	do	8.62		1.12	.32	4.35	47.50	37.88	Ignition loss: NaCl, 0.15; CO_2, 45.80; H_2O, 1.35.
	1921									
M-50	Jan. 30	do	8.18		1.17	.17	4.28	46.90	39.30	Ignition loss: CO_2, 45.50; H_2O, 1.43.
M-51								8.18		
M-52								6.69		
	1920									
M-53	Nov. 9	Henriques	2.25		.35	.92	.0	31.28	65.30	
M-57	do	Riddell	12.20		.32	.84	6.10	43.42	37.07	Moisture, 2.15; Comb. H_2O, 1.90; CO_2, 39.20.
	1921									
M-60	Jan. 21	Henriques	1.27		.19	.05	1.22	52.7	44.62	Soft portion.
M-60	do	do	.26		.08	.22	1.22	52.0	46.22	Hard.
M-61	do	do	1.76		.35	.16	3.13	50.09	44.51	

RATE OF THERMAL DECOMPOSITION OF NATURAL CARBONATES OF MAGNESIUM AND CALCIUM

In order to ascertain the rates at which magnesite and dolomite can be calcined to form plastic magnesia, a series of tests of pieces of various sizes was designed to determine the rates of thermal decomposition. A few tests of limestone and of calcite were also made for comparison. Our work covered the temperature range of 500 to 850° C. for the magnesites and higher temperatures for the calcium carbonate products.

DISSOCIATION TEMPERATURE OF MAGNESIUM CARBONATE

Practically no work on rates of decomposition had been done before, although time-temperature curves had been used in locating the temperature at which the dissociation pressure of these carbonates reaches 1 atmosphere. Table 3 gives the references and the results of previous work on the dissociation temperature of magnesium carbonate.

The average of the results of Hedvall (10)[2] is 546° C. Our work shows that $MgCO_3$ can not be decomposed thermally with noticeable velocity until the temperature is about 575° C., a figure in fair agreement with those of Friedrich (7) and of Grünberg (9). All these figures apply to cryptocrystalline (amorphous) magnesite. The work of Marc and Simek (11) shows 1 atmosphere pressure of carbon dioxide, when in true equilibrium, at 402° C., but so many disturbing factors had to be eliminated in obtaining this figure that it is of little practical value, and we prefer to use 575° C. as the more probable figure, at least for practically attainable conditions. For calcium carbonate, a dissociation temperature of 898° has been determined by Johnston (13), which is in fair agreement with figures varying from 900 to 920° C. obtained by many previous investigators.

The distinction between equilibria and kinetics in the foregoing paragraph must be noticed. Although the work of Marc and Simek indicates that true equilibrium with 1 atmosphere of CO_2 takes place at 402° C., a noticeable velocity of thermal decomposition at 1 atmosphere is not evident until the temperature reaches 575° C. Likewise, for calcium carbonate, the work of Johnston indicates

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[2] Numbers in parentheses refer to the investigations cited in Table 3.

that a true equilibrium at 1 atmosphere is met at 898° C.; but experience shows that a noticeable velocity of thermal decomposition at the same pressure is not attained until the temperature reaches about 950° C. Under one condition a superheat of at least 175° is needed, and under the other a superheat of 50°.

With further reference to the work of Marc and Simek, our experimental results indicate that magnesium oxide can be recarbonated at 420° C., although the rate is quite slow. Evidently the carefully determined figure of Marc and Simek of 402° C. for equilibrium is too low.

TABLE 3.—*Thermal dissociation of $MgCO_3$*

Observer	Dissociation Temperature °C.	Kind of material	Method
H. Rose [1]	Low red heat	Basic magnesium carbonate.	Determination by loss in weight.
W. Anderson [2]	810	"Heavy" $MgCO_3$	Do.
A. Michaelis[1]	Over 300	Magnesite	Do.
Do [3]	300	$MgCO_3 . 3H_2O$	Do.
A. Vesterberg [4]	500 (estimated)	Magnesite	Do.
E. Wulfing [5]	500+	do	Do.
O. Brill [6]	500–550	$MgCO_3$ made by heating $MgCO_3.3H_2O$ in CO_2.	Do.
K. Friedrich [7]	570–600	Magnesite	Temperature measurements.
O. Kallaunder [8]	500–620	Amorphous magnesite	Determination by loss in weight.
K. Grünburg [9]	570±15	Magnesite	Do.
J. A. Hedvall [10]	546 (average)	Precipitated $MgCO_3$	Temperature measurements.
R. Marc and A. Simek.[11]	402		Pressure measurements: 100°=0.04 mm, 200°=2.0 mm, 300°=47 mm, 402°=760 mm, Q=23,200.
A. V. Bleininger and W. E. Emley.[12]	750	Magnesian limestone	Temperature measurements. Note more likely dicsociation temperature of dolomite.
J. Johnston [13]	898	Precipitated $CaCO_3$	For comparison.

[1] Rose, H., ———, Pogg. Ann., Bd. 83, 1851, p. 423.

[2] Anderson, W. C., The formation of magnesia from magnesium carbonate by heat, and the effect of temperature on the properties of the product: Proc. Chem. Soc., vol. 21, 1905, p. 11.

[3] Michaelis, A., Lehrbuch der Chemie. Leipzig, 5 ed, 1884, Bd. 2, pt. 3, p. 748.

[4] Vesterberg, Alb., Chemische Studien über Dolomit und Magnesit: Bull. Geol. Inst., Univ. Upsala, vol. 5, 1900, p. 127.

[5] Wülfing, E. A., Untersuchung des bunten Mergels der Keuperformation auf seine chemischen und mineralogischen Bestandteile: Jahres. Ver. vater. Natur., Württemberg, Bd. 56, 1900, pp. 1–46.

[6] Brill, Otto, Über die Dissoziation der Karbonate der Erdalkalien und des Magnesiumkarbonats: Ztschr. anorg. Chem., Jahrg. 45, 1905, pp. 282–291.

[7] Friedrich, K., Beiträge zur Kenntnis thermischen Dissoziation und der Konstitution leicht zerlegbarer Mineralien: Centralb. Mineral., Geol., u. Palaontol., Jahrg. 1, 1912, p. 653.

[8] Kallauner, Otto, Die thermische Dissoziation des amorphen Magnesits: Chem. Ztg., Jahrg. 37, 1913, pp. 182, 183.

[9] Grünberg, Karl, Beitrag zur Kenntnis der naturlichen krystallisieren Karbonate des Calciums, Magnesiums, Eisens, und Mangans: Ztschr. anorg. Chem., Bd. 80, 1913, pp. 337–396.

[10] Hedvall, J. A., ———, Ztschr. anorg. Chem., Bd. 98, 1916, p. 47.

[11] Marc, R. and Simek, A., Über die thermische Dissoziation des Magnesiumkarbonats: Ztschr. anorg. Chem., Bd. 82, 1913, pp. 17–49.

[12] Bleininger, A. V., and Emley, W. E., The burning temperature of limestone: Am. Cer. Soc., vol. 13, 1911, pp. 618–638.

[13] Johnston, John, The thermal dissociation of calcium carbonate: Jour. Am. Chem. Soc., vol. 32, 1910, pp. 938–946.

EXPERIMENTS BY THE AUTHORS

The experimental work on rate of decomposition was done in the familiar Victor Meyer apparatus, arranged as shown in Plate I, *A.*, page 32. Details are shown in Figure 1. Our apparatus was similar to that used by Bole.[3]

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[3] Bole, G. A., An apparatus for studying the dissociation of carbonate rocks: Jour. Am. Cer. Soc., vol. 2, 1919, pp. 410–417.

The temperatures were measured with two standardized platinum-rhodium thermocouples, and a Leeds and Northrup potentiometer, and are accurate to ±5°. An electric furnace was used for heating, and the temperature control was within 10° (±5°). The volume of carbon dioxide evolved was measured over mercury to within 0.5 c. c. Samples of the carbonate of about 0.5 gram were weighed into a silver or a silica crucible and hung from the trigger by a fine nichrome wire. The crucible was dropped from the trigger into the bottom of the silica tube and the volume of gas evolved was re-

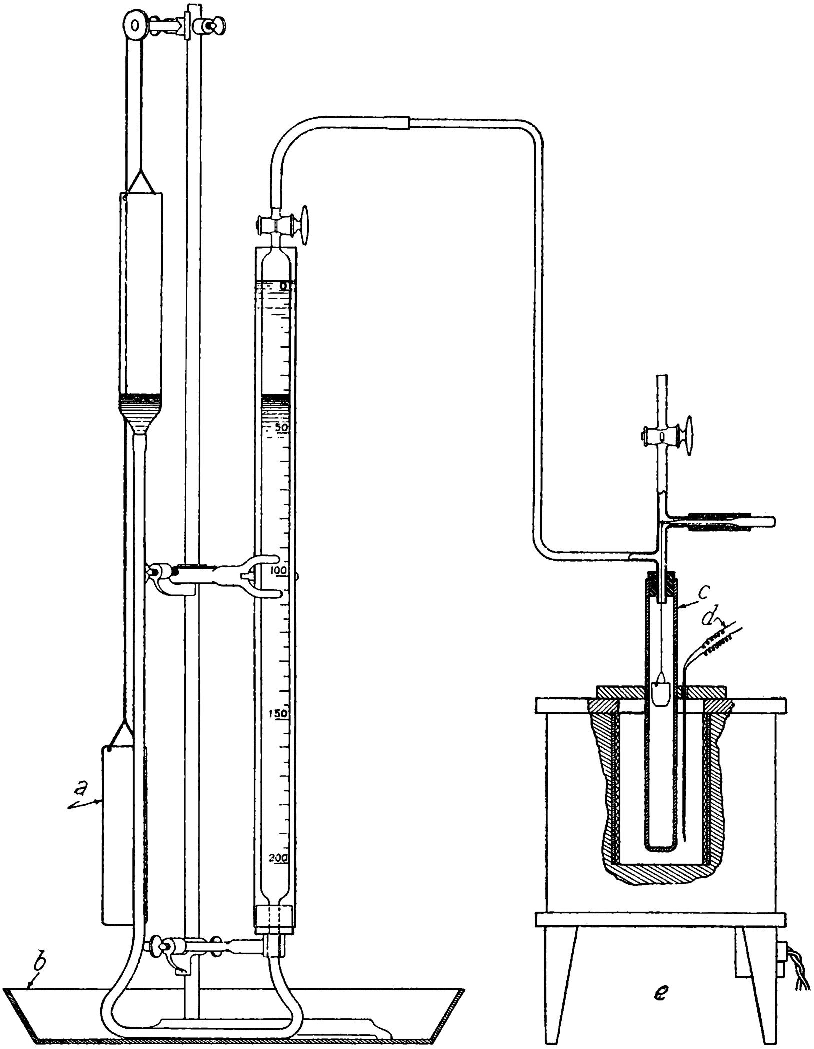

FIGURE 1.—Victor Meyer apparatus for studying decomposition of magnesite: *a*, Counterweight; *b*, tray; *c*, silica tube; *d*, thermocouple leads; *e*, electric furnace

corded each minute with a stop-watch, until the evolution of the gas ceased. The percentage decomposition is calculated by dividing the volume of gas liberated in various intervals of time by the total volume of gas evolved. The results in the curves are for materials screened to a definite size—through a 28-mesh and on a 35-mesh screen (0.586 mm. to 0.417 mm. openings, respectively). The pressure of carbon dioxide in the silica tube was approximately 1 atmosphere.

Table 4 gives the analyses of the materials used. The results of our measurements are given in the curves of Figures 3 to 15, which will be discussed later.

LIBERATION OF CO_2 BY MAGNESITE AT CALCINING TEMPERATURE

To determine the effect of size of grain on the rate of liberation of carbon dioxide for magnesite at a representative calcining temperature, we collected the following figures for 750° C. (See Tables 5 and 6.)

TABLE 4.—*Analyses of materials used in the plastic magnesia investigation*

	California magnesites					Washington magnesites (Chewelah)		Dolomites		Calcium carbonates	
	Tulare	White Rock	Red Mountain	Porterville	Sampson			Chewelah	Owens Lake	Mount Q. limestone	Pure calcite crystals
	M-18	M-10	*M-13	M-11	M-60	M-1	M-29	M-15	M-48	M-26	C-1
SiO_2	1.35	4.50	1.2	1.15	0.6	4.20	7.65	1.47	0.50	0.12	Trace.
Al_2O_3	.06	.3	.01	2.5	.23	.41	.30	.70	.15	.10	Do.
Fe_2O_3	.14	2.2	.43	.3	1.01	.96	.70	.82	.03	.05	Do.
CaO	.30	.1	.5	.7	.5	2.76	.03	25.2	30.2	55.10	55.9.
MgO	46.7	43.8	46.3	45.1	46.43	42.52	43.5	24.5	21.6	.70	Trace.
CO_2	51.3	48.6	51.4	50.0	51.0	48.6	48.0	47.2	47.6	44.1	43.8.
H_2O	.26	.7	.2	.2	.2	.06	.08	.1	.08	-------	-------
Equivalent per cent $CaCO_3$	.53	.17	.9	1.2	.98	4.93	.05	45.0	53.9	98.1	99.9.
Equivalent per cent $MgCO_3$	97.8	92.0	97.1	94.6	97.5	89.5	91.3	51.4	45.4	1.47	-------

TABLE 5.—*Cryptocrystalline magnesite at 750° C. (sample M-13)*

Size	28 to 35 mesh	0.3 cm. 1/8 in.	0.8 cm. 2/8 in.	1.0 cm. 3/8 in.	1.3 cm. 4/8 in.	2.0 cm. 6/8 in.
Number pieces	3,000	6	1	1	1	1
Weight	0.5000	0.5007	1.4895	2.7640	5.395	16.875
Loss in weight	0.2520	0.2553	.7625	1.406	2.768	8.640
Volume CO_2 evolved	127	131	385	690	1,350	4,110
Time, minutes	6	8	20	24	29	38
C.c. CO_2 per gram, $MgCO_3$ per minute	89	53	22.0	22.5	16.4	13.6

TABLE 6.—*Crystalline magnesite at 750° C. (sample M–29)*

Size	28 to 35 mesh	0.3 cm.	0.8 cm.	1.0 cm.	1.3 cm.	2.0 cm.
Number pieces	3, 000	6	1	1	1	1
Weight	0. 5000	0. 5008	1. 6655	3. 053	7. 216	18. 532
Loss in weight	. 2340	. 2383	. 8335	1. 511	3. 910	. 083
Volume CO_2 evolved	120	127	422	735	1, 435	4, 425
Time, minutes	14	17	25	35	42	65
C. c. CO_2 per gram, $MgCO_3$ per min.	39	27. 9	18. 6	15. 9	9. 2	8. 6

EFFECT OF FINENESS OF PARTICLES

The data from Tables 5 and 6 are plotted in Figure 2, which shows the rates at which carbon dioxide is evolved from particles of different sizes when heated to 750° C. The important point is that the rate of decomposition of magnesite increases greatly with the decrease in particle size. Also, the cryptocrystalline (amorphous) magnesite from California decomposed much more rapidly than the crystalline magnesite from Washington. In general this was true of all the samples tested, as can be seen by consulting Figures 3 to 15, inclusive—particularly Figures 14 and 15, which compare the two types at 650° and 750° C., respectively. Since plastic magnesia is to be used in a finely divided condition, the magnesite before burning should be ground to the finest size economically feasible, in order to insure rapid decomposition of the mineral and efficient utilization of heat.

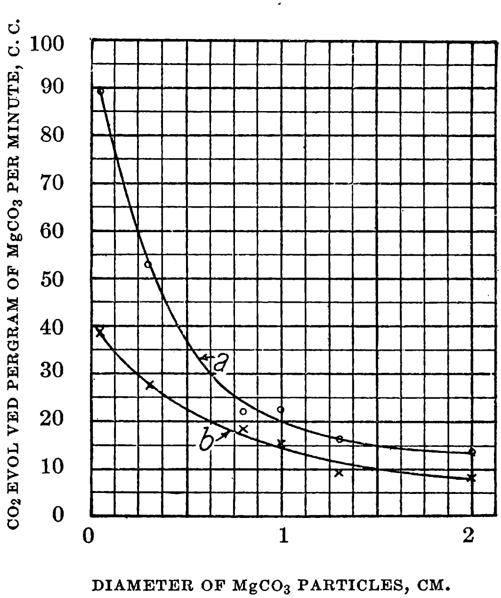

FIGURE 2. Curves showing the rates at which carbon dioxide is evolved from particles of different sizes when heated to 750° C.: *a*, Amorphous magnesite; *b*, crystalline magnesite.

EFFECT OF TEMPERATURE

The curves above mentioned show that magnesite begins to decompose with appreciable velocity at about 600° C. and the velocity of decomposition increases rapidly at higher temperatures. However, experience has shown that the magnesia produced is valueless for making cements if it has been altered to the crystalline variety MgO, called

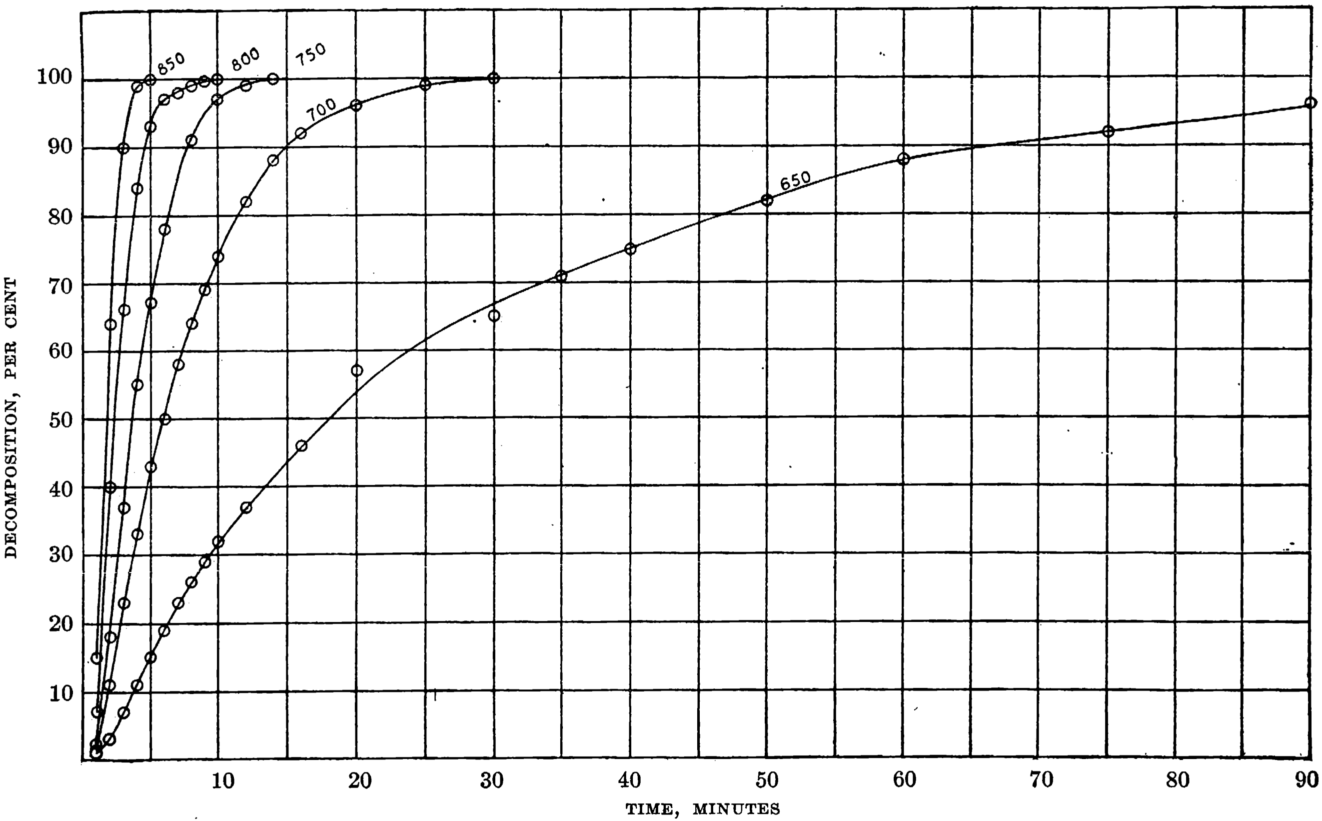

FIGURE 3.—Curve showing rate of decomposition, at different temperatures, ° C., of crude magnesite from Chewelah, Wash.

periclase. This change takes place at higher temperatures, particularly above 1,000° C., and in the presence of iron compounds is decidedly rapid. Therefore, calcining to produce plastic magnesia is done at temperatures below 1,000° C., and some of the carbon dioxide is not expelled during the burning. In fact, as will be seen later, the best plastic magnesia contains a small percentage of carbon dioxide that has never been removed by calcination. This means that the material is removed from the furnace at some point on the decomposition curves of Figures 3 to 9 which corresponds to about 80 per cent decomposition or more. If a good supply of heat be assumed, the necessary time for calcination can be approximated from our curves for any definite temperature.

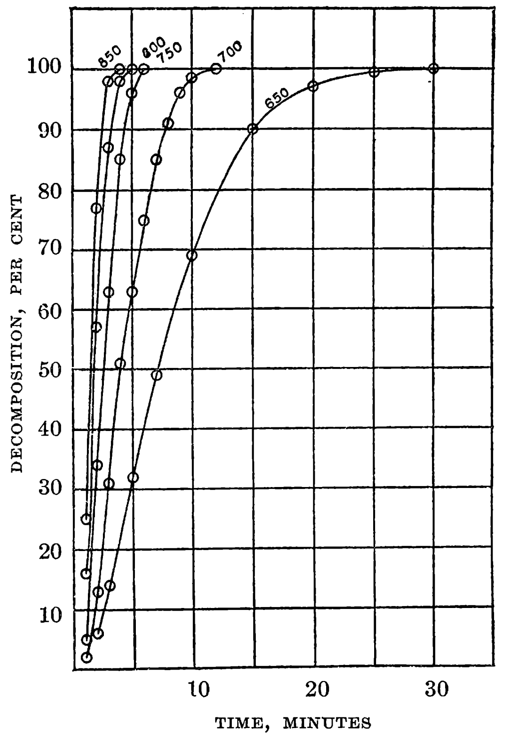

Figure 4.—Curve showing rate of decomposition, at different temperatures, °C., of crude magnesite from White Rock mines, Rutherford, Calif.

DECOMPOSITION OF DOLOMITE

The decomposition curves for dolomite were highly interesting. The California dolomite is a true dolomite (Fig. 11), and a comparison of its decomposition curves with those for magnesites shows that, at temperatures (600° to 750° C.) by which magnesite can be completely decomposed in 10 to 30 minutes, the Owens Lake delomite was decomposed very slightly. However, at temperatures above 750° and up to 900° C., the dolomite lost much carbon dioxide; this loss approached a maximum of about 50 per cent which corresponds to the complete decomposition of the $MgCO_3$ portion of the dolomite. At still higher temperatures further loss of carbon dioxide began and the calcium carbonate decomposed.

OWENS LAKE DOLOMITE

The inference to be drawn from the curves presented in Figure 11 is that the Owens Lake dolomite contains no free magnesite as

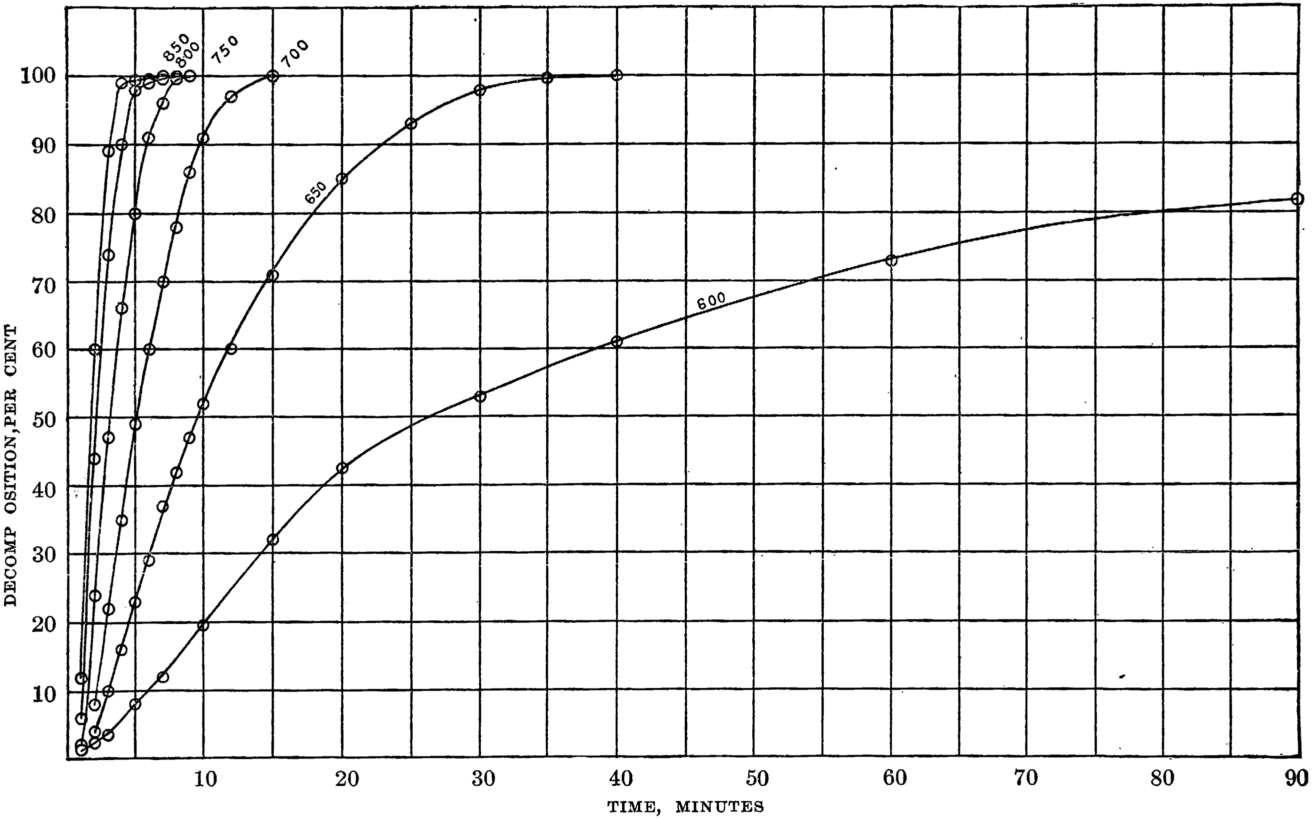

FIGURE 5.—Curve showing rate of decompoposition, at different temperatures, °C., of crude magnesite from Tulare Mining Co., Porterville, Calif.

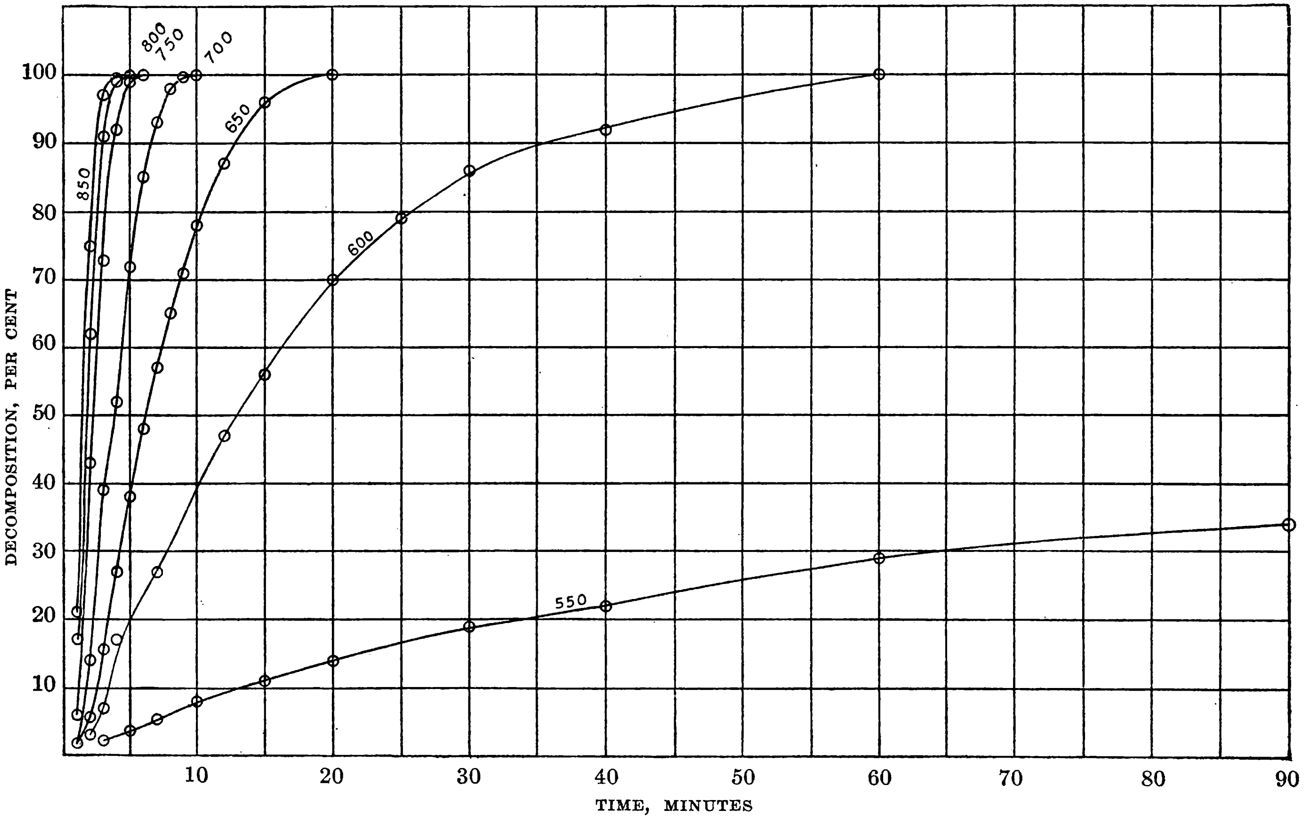

FIGURE 6.—Curve showing rate of decomposition, at different temperatures, °C., of crude magnesite from the Western Magnesite Development Co., Livermore, Calif.

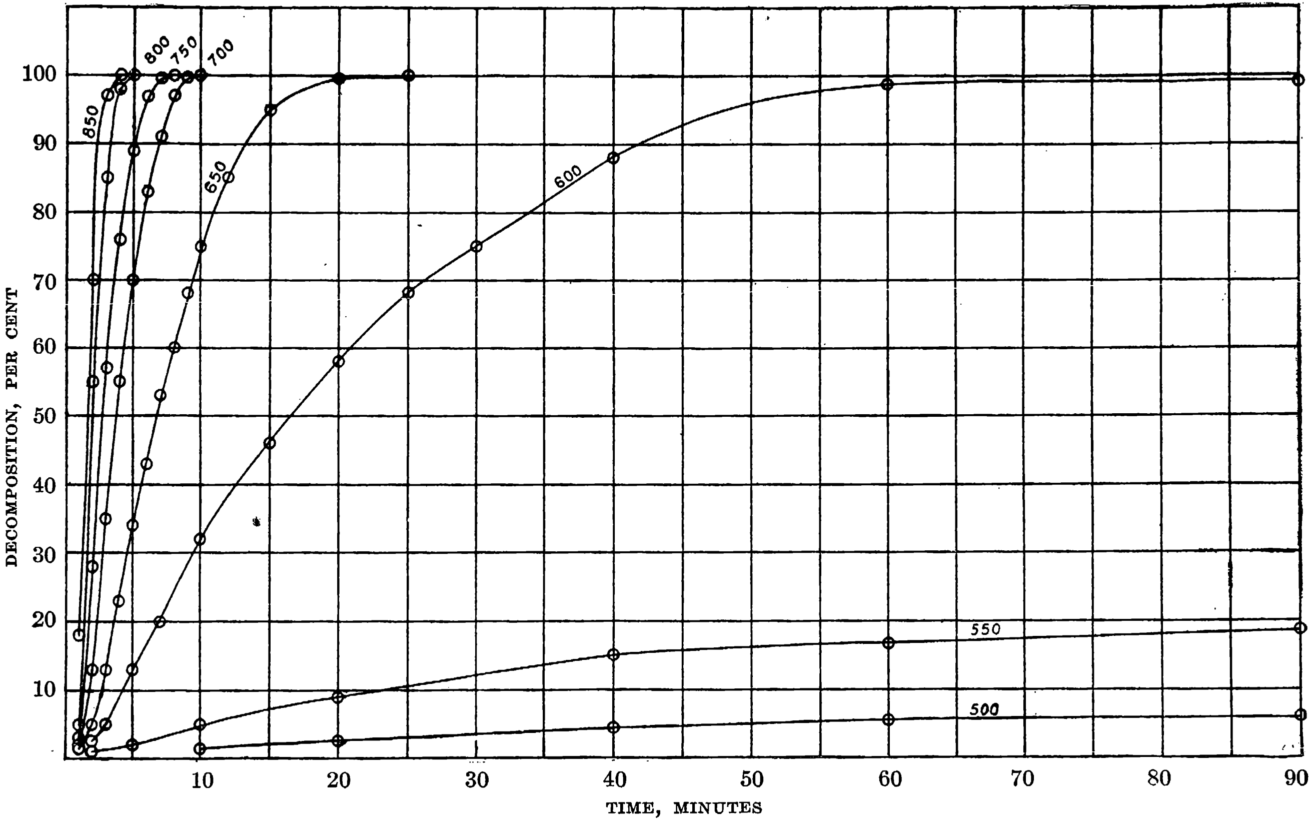

FIGURE 7.—Curve showing rate of decomposition, at different temperatures, ° C., of crude magnesite from Tulare Mining Co., Porterville, Calif.

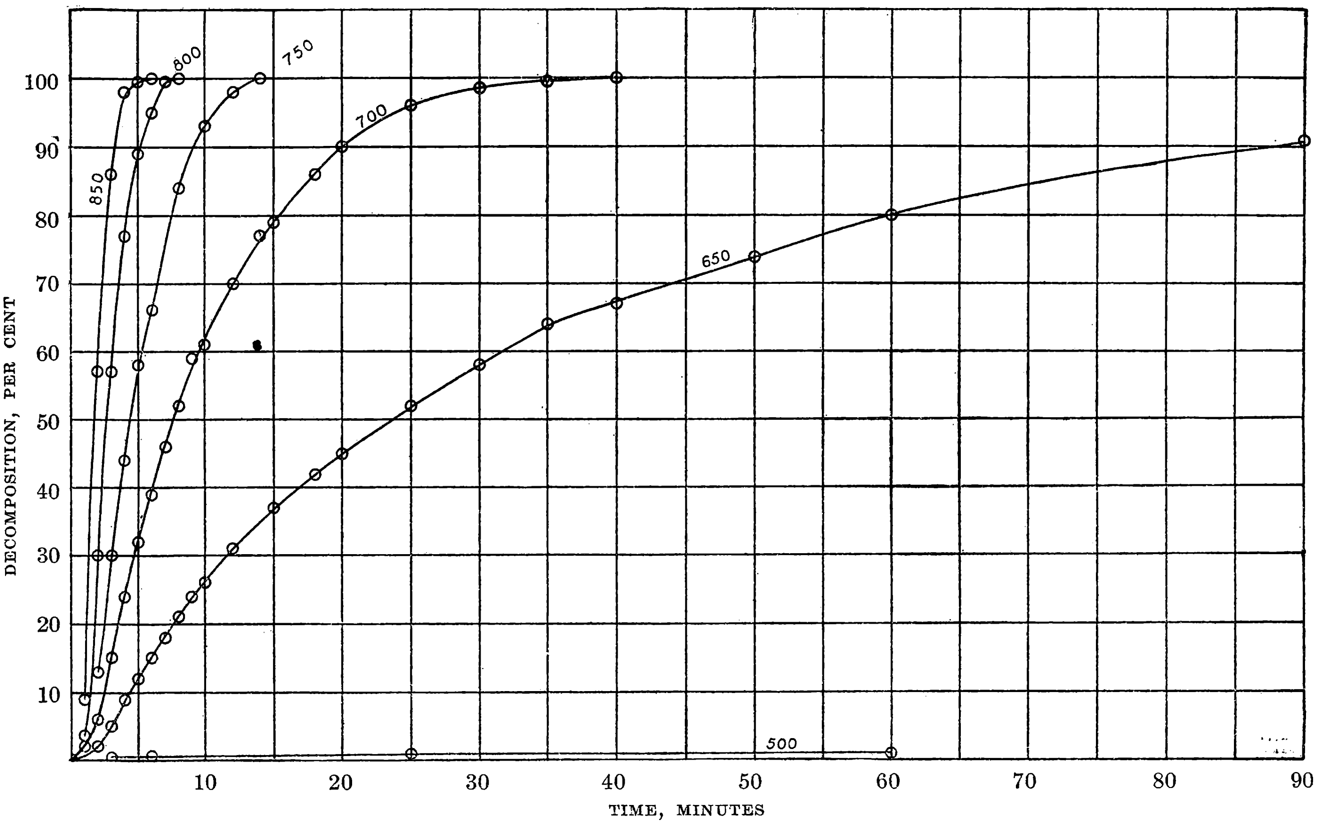

FIGURE 8.—Curve showing rate of decomposition, at different temperatures, ° C., of crude magnesite from Northwest Magnesite Co., Chewelah, Wash.

such, and that the first rapid evolution of carbon dioxide results from the breaking down of the dolomite crystals and the simultaneous decomposition of the resulting magnesium carbonate. The residual calcium carbonate remained unaltered under a pressure of 1 atmosphere of carbon dioxide until the temperature exceeded 900° C.

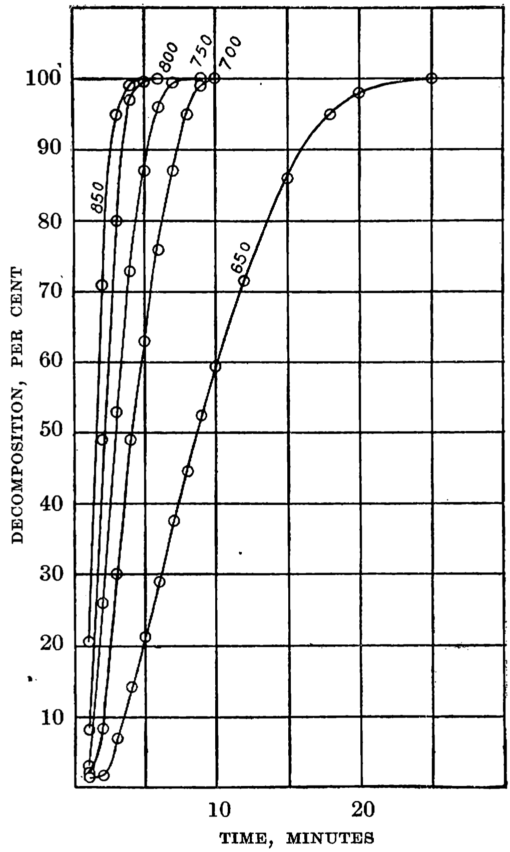

FIGURE 9.—Curve showing rate of decomposition, at different temperatures, ° C., of crude magnesite from C. S. Maltby, Porterville, Calif.

CHEWELAH DOLOMITE

The curves for the Chewelah dolomite, shown in Figure 10, differ somewhat from those for the Owens Lake dolomite. The sample of Chewelah dolomite came from the vicinity of the magnesite deposit and might be expected to contain some free magnesite. Its chemical analysis showed more magnesium carbonate than calcium carbonate. Therefore, it was not surprising to find that at a temperature between 650° and 700° C. this dolomite lost about 22 per cent of its total CO_2, and then came to equilibrium with the carbon dioxide atmosphere. Heating to 750°, but not above 900° C., caused further dissociation, and the system again came to rest when 60 per cent of the total CO_2 had been driven off. Heating to temperatures above 900° C. decomposed the remaining calcium carbonate. In other words, the decomposition was in three stages, as follows: First the carbon dioxide of the magnesite was liberated, then the carbon dioxide of the magnesium carbonate in the form of dolomite was liberated, and finally the carbon dioxide of the calcium carbonate in the dolomite or in free calcium carbonate was liberated.

This method of observing the thermal decomposition of dolomite may apparently be used as a method for determining the mineralogical character of the constituent carbonates. Microscopic study to check the results of our observations seems desirable.

WORK OF BOLE AND SHAW

Bole and Shaw,[4] in recent large-scale experiments, have heated dolomites in iron or clay retorts in order to maintain an atmosphere high in CO_2 and thus liberate the CO_2 combined with the magnesia, but not that combined with the lime of the dolomite. Free lime is known to be very detrimental to magnesian cements, whereas our work and that of the Dow Chemical Co. has proved that calcium carbonate in the cements is practically inert. Our work on the preparation of plastic magnesia from dolomites is described later in this bulletin.

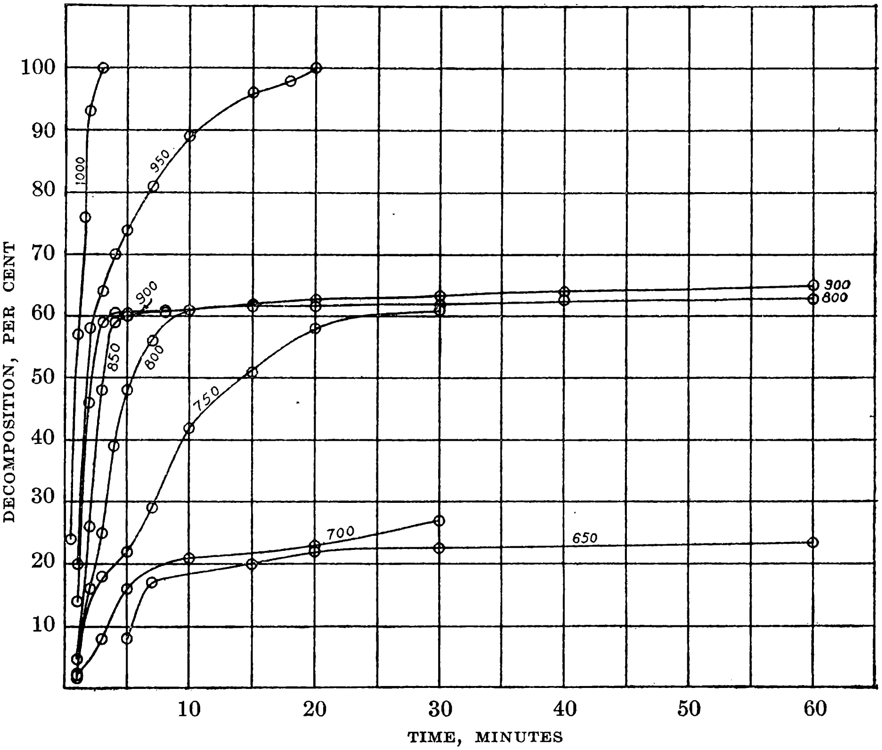

FIGURE 10.—Curve showing rate of decomposition, at different temperatures, ° C., of crude dolomite from Chewelah, Wash.

Bole and Shaw found that by heating dolomite to about 725° to 750° C. not more than 0.5 per cent free lime was formed, and the product made good magnesian or Sorel cements. They inferred that

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[4] Bole, G. A., and Shaw, J. B., The caustic calcination of dolomite and its use in Sorel cements: Jour. Am. Ceramic Soc., vol. 5, 1922, pp. 817–822.

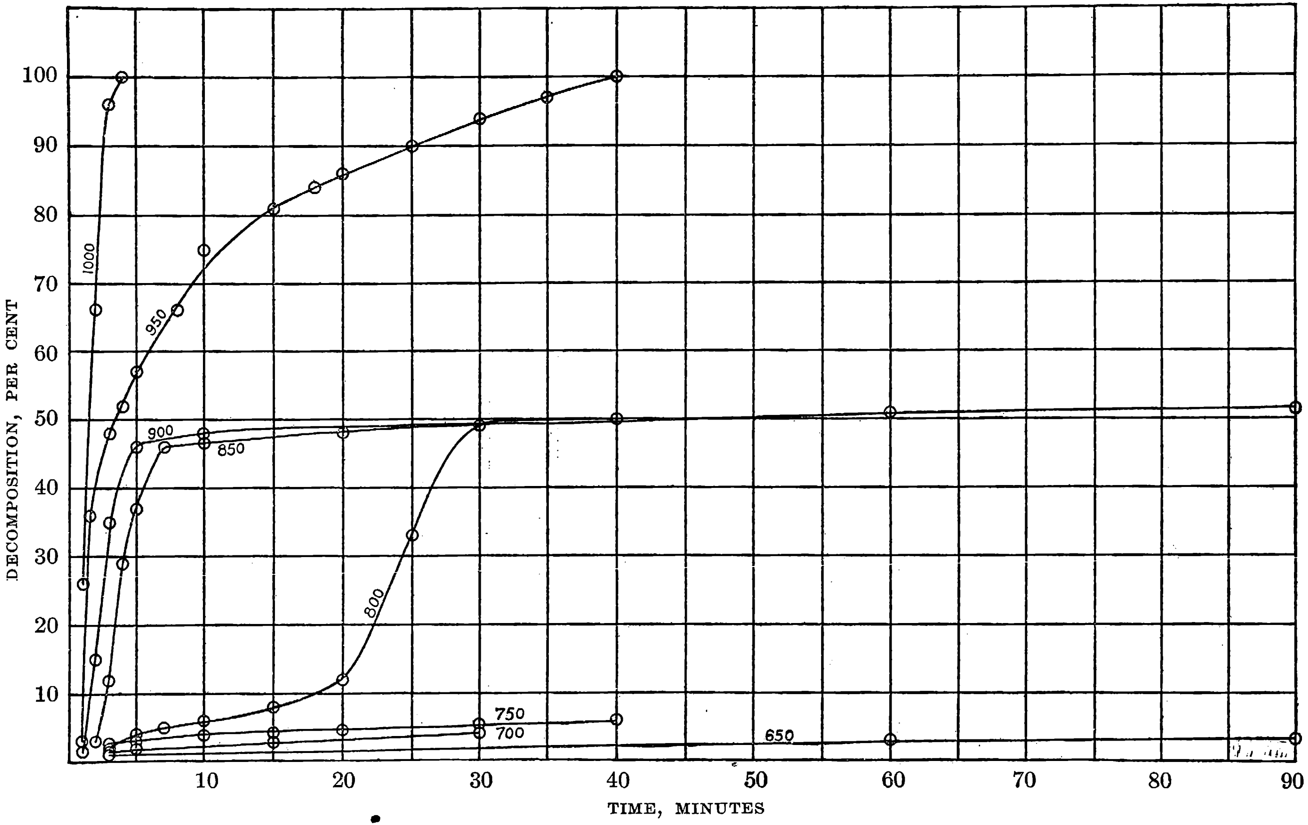


FIGURE 11.—Curve showing rate of decomposition, at different temperatures, ° C., of dolomite from California Alkali Co., Cartago, Calif.

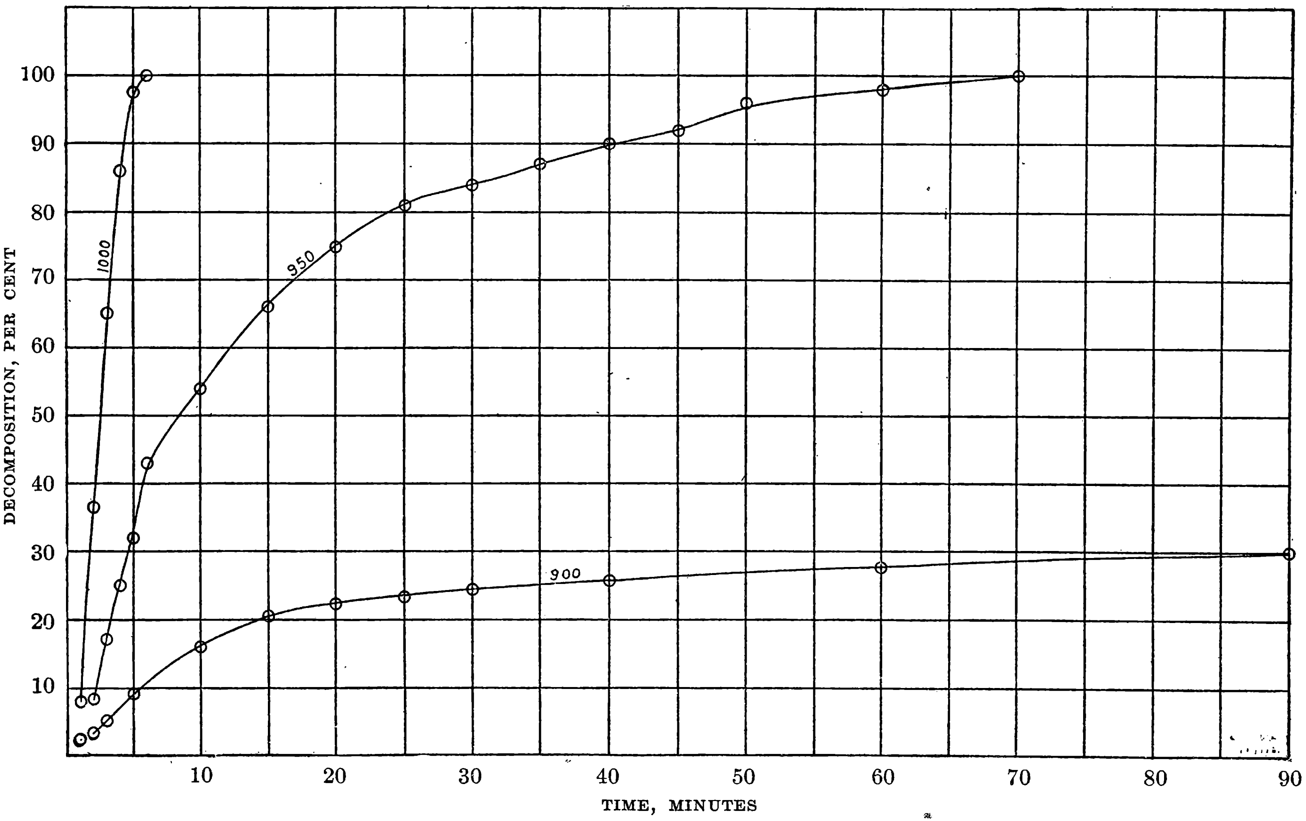


FIGURE 12.—Curve showing rate of decomposition, at different temperatures, ° C., of limestone from Pacific Portland Cement Co., Auburn, Calif.

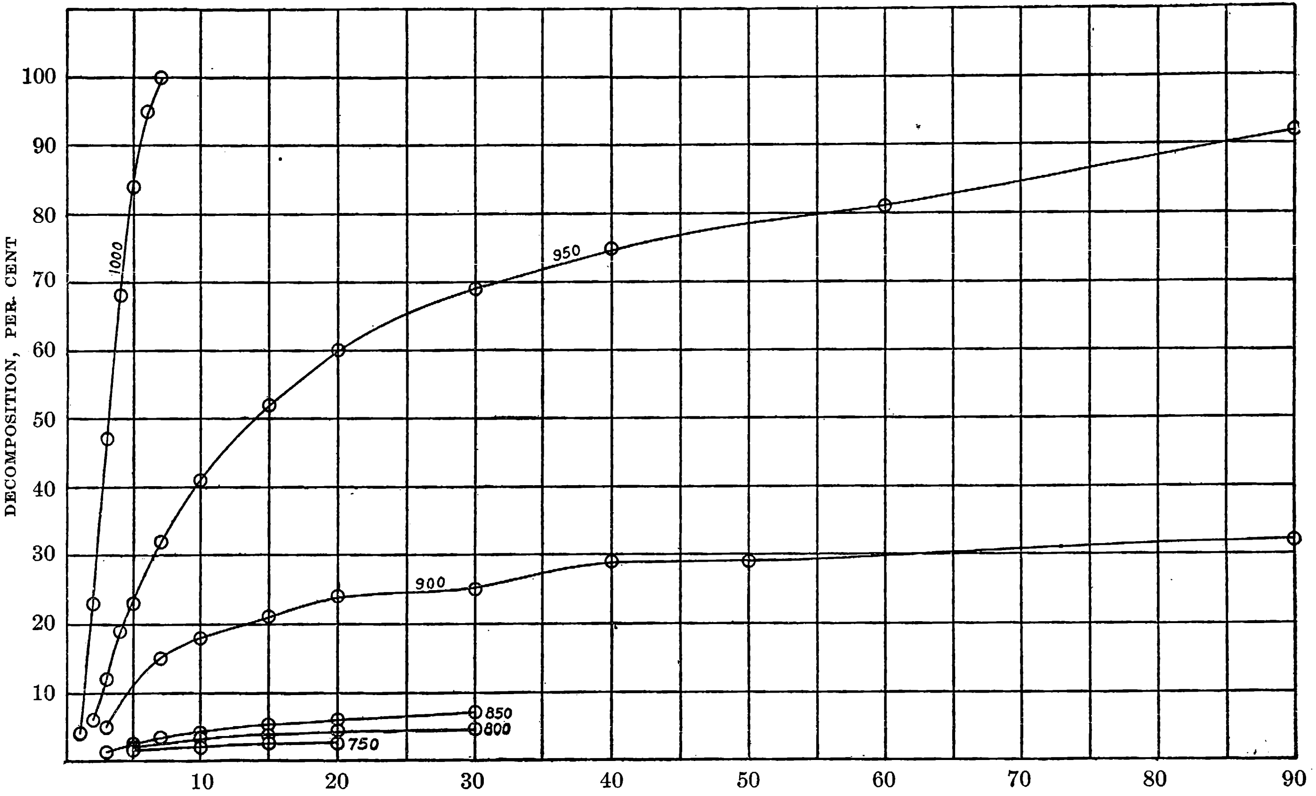


FIGURE 13.—Curve showing rate of decomposition, at different temperatures, °C., of calcite

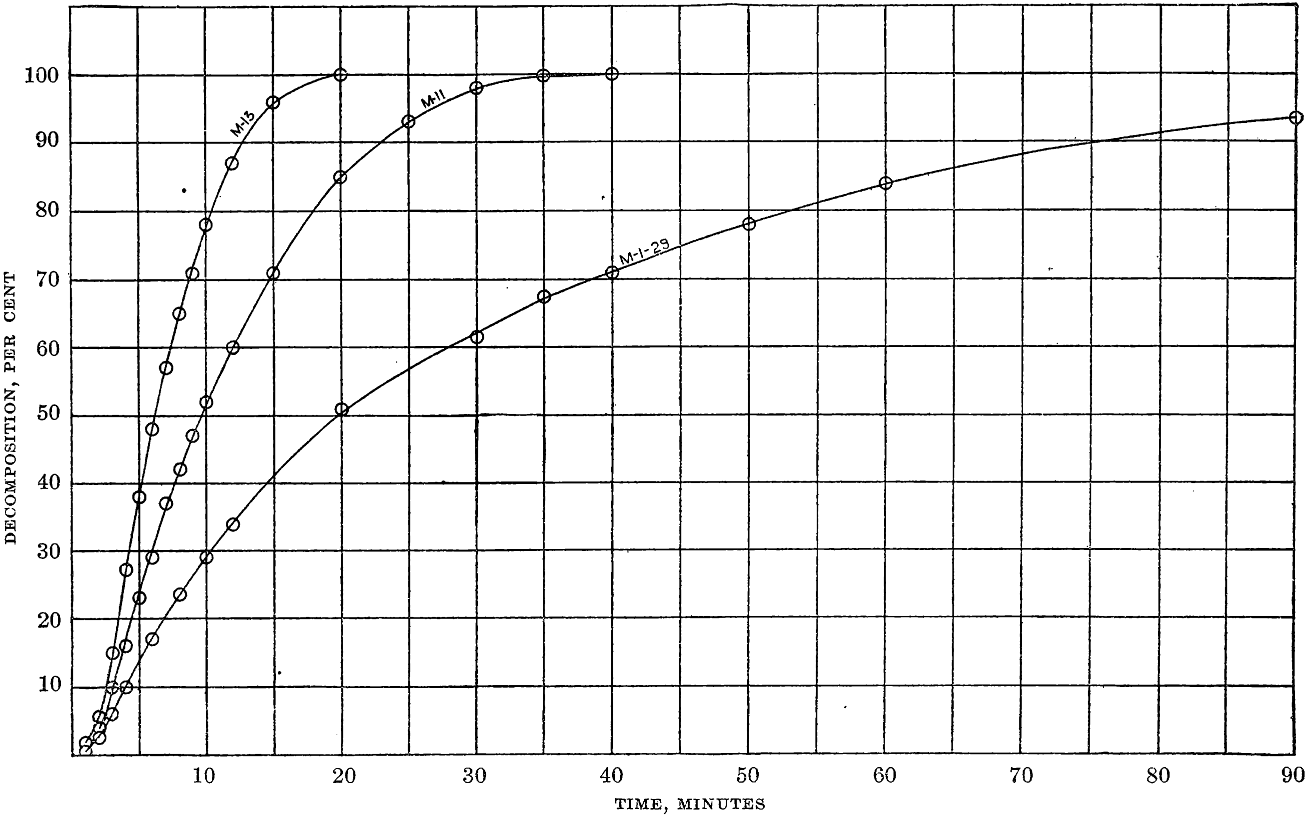


FIGURE 14.—Curve showing comparative rates of decomposition of crude magnesites M–13, M–11, and M–1–29 at 650° C.

some dolomites are solid solutions, others double salts, and still others a mixture of both types. High-silica dolomites were inferior. Evidently the Owens Lake dolomite can be regarded as a true double salt. The Chewelah dolomite, however, must have contained some magnesite in solid solution as well as free; the chemical analysis indicates only about 6.4 per cent more magnesite than is necessary for forming dolomite with the lime present, whereas 22 per cent of the total carbon dioxide was liberated at temperatures high enough to decompose the magnesium carbonate only. This work of Bole and Shaw, performed since our work was done, has helped greatly to explain the behavior of dolomites during calcination and to show the possibility of making magnesian cements from dolomite that had been properly calcined.

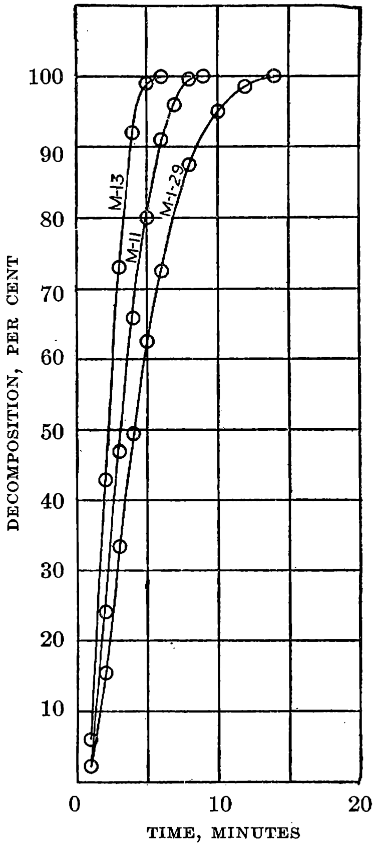


FIGURE 15.—Curve showing comparative rates of decomposition of crude magnesites M–13, M–11. and M–1–29 at 750° C.

EFFECT OF TEMPERATURE ON $CaCO_3$ DECOMPOSITION

Calcium carbonate is not decomposed much at temperatures below 900° C., if, as in this set of measurements, the pressure of CO_2 in contact with it is maintained at 1 atmosphere. Of course, the apparatus, from the way it was operated, contained only air at the beginning of an experiment and this air was quickly swept out by the carbon dioxide generated by the decomposition of the carbonates. As a result the curves for calcite at temperatures below 900° C. (Fig. 13) show that decomposition is slight. The decomposition of limestone and of calcite became vigorous at 950° C., as shown in Figures 12 and 13, and was rapid only at 1,000° C. A comparison of the two sets of curves for 950° C. shows that the limestone decomposed more rapidly than the calcite—as might be expected from the close packing of molecules in the crystalline calcite. One might therefore expect marble, which is crystalline, to decompose more slowly than limestone, which is cryptocrystalline.

PRACTICAL CONCLUSIONS

A magnesite containing calcium carbonate can be safely calcined at any temperature below 900° C. without liberation of free lime provided the pressure of carbon dioxide is maintained at 1 atmosphere. However, this requirement would necessitate retort heating to prevent the gases of combustion from mingling with and reducing the partial pressure of the carbon dioxide from decomposition.

As reference to Figure 19, p. 82, will show, the decomposition pressure of calcium carbonate approaches zero at about 700° C., although it is not very high at 750° C.; and it is quite possible to calcine magnesite at this temperature and still have enough partial pressure of carbon dioxide in the flue gases to prevent the formation of free lime through the decomposition of calcium carbonate. For dolomites, however, our work indicates that a calcination temperature of about 850° C. is necessary, and at this temperature the decomposition pressure of calcium carbonate is one-half atmosphere. This percentage of carbon dioxide is too high for maintenance in a direct-fired furnace, even if allowance be made for the carbon dioxide resulting from the decomposition of magnesium carbonate. Hence Bole and Shaw were correct in choosing a muffle furnace for the calcining of dolomite to make plastic magnesia. However, the velocity of decomposition of $CaCO_3$ at 850° C. is low, and less of it breaks up in an open furnace than might be anticipated.

It would seem, therefore, that a high content of calcium carbonate in a magnesite is no deterrent to the preparation of plastic magnesia with a low content of free lime; and that any lime present either as dolomite [$CaMg(CO_3)_2$] or calcium carbonate ($CaCO_3$) can be left in the calcine merely as inert material, if the burning temperature in any ordinary direct-fired furnace does not exceed 750° C. For some of the materials 800° or even 850° C. is a safe calcining temperature.

CALCINATION OF MAGNESITE FOR PLASTIC MAGNESIA

INTRODUCTION

Having determined that the best temperature range for the calcination of magnesite is 700 to 900° C., as far as rapidity of calcination is concerned, and knowing that this temperature range is frequently used in practice, we tested the effects of various temperatures and times of burning on the physical properties of the cements made from the resulting plastic magnesia. For magnesites high in lime the CO_2 content of the furnace atmosphere was varied.

In addition to obtaining the fundamental data in regard to the calcination of magnesite, we considered the type of furnace best suited for calcining magnesite on a large scale. The multiple-hearth roaster of the McDougal type had not yet been used for this purpose, and early in the investigation the suggestion was made that this furnace might be particularly suitable. Large-scale calcination tests were accordingly made in a laboratory-size Herreshoff furnace loaned for the purpose by the Pacific Foundry Co. Mr. E. J. Fowler of that company kindly made this furnace available. The tests yielded data not only on the effect of the time and temperature of calcination, but also on the rate at which heat was absorbed by a bed of magnesite. This information is essential in connection with furnace design.

As a preliminary to the tests with the Herreshoff furnace, experiments were made with various electrically heated laboratory furnaces in order to obtain preliminary information on the calcining behavior of the various types of magnesite that were to be studied.

PRESENT PRACTICE IN BURNING PLASTIC MAGNESIA

At present, magnesite for plastic magnesia is calcined in rotary cylindrical kilns similar to those used in making cement clinker, in vertical stack kilns resembling those used for burning lime, or in the Scott furnaces used chiefly for distilling quicksilver from its ores. The multiple-hearth McDougal-type roaster has not been used for this purpose, but certain theoretical considerations on heat transfer made us think that this type of furnace would be better adapted to burning magnesite for plastic magnesia than any of the furnaces now used commercially; for this reason much time was spent in collecting data from the laboratory-size Herreshoff furnace. On pages 55 to 58 further data on present practice are given for comparison.

ROTARY COMBUSTION-TUBE FURNACE

The first tests were with a silica tube (60 cm. long and 3 cm. inside diameter) placed inside a regular electrically heated combustion-tube furnace and rotated by suitable pulleys, reducing gear and motor as shown in Plate I, *B*; the whole apparatus was mounted on a unit baseboard. The speed of rotation ranged from 2 to 6 revolutions per minute and by changes in the slope of the furnace the capacity could be varied from 10 to 100 grams an hour. The heating element was 30 cm. long, and 5 cm. from each end, the temporature in the tests was 10° C. below that at the center of the element. The material remained in the hot zone for periods ranging up to 30 minutes, according to the rate at which it was being fed through. The feeding device used consisted of a tube and an old half-inch auger, the latter being run by pulleys attached to the speed-reducing gear (not shown in the figure).

This furnace proved useful for calcining small amounts of material in order to observe the rate of burning, color of calcine, and the chemical changes that took place. However, it did not produce calcine enough for any physical tests except those on setting time. The calcine had to be discharged into a closed receptacle to prevent contact with the moist air.

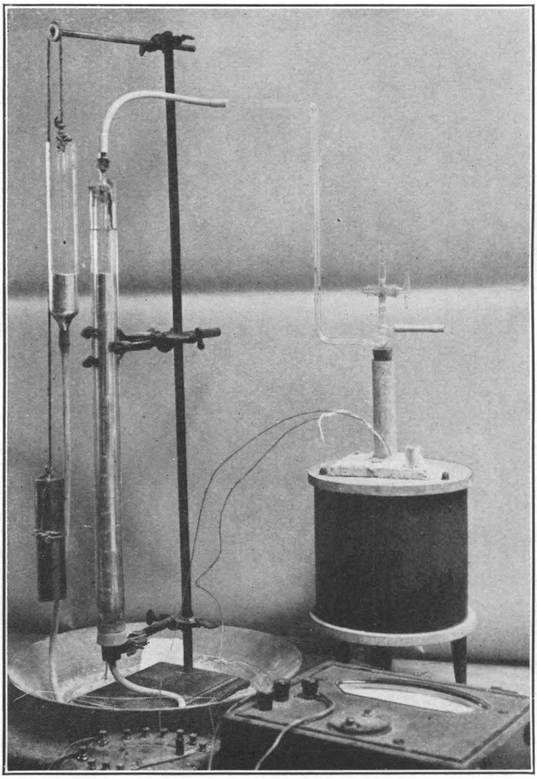
ELECTRIC MUFFLE CALCINER

A series of tests was also made in the electric muffle for calcining magnesite to plastic magnesia. As much as 10 pounds of magnesite can be calcined in the ordinary heavy-duty Hoskins type of muffle and thus enough plastic magnesia for more extended physical tests can be obtained. Our chief use of the muffle, however, was for further tests of the time of calcination necessary to decompose various sizes of magnesite at various temperatures. Samples removed at 10, 15, and 30 minute intervals showed that at all temperatures above 700° C. the calcination was practically complete in 10 minutes, except that half-inch pieces at 750° C. or lower gave evidence of not being completely calcined in that time.

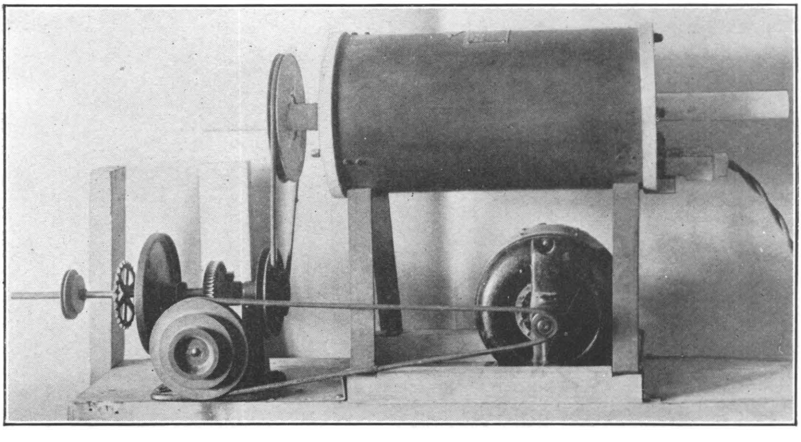
ELECTRICALLY HEATED ROTARY KILN

A rotary electric kiln, 5 feet long and 4 inches inside diameter, was constructed in the laboratory. The heating element was a nichrome winding buried in the lining. Current was supplied through collector rings on the outside of the furnace shell.

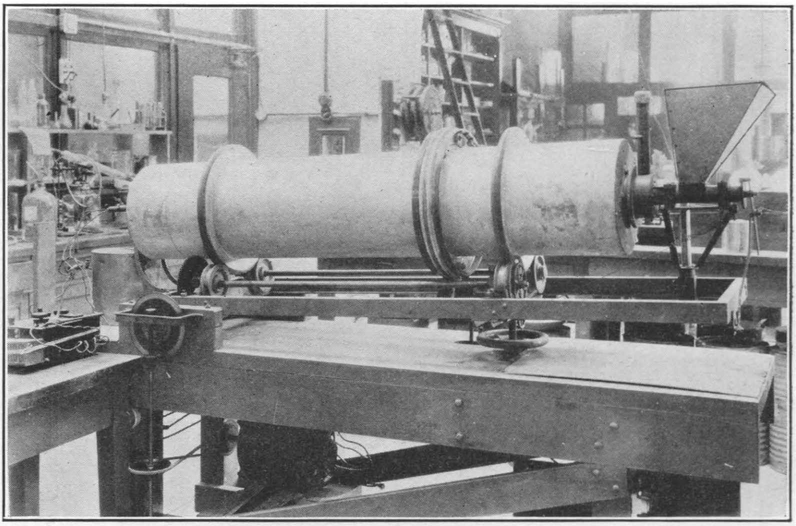
Plate II, *A*, shows the feeding arrangement and Plate II, *B*, the discharge end of the kiln. Alternating current at variable voltages was obtained from a transformer and voltage-regulator set shown in



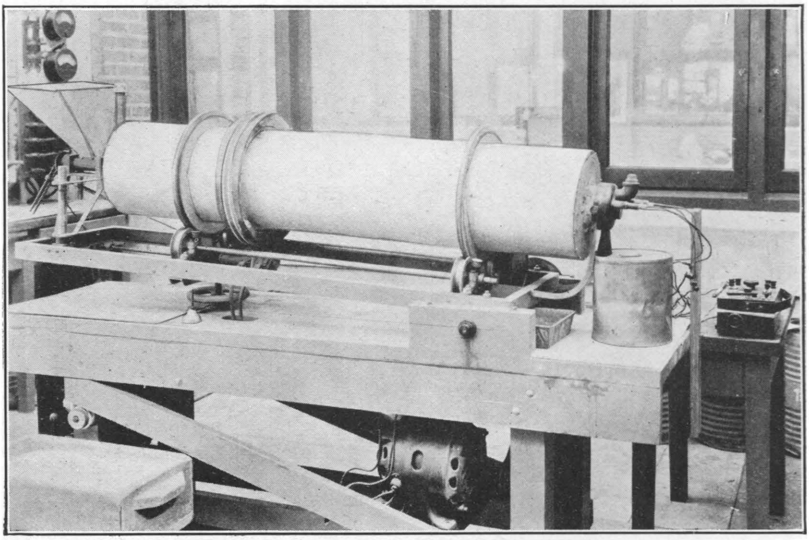
A. VICTOR MEYER APPARATUS FOR STUDYING COMPOSITION OF MAGNESITE



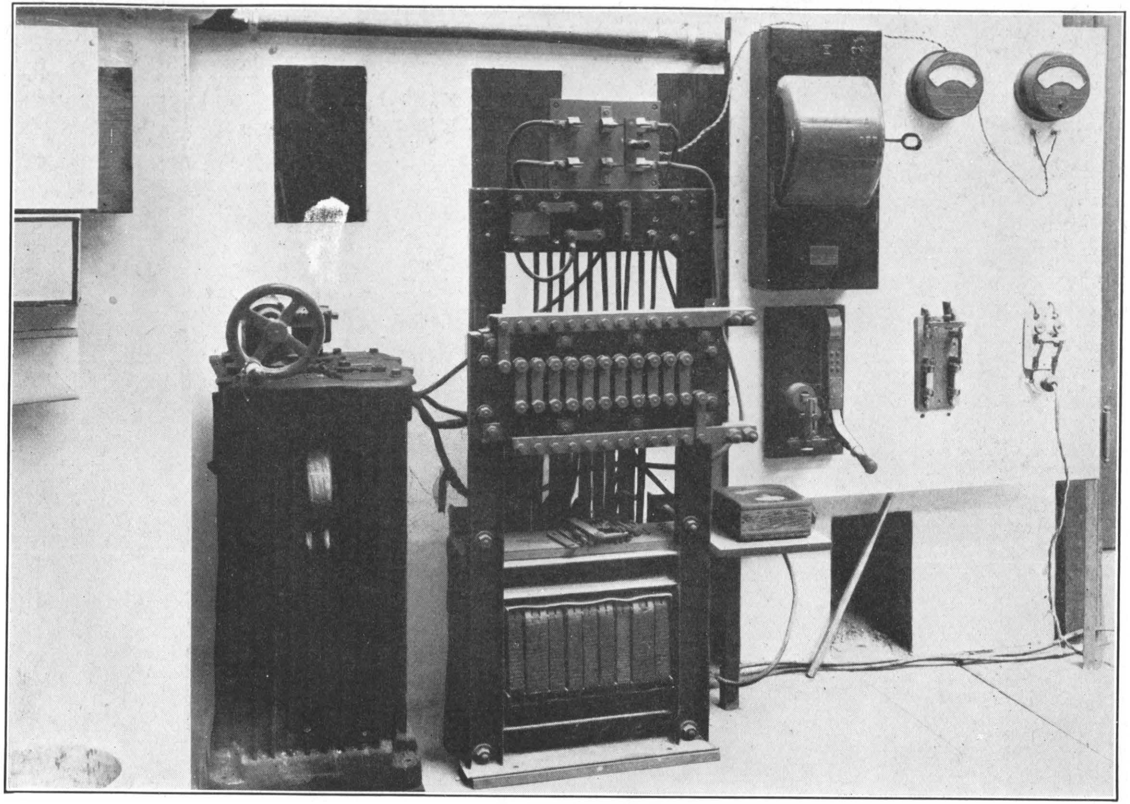
B. ROTARY COMBUSTION-TUBE FURNACE



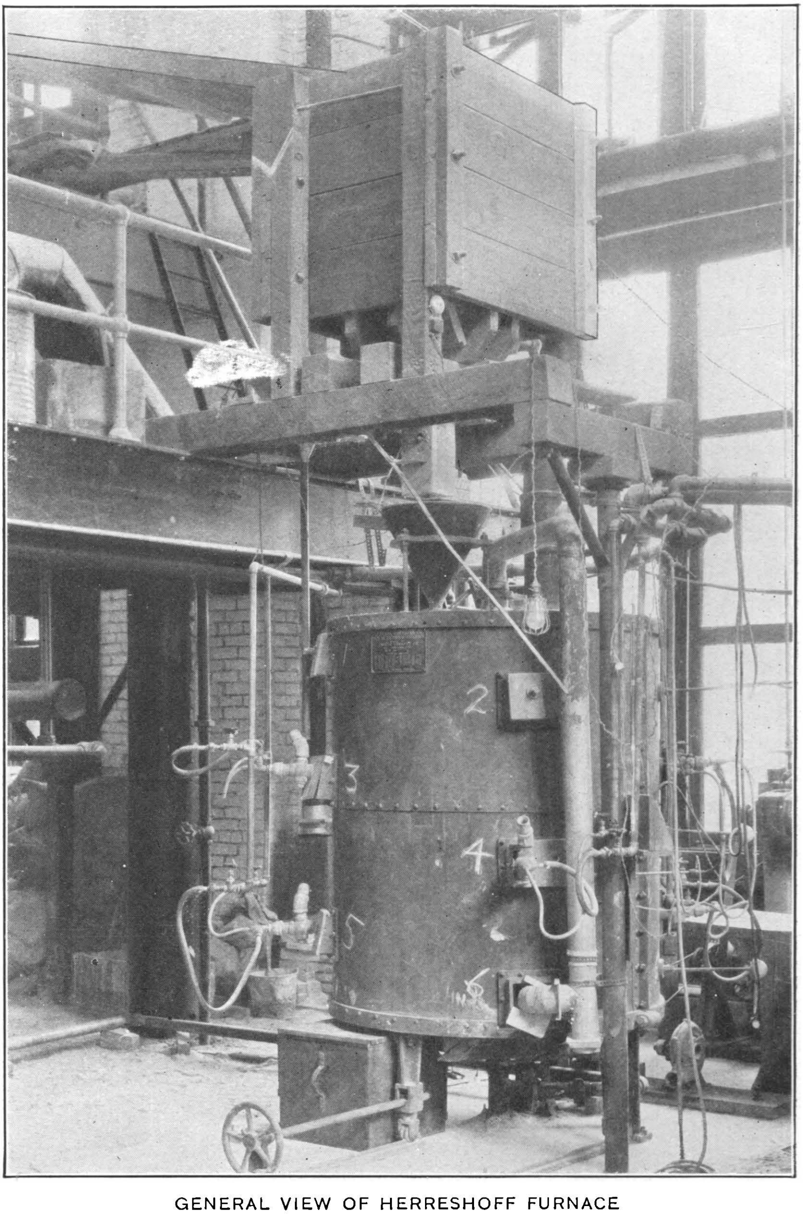
A. ELECTRICALLY HEATED ROTARY KILN, FEED HOPPER, ADJUSTABLE FEEDING MECHANISM, AND DRIVE



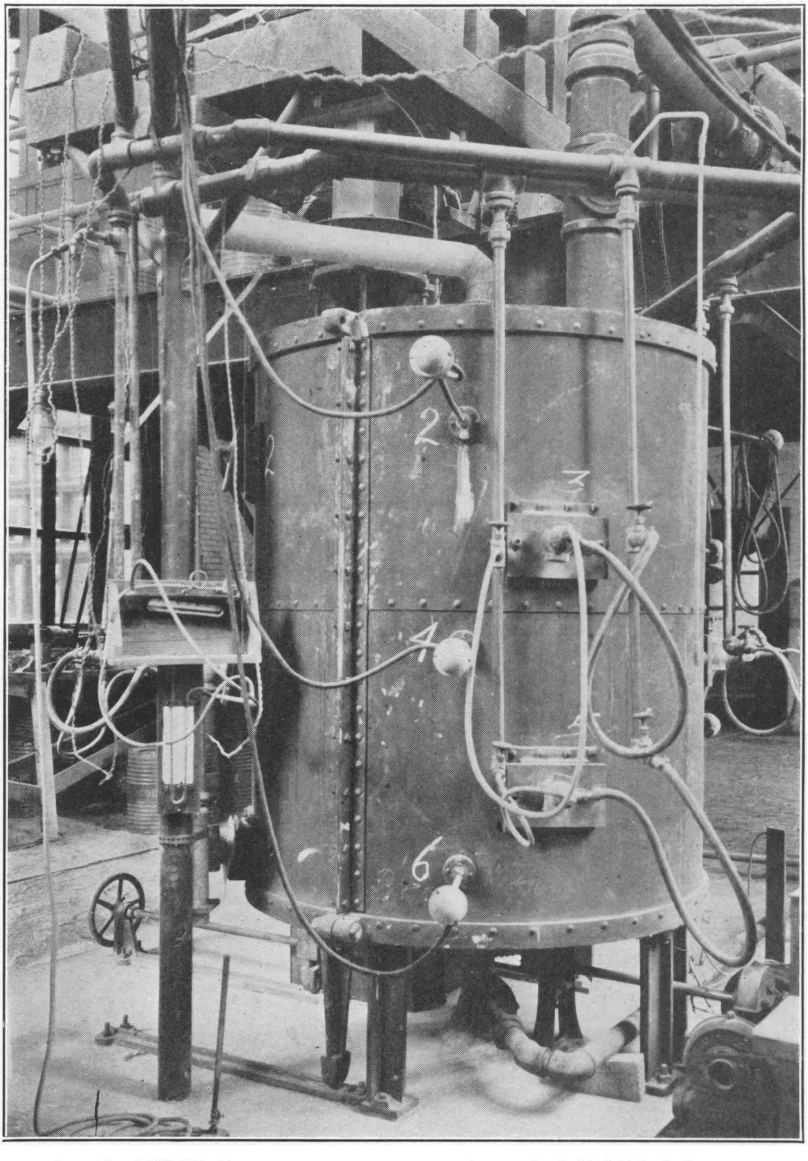
B. DISCHARGE AND THERMOCOUPLES FOR ELECTRICALLY HEATED ROTARY KILN



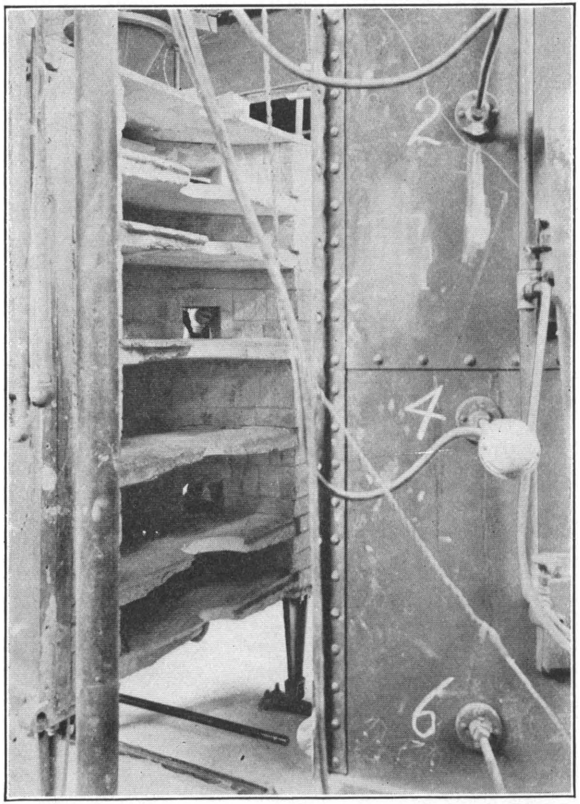
VOLTAGE REGULATOR, MULTIPLE-TAP TRANSFORMER, AND SWITCHBOARD FOR ELECTRICALLY HEATED ROTARY KILN



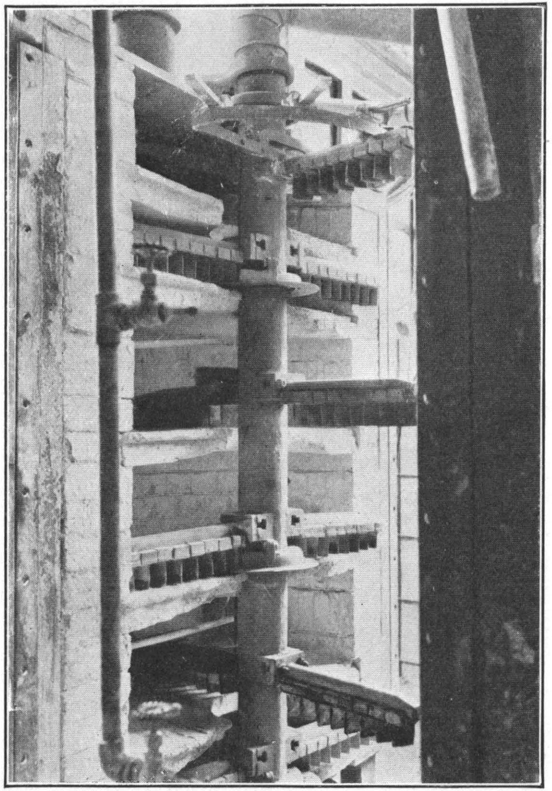
GENERAL VIEW OF HERRESHOFF FURNACE



HERRESHOFF FURNACE, DRIVING MECHANISM, GAS BURNERS, THERMOCOUPLES, AND GAUGES



A. HERRESHOFF FURNACE, SHOWING ONE HALF OF THE INTERIOR WITH TWO GAS BURNERS IN PLACE



B. OTHER HALF OF INTERIOR OF HERRESHOFF FURNACE, SHOWING COLUMN AND RABBLE ARMS

Plate III. Any desired rate of feed was obtainable through the variable-speed feed device. The whole furnace shell was set in a frame and its slope could be changed by manipulation of a hand wheel. An adjustable friction disk in the reducing gear from the driving motor permitted variations in speed.

With this furnace heated to a maximum of 1,000° C. because nichrome windings deteriorate rapidly at higher temperatures, magnesia could be produced continuously at the rate of about 2 kg. per hour. In most of the tests the furnace speed varied from 0.5 to 2 revolutions per minute. When a "steady state" had been established under a given set of operating conditions, the point of maximum temperature in the furnace was between the center and the discharge end. This location was determined in part by the heat losses from the ends of the furnace and in part by the absorption of heat reaching its maximum rate at the point where the magnesite was decomposing most rapidly. Although the maximum temperature of the furnace could be determined quite accurately, it was difficult to determine how long the material under treatment had been exposed to any given temperature. Furthermore, the conditions within the furnace, unless air was deliberately passed through it, corresponded closely to muffle heating because the furnace atmosphere was very high in carbon dioxide. Obviously, these conditions are quite different from those in a fuel-fired furnace where the concentration of carbon dioxide is not likely to exceed 30 per cent. This electric furnace was therefore used only for preliminary calcining tests, and the gas-fired Herreshoff furnace was used to obtain the final data.

GAS-FIRED HERRESHOFF FURNACE

As we used the smaller furnaces mainly for preliminary work, we give none of the data they yielded, but we call attention to the data collected from the operation of the laboratory-size gas-fired Herreshoff furnace loaned by the Pacific Foundry Co. This furnace had six hearths and was 5 feet 5 inches high by 36 inches internal diameter. It was operated for long periods of time on large lots of material in order to make heat measurements after thermal equilibrium had been attained. With these measurements it was possible to construct a heat balance and to compute the losses per unit area of exposed surface and per unit weight of products obtained. From this computation it was possible also to calculate the rate at which heat had been absorbed per unit surface of magnesite exposed. All these unit figures were then used for calculating data for a full-sized Herreshoff type of furnace and for comparison with furnaces of other types.

OBJECT OF RUNS

In all 29 runs were made. Their average duration was 11 hours. Run 28 was made to obtain as nearly as possible a perfect thermal steady state, the criterion of which is the attainment of a constant average temperature over the outside of the furnace. Attainment of this state required 16 hours. Because their conditions had been more favorable than the others, four of the tests were selected for calculating the heat balances given in the following pages.

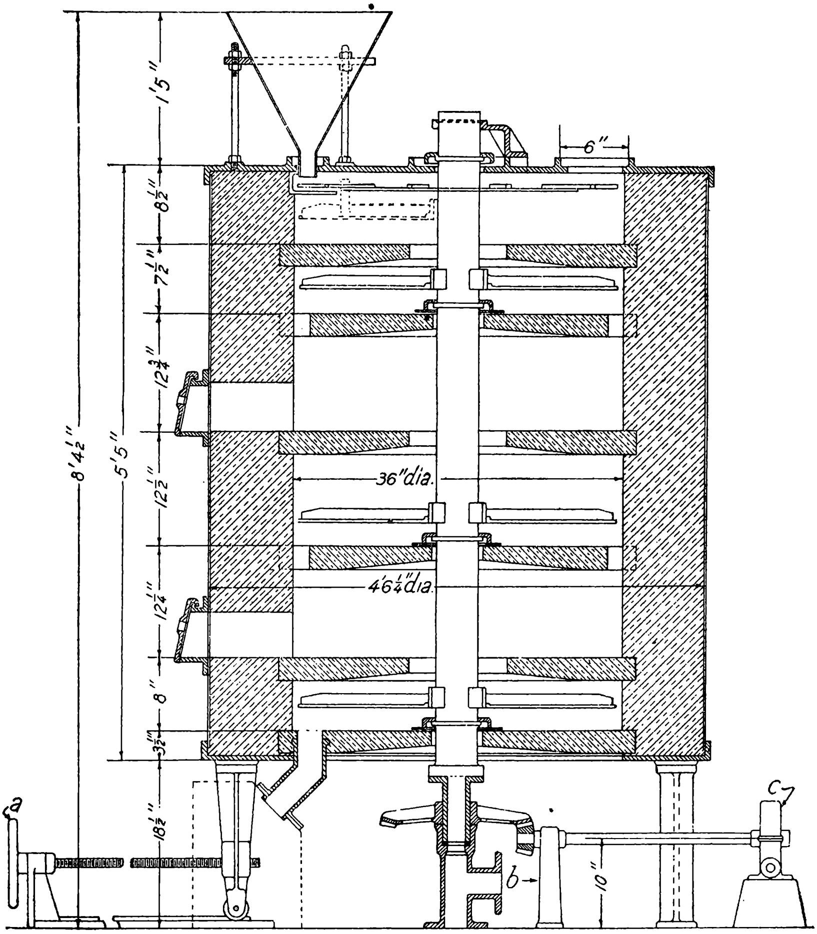


FIGURE 16.—Vertical section of the new Herreshoff pressure air-cooled type of furnace: *a*, 11-inch hand wheel; *b*, to blower; *c*, worm reduction set (rabble teeth not shown)

DESCRIPTION OF HERRESHOFF FURNACE

Figure 16 shows a vertical section of the Herreshoff furnace used. General views of the furnace are shown in Plates IV and V. The hearths were monolithic fire-clay shapes set into niches of the fire-brick lining of the furnace. Both the roof and the bottom or cooling hearth were relatively thinner than they would be in a commercial furnace and radiated an undue amount of heat. The walls were 9 inches thick and were not insulated; in consequence the loss of heat by convection and radiation to the outside atmosphere was considerable.

The rabble arms were cooled, air being supplied through the central rotating shaft by a small blower. The furnace shell and lining were divided vertically into halves—one half was mounted on rollers so that it could be moved far enough to allow the furnace to be cleaned and repaired. Around each hearth were suitable openings, shown both in Figure 16 and in Plate VI, *A* and *B*, which allowed gas burners and thermocouples to be inserted at any point.

A feed hopper permitted material to pile up on a little shelf beneath it and several feed scrapers on the rabble shaft swept off this material at each rotation of the shaft. Under the action of the rabbles shown in Plate VI, *B*, the material then passed to the center of the top hearth, dropped to the second, passed to the circumference of the second, dropped through suitable holes in the periphery to the third hearth, and so on.

Plate IV gives a general view of the furnace with all accessories installed for the tests. Plate V gives a closer view, showing the driving worm, gas burners, and thermocouples on one side of the furnace, also the pitot-tube gages and draft gages. Plate VI, *A*, gives a close-up view of one half of the interior of the furnace and shows the gas burners in place at two of the entrances of the furnace, as well as the thermocouples installed through suitable holes in hearths 2, 4, and 6. A view of the other half of the inside of the furnace, printed as Plate VI, *B*, shows the rabbles on the rabble arms that extend horizontally from the hollow verical drive-shaft and the feed scrapers above the rabble arms on the top hearth.

OPERATION OF THE FURNACE

A Wilson-Maeulin indicating pyrometer, graduated in the centigrade scale and connected by a multiple-pole switch to Wilson-Maeulin "pyrods" (iron-constantan thermocouples) was used. The accuracy of the thermocouples was determined to be of the order of 7° C. One pyrod was inserted on each hearth in the gas space above the rabble arms and, about midway between the fuel-gas ports, a 20-gage iron-constantan couple was placed in the stack opening. A pipe was provided by which hot air from the rabble shaft could be returned for use in combustion on hearth 6, and the temperature of this air was likewise measured. A small, 20-gage, exploring couple was used to determine the temperature of the calcine as it dropped from hearth 5 to hearth 6, and as it dropped into the final storage can. A thermocouple covered with asbestos to prevent loss of heat by radiation was used to measure the outside temperature of the furnace shell at various points, and special precautions were taken to measure the true temperature of the furnace jacket.

Pitot tubes measured the amounts of cooling air and of warm air entering the furnace. The fuel gas was passed through a large standard "100-light" gas meter loaned by the Pacific Gas & Electric Co. Subsequent checking showed the readings were accurate to within 1 per cent. The primary air for combustion was obtained, under high pressure, from the air lines of the building, and was released through a reducing valve.

Samples of both the fuel gas and the gases of combustion were taken frequently and analyzed in an Orsat apparatus. Oxygen and carbon monoxide were determined together. Samples of the magnesite and of the plastic magnesia were taken and all weights were kept carefully. The determination of ignition loss was made by weighing calcines as soon as they had cooled.

DATA ON RUN 28

The principal averages of temperatures, weights, and volumes during run 28, for which more complete data are obtained than for preceding runs, are given below. We have used English units throughout, in accordance with the usual American practice of reporting such data.

Average temperatures:		
Hearth 6	°Fahr.	615
Inside the furnace	do	1,168
Material dropping from hearth 5	do	[a] 1,375
Calcined material dropping from furnace	do	700
Temperatures:		
Outside air	do	64
Air from rabbles	do	726
Gas in upper stack	do	500
Gas in lower stack	do	754
Fuel gas	do	57
Pressure:		
Fuel gas	inches of water	9.3
Air to burners	pounds per square inch	8.0
Weight:		
Feed	pounds per minute	2.414
Calcine	do	0.93
CO_2 from calcining	do	.894
Flue dust	do	.576
Approximate time material in furnace	minutes	65
Draft	inches of water	.145
Fuel gas	cubic feet per minute	8.65
Rabble arms movement	revolutions per minute	.731
CO_2 in stack gases	per cent	13
Ignition loss of CO_2 in calcine	do	2.87
O_2+CO in stack gases	do	11.2
Total solid oxides lost in flue dust	do	26.6

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[a] 746° C.

TABLE 7.—*Record of temperatures in different hearths of the Herreshoff furnace.*[a]

Hearth No.	Temperature, ° F.		
	Maximum	Minimum	Average
1	625	605	615
2	1, 195	1, 160	1, 175
3	1, 420	1, 400	1, 410
4	1, 465	1, 405	1, 435
5	1, 490	1, 435	1, 455

[a] Material M–45, sized to pass an 8-mesh screen.

TABLE 8.—*Metallurgical balance sheet of Herreshoff furnace*

	Insoluble		Al_2O_3		Fe_2O_3		CaO		MgO		CO_2		H_2O		$MgCO_3$		$CaCO_3$		CaO left free		MgO left free	
	Per cent	Pounds	Per cent	Pounds	Per cent	Pounds	Per cent	Pounds	Per cent	Pounds	Per cent	Pounds	Per cent	Pounds	Per cent	Pounds	Per cent	Pounds	Per cent	Pounds	Per cent	Pounds
Run 28																						
Feed, 2.414 pounds per minute	4. 44	0. 1072	0. 79	0. 0191	0. 92	0. 0222	1. 77	0. 0427	43. 07	1. 0390	48. 48	1. 170	0. 53	0. 0128	90. 16	2. 1764	3. 16	0. 0763	0. 00		0. 00	
Calcines, 0.93 pound per minute (73.4 per cent solid oxides)	8. 36	. 0787	1. 52	. 0141	1. 76	. 0164	3. 38	. 0314	82. 04	. 7624	2. 87	. 027			3. 70	. 0344	2. 14	. 0199	2. 18	0. 0204	80. 27	0. 7460
Flue dust 0.576 pound per minute (26.6 per cent solid oxides)	4. 95	. 0285	. 89	. 0051	1. 02	. 0059	1. 98	. 0114	47. 9	. 2760	43. 3	. 249			79. 90	. 4601	3. 51	. 0202			9. 73	. 0560
Gases												. 894		. 0128								
Run 29																						
Feed, 5.69 pounds per minute	4. 44	0. 2528	0. 79	0. 0449	0. 92	0. 0523	1. 77	0. 1007	43. 07	2. 4511	48. 48	2. 7590	0. 53	0. 0302	90. 16	5. 1250	3. 16	0. 1798				
Calcines, 2.21 pounds per minute (69.1 per cent solid oxides)	7. 92	. 1745	1. 41	. 310	1. 63	. 0360	3. 13	0. 0692	76. 65	1. 6926	9. 26	. 207			13. 87	. 3065	4. 85	. 1071	0. 41	0. 0091	70. 0	1. 5461
Flue dust, 1.582 pounds per minute (30.9 per cent solid oxides)	4. 95	. 0782	. 89	. 0139	1. 02	. 0162	1. 98	. 0313	47. 9	. 758	43. 3	. 685			79. 90	1. 2640	3. 51	. 0556			9. 73	. 1538
Gases												1. 8670		. 0302								
Runs 3 and 4																						
Feed, 5.6 pounds per minute	4. 63	0. 255	0. 41	0. 0226	0. 94	0. 0518	2. 09	0. 115	44. 21	2. 432	47. 22	2. 60	0. 5	0. 0275	92. 9		3. 73					
Calcines, 2.09 pounds per minute (68.6 per cent solid oxides)	8. 39	. 1755	. 444	. 0156	1. 705	. 0357	3. 74	. 0782	80. 13	1. 675	5. 3	. 112				0. 0964		0. 140				1. 629
Flue dust, 1.58 pounds per minute (31.4 per cent solid oxides)	5. 04	. 0795	. 443	. 0070	1. 02	. 0161	2. 33	. 0368	47. 87	. 757	43. 3	. 6836				1. 25		. 0657				. 162
Gases												1. 804		. 0275								

FUEL GAS ANALYSES, RUN 28

Three samples of the fuel gas were taken during the run and sent to the Oakland laboratories of the Pacific Gas & Electric Co. for complete analysis. The reported average heating value of 570 B. t. u. per cubic foot refers to the gas under standard conditions and was calculated by the Oakland laboratories from the following analysis (Table 9) by a method that is claimed to approximate closely the actual calorimetric determinations:

TABLE 9.—*Analyses of fuel gas*

Compound	Per cent by volume	Weight per cubic foot at 57° F. and 9.3 inches water, pounds	Mean weight per cubic foot, pounds	Weight of air per cubic foot, pounds	Specific weight
Carbon dioxide (CO_2)	4.5	0.1195	0.00538		
Benzene (C_6H_6)	1.8	.2105	.00390		
Ethane (C_2H_4)	2.93	.0763	.00224		
Oxygen (C_2)	.77	.864	.00067		
Carbon monoxide (CO)	10.7	.0756	.00809		
Hydrogen (H_2)	47.2	.00543	.00256		
Methane (CH_4)	28.4	.0434	.01233		
Nitrogen (N_2)	3.7	.073	.00270		
			.03787	0.0782	0.483

From this we find the weight of gas used per minute was 0.3265 pound.

CHECKING CALORIFIC VALUES

To check the calorific value of the gas as given above, consider the data for heating values given in "Metallurgical Calculations" by Richards, corrected to the conditions obtaining during the test.

TABLE 10.—*Heat of combustion of components of fuel gas per cubic foot at 57° F. and 14.96 pounds pressure*

Compound	Lower value
H_2	284
CO	331
CH_4	917
C_2H_4	1,566
C_6H_6	3,765
B. t. u. of gas sample (water not condensed)	542
B. t. u. of gas sample (water condensed)	599

In our calculations we have used the lower value, 542 B. t. u., which is to be compared with the 570 B. t. u. used by the Pacific Gas & Electric Co. We have chosen the lower heating value because it represents the heat actually given to the furnace, all of the water passing up the stack as vapor. The calorimetrically obtained value of 570 given by the gas company is about halfway between the lower value of 542 and the higher of 599; and in view of the large hydrogen content of the gas—about 16.5 per cent by weight—it seems more logical to charge the furnace with the lower heating value of the fuel instead of the higher. Complete combustion of the fuel gas would give 0.485 pound of water per minute and produce a partial pressure of 1.377 pounds per square inch. At this pressure the latent heat of evaporation of water is 1,028 B. t. u. per pound; therefore the latent heat in the stack gases per minute is 0.485×1,028=499 B. t. u., or, referred to 1 cubic foot of gas, 57.7 B. t. u.

One pound of the above gas requires 10.6 pounds of air for complete combustion, and if no excess air were used the final gases, including the CO_2 from the magnesite, would have the following composition:

TABLE 11.—*Analysis of final gases, with no excess air*

Constituent	Pounds per minute	Per cent by volume, water free
Carbon dioxide (CO_2)	1.513	26.4
Nitrogen (N_2)	2.682	73.6
Water vapor (H_2O)	0.485	

The actual analysis of gases was as follows:

TABLE 12.—*Analysis of final gases, as sampled*

Constituent	Per cent by volume
Carbon dioxide (CO_2)	13.0
Oxygen and carbon monoxide (O_2+CO)	11.2
Nitrogen (N_2)	75.8

Computation shows that 1.03 volumes of air should be added to 1 volume of gas (Table 11) to give the actual analysis (Table 12).

With this value of 1.03 for excess air, the actual analysis by volume and by weight can be calculated:

TABLE 13.—*Calculated analysis of final gases*

Constituent	Per cent by volume	Per cent by weight
Carbon dioxide (CO_2)	13.0	18.75
Nitrogen (N_2)	76.3	70.00
Oxygen and carbon monoxide (O_2+CO)	10.7	11.25

The check between the observed O_2+CO (11.2) and the calculated one (10.7 per cent) is fairly good.

Calculating the excess air:

$$\text{Per cent excess air} = \frac{0.1125\times1.513}{.232\times.1875\times3.46} = 113.1 \text{ per cent.}$$

Weight of surplus air per minute, 3.91 pounds.
Total weight of air per minute, 7.37 pounds.

From the data given the total weight per minute of the stack gases and their thermal content can be tabulated.

TABLE 14.—*Total weight and heat content of stack gases*

Constituent	Weight per minute	B. t. u. per pound	Total B. t. u.
Carbon dioxide (CO_2)	1, 513	155. 7	235. 5
Moisture (H_2O)	. 500	323. 9	162
Nitrogen (N_2)	5. 682	172. 3	980
Oxygen (O_2)	. 907	150. 9	136. 8
Total	8. 60	----------	1, 514

The moisture content above includes the moisture in the raw feed and in the air for combustion.

HEAT IN FLUE DUST

The heat lost in the flue dust is tabulated in Table 15.

Table 15.—Heat lost in flue dust

Constituent	Weight per minute	B. t. u. per pound at 754–764°F	Total per cent
Iron oxide, alumina, and silica (Al_2O_3, Fe_2O_3, SiO_2)	0. 0395	154. 9	6. 1
Magnesia (MgO)	. 0560	181. 6	10. 2
Calcium carbonate ($CaCO_3$)	. 0202	171. 5	3. 5
Magnesium carbonate ($MgCO_3$)	. 4601	195. 7	90. 2
Total	. 5758	----------	100. 0

HEAT OF DECOMPOSITION

From the metallurgical balance in Table 8 we find that the amount of MgO produced per minute was 0.802 pound and of CaO, 0.0204 pound.

Heat of decomposition of $MgCO_3 = 0.802 \times 1{,}290 = 1{,}035$ B. t. u.; heat of decomposition of $CaCO_3 = 0.0204 \times 1{,}375 = 28$ B. t. u. Total for $MgCO_3$ and $CaCO_3$ 1,063 B. t. u.

HEAT IN CALCINE

The average temperature of the calcine discharged was 700° F. The calculated heat content is given in Table 16.

TABLE 16.—*Heat lost in calcine*

Constituent	Pound per minute	B. t. u. per pound at 700–64	Total B. t. u.
Iron oxide, alumina, and silica (Al_2O_3, Fe_2O_3, SiO_2)	0.1092	152.8	16.7
Magnesia (MgO)	.7460	180.8	134.9
Lime (CaO)	.0204	130.1	2.7
Magnesium carbonate ($MgCO_3$)	.0344	177.8	6.1
Calcium carbonate ($CaCO_3$)	.0199	156.0	3.1
Total	.9299		163.5

HEAT BALANCE

Summing the above factors, with a few that are self-evident, into a partial heat balance gives the following tabulation:

TABLE 17.—*Heat balance*

Item	Input, B. t. u.	Output	
		B. t. u.	Per cent of total
Heat in fuel gas (lower value)	4,710		
Heat of decomposition		1,063	22.6
Sensible heat in stack gases		1,514	32.1
Sensible heat in flue dust		100	2.1
Sensible heat in calcine		164	3.5
Heat of evaporation of water in feed		14	.3
Not accounted for in above items		1,855	39.4
Total	4,710	4,710	100.0

In Table 17 the heat not accounted for is that due to all other losses, such as conduction through and radiation from the walls, top, and bottom of the furnace. In the paragraph that follows an attempt is made to check these losses by calculation and comparison to see if the unaccounted-for loss is reasonably near other known furnace losses.

CALCULATION OF RADIATION AND CONVECTION LOSSES

Heat is dissipated from the outside of the furnace by radiation and by convection. The radiated heat is transmitted directly to objects according to the Stefan-Boltzman law; the heat lost by convection is carried in air currents induced by the warming of the air near the furnace. Some heat was lost in the pipe through which hot air from the central rabbling shaft returns to the bottom hearth for combustion. Two thermocouples placed near the two ends of this pipe gave readings of 748° F. and 549° F., respectively, so that a temperature drop of 200° F. is indicated. A Pilot tube in this pipe indicated that the flow of air was 3.73 pounds per minute; the consequent loss of heat was therefore 204 B. t. u. per minute. Subtracting this 204 B. t. u. from the 1,855 B. t. u. unaccounted for in

Table 17 (the heat balance) leaves 1,651 B. t. u. lost by radiation and convection from the furnace itself.

RADIATION LOSSES

The Stefan-Boltzman law states that the energy radiated by a hot body is proportional to the difference between the fourth powers of the absolute temperatures of the hot body and its surroundings. An emissivity coefficient is necessary in order to calculate the actual amount of heat radiated, and for conditions similar to those of this investigation this coefficient, E, equals about 0.65. We used this equation:

$$R=28.8\ E\left(\frac{T_h^4}{1,000}-\frac{T_c^4}{1,000}\right)=\text{B. t. u. per square foot per minute.}$$

This equation was used in calculating the radiation from all sections of the furnace, but we calculated the radiation from each hearth wall and the top of the furnace separately. The data are shown in Table 18.

TABLE 18.—*Radiation from furnace shell*

	T_h° F.	T_c° F.	Depth of zone, feet	Radiation, B. t. u. per minute
Hearth 1	164	64	0.7	14.0
Hearth 2	183	64	.75	18.7
Hearth 3	206	64	1.05	33.8
Hearth 4	214	64	1.1	37.8
Hearth 5	208	64	1.05	33.7
Hearth 6	182	64	.75	18.8
Top	243	68		49.2
Total				206.0

Some of the furnace dimensions not mentioned in Table 18 are as follows:

Height of cylindrical shell	feet	5.4
Circumference of shell	do	14.1
Area of cylindrical shell	square feet	72.2
Area of top	do	16.6

The sides of the furnace were lined with 9-inch standard fire brick; the top was of unlined cast iron; the bottom was a 2-inch fire-clay tile. Deducting from 1,651 B. t. u., the radiation loss, 206 B. t. u., of the furnace shell leaves 1,445 B. t. u. to be accounted for by convection.

CONVECTION LOSSES

Three convection formulas have been used for estimating this loss. The formula of Lorenz,[5] which has been favorably noted by Lang-

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[5] Lorenz, L., Über das Leitungsvermögen der Metalle fur Wärme und Electricität: Pogg. Ann., vol. 13, 1881, p. 583.

muir,[6] given in the original in C. G. S. units but converted by us for B. t. u., is derived from a consideration of the amount of heat carried off by air set in motion by being warmed at a heated surface. The formula is—

$$C = 0.00009868\ H^{-0.25}(T_h - T_c)^{1.25}$$

Where

C = Convection loss.
H = Height of body in centimeters.
T_h = Temperature of hot body.
T_c = Temperature of surroundings.

By using this formula with the data of run 28 and reducing them to the average temperature of the furnace shell, a convection loss of 94 B. t. u. per minute was obtained. If the whole shell heated to the temperature of the hottest spot, the calculation gives only 110 B. t. u. per minute.

The formula of Langmuir, noted above, is based on the consideration that convection losses are really to be considered conduction through a layer of still air next to the hot surface and his mean value for the thickness of this layer is 0.45 cm. for vertical surfaces and 0.41 cm. for horizontal. This results in 71 B. t. u. per minute convected from the top and 134 B. t. u. from the sides—a total of 205 B. t. u. per minute.

Snyder[7] uses a formula developed empirically by J. W. Richards which is given in the earlier editions of his "Metallurgical Calculations," and is embodied in a set of curves that gives the combined radiation and convection losses. For the present purpose the computation gives a loss per minute of 500 B. t. u. from the sides and 180 B. t. u. from the top of the furnace, making a total combined radiation and convection loss of 680 B. t. u. per minute. By use of Snyder's curves, and after our figure of 206 B. t. u. radiation loss is subtracted, a convection loss of 474 B. t. u. per minute still exists. To this may be added another 65 B. t. u. convected and about 50 B. t. u. radiated per minute through the bottom of the furnace; since Snyder's curves are derived from a great deal of practical data, his loss computations are used rather than those of Lorenz or Langmuir. The total radiated and convected heat computed by Snyder is 795 B. t. u. per minute, which subtracted from 1,651 B. t. u. (the amount of heat for which we are trying to account) leaves 856 B. t. u. per minute still unaccounted for.

From a total of 4,710 B. t. u. entering the furnace this loss of 856 B. t. u. per minute represents nearly all the errors in the work; how-

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[6] Langmuir, Irving, Convection and radiation of heat: Trans. Am. Electrochem. Soc., vol. 23, 1913, p. 299–330.

[7] Snyder, F. T., The flow of heat through furnace walls: Trans. Am. Electrochem. Soc., vol. 18, 1910, p. 239.

ever, some extra heat is lost by radiation and convection of heat and by passage of gas currents out through the ports, which are not as well insulated as the remainder of the furnace walls, some heat is also lost at sharp corners of the furnace. In view of all the averaging that had to be done in collecting figures for this calculation, and all the possible sources of error, the agreement in the above computations is considered very good, since they account for 81.8 per cent of the heat entering the furnace.

HEAT TRANSFER NUMBERS, RUN 28

The furnace can be divided into three zones—one of preheating of the charge, one of calcination, and one of cooling the charge by the incoming gases or by radiation and convection, although the defining of the boundaries of these zones is necessarily somewhat arbitrary. Then a heat balance can be drawn for each zone and the amount of heat that has been transferred from the combustion gases to the charge, to the walls, or to the rabble arms, per unit of area per unit time can be calculated.

The original material had a total volatile content (ignition loss) of 49.01 per cent. By comparing the ignition-loss determinations of samples from the various hearths during calcination it is possible to judge on which hearths most of the calcination took place. Table 19 gives these figures, and shows that there was little calcination on hearth 2; most of it was on hearths 3, 4, and 5. We have therefore assumed hearths 1 and 2 to be the preheating, hearths 3, 4, and 5 the calcining, and hearth 6 the cooling zone.

TABLE 19.—*Ignition loss on different hearths of furnace*

Hearth No.	Temperature, ° F.	Ignition loss, per cent
2	1,148	45.8
3	1,409	32.3
4	1,427	6.65
5	1,454	1.70
6	1,022	2.35

From the above table the heat balances in the different sections of the furnace can be computed. These balances are given in Tables 20, 21, and 22.

TABLE 20.—*Heat balance in preheating section, hearths 1 and 2*

Input			Output		
Item No.	Item	B. t. u.	Item No.	Item	B. t. u.
9	Heat in gases from hearth 3	3,007.0	1	Heat in stack gases	1,508.0
			2	Heat in flue dust	100.0
			3	Decomposition heat of flue dust	77.0
			4	Evaporation of water	14.0
			5	Proportionate heat of decomposition	124.0
			6	Warming return air	98.0
			7	To solids, 64°–1,110° F	551.0
			8	Proportionate radiation and convection losses	349.0
			8a	Unaccounted for	186.0
		3,007.0			3,007.0

TABLE 21.—*Heat balance in calcining section, hearths 3, 4, and 5*

Input			Output		
Item No.	Item	B. t. u.	Item No.	Item	B. t. u.
	Fuel gas	4,710.0	9	Heat in gases	3,007.0
7	Solids	551.0	10	Proportionate radiation and convection losses	1,330.0
15	Hot air	865.0	11	Warming return air	345.0
			12	Proportionate heat of decomposition	862.0
			13	Raising CO_2 evolved from 1,110 to 1,300° F	47.0
			14	Heat in calcine at 1,375°	335.0
			------	Unaccounted for (excess)	200.0
		6,126.0			6,126.0

TABLE 22.—*Heat balance in cooling section, hearth 6*

Input			Output		
Item No.	Item	B. t. u.	Item No.	Item	B. t. u.
6, 11, 18	Heat in 3.73 pounds air	492.0	15	Hot air	865.0
14	Heat in calcine	335.3	16	Heat in calcine, 700°–764°	163.5
14a	Unaccounted for	599.0	17	Proportionate radiation and convection losses	348.0
			18	Warming return air	49.0
		1,426.0			1,426.0

The heat balances in Tables 20, 21, and 22 are only approximations because some of the values were obtained by distributing the total for the furnace among the parts of the furnace in reasonable proportions. Item 5 is the heat of decomposition in the heating zone; it is taken from the metallurgical balance sheet and from the data of Table 19. Items 8, 10, and 17 had to be proportioned according to the proportions used in calculating the heat loss by convection and by radiation of the whole furnace, which are: Section 1, 20 per cent; section 2, 70 per cent; and section 3, 10 per cent. These same percentages were used in proportioning items 6, 11, and 18.

Item 7 required the postulation of a temperature at which active decomposition began—in this instance, 1,110° F. (594° C.). This figure is somewhat higher than the figure 575° C. given on page 12, but was deduced by rough proportion from the time, 20 minutes, required for material to reach the discharge of hearth 2, when 12 per cent of the material was decomposed. We assumed that decomposition took place during the last half of the time of travel over hearth 2.

By use of the above heat balances the heat transfer numbers, which may be defined as the number of thermal units per square foot per hour per degree Fahrenheit of temperature difference between the material and the hot gases, can be calculated.

HEATING ZONE

For the heating zone we calculate the following heat balance:

Deviation of heat transfer number

Portion of heat of decomposition in heating zone	B. t. u. per minute	124
Heating of material from 64° to 1,110° F	do	551
Evaporation of water in charge	do	14
Total heat transferred from gas to solids	do	689
Average gas temperature (average of hearths 2 and 3 and exit gases)	° Fahr	1, 023
Average temperature of material $\frac{66+1110}{2}$	do	587
Mean temperature between gas and material (difference)	do	436
Hearth area	square feet	12
Transfer number $\frac{689}{436\times12}\times60$		7. 9

To this must be added the heat transferred to the stack dust, which makes the total heat transferred 866 B. t. u.; and the resulting heat-transfer number in the preheating zone is 9.9 B. t. u. per square foot of hearth area per degree Fahrenheit difference in temperature per hour.

CALCINING ZONE

Attention is called to the fact that the heat in the calcines entering the calcining zone is 551 B. t. u., whereas the heat in the calcines leaving the zone is only 335 B. t. u.; the difference, 216 B. t. u., is heat derived from the material itself, and should not enter the transfer number. The total heat work done in this zone can be calculated to be 862 B. t. u., heat of decomposition plus the 47 B. t. u. necessary to heat the evolved CO_2 from 1,110° F., the decomposition temperature, to 1,300° F., the temperature of the gases. Deducting the 216 B. t. u. above noted from this sum (909 B. t. u.), gives the net, 693 B. t. u. The data for the heat transfer number are then as follows:

Derivation of heat transfer number

Heat transferred from gas to material	B. t. u. per minute	693
Average temperature of hearths 3, 4, and 5	°Fahr	1,433
Temperature of material dropping from hearth 5	do	1,375
Average temperature of material, $\frac{1375+1110}{2}$	do	1,243
Mean temperature difference between gas and material	do	190
Area of hearths 3, 4, and 5	square feet	18.5
Transfer number, $\frac{695}{190\times 18.5}\times 60$		11.85

This transfer number is somewhat higher than that obtained for the preheating zone, but this might be expected because of the greater agitation of the gas currents, caused by burning the fuel directly over the material, and because of direct radiation from the flame to the material near it.

These transfer numbers are of interest in comparison with those obtained in the utilization of waste heat boilers, which range from 3.5 to 5.5.[8]

COOLING ZONE

As heat passes outward through furnace walls, transfer numbers can be calculated to show how the flow of heat from the inside of the furnace to the outside compares with the rate of flow into the material being calcined. Table 23 summarizes the essential data.

TABLE 23.—*Rates of heat transfer in three zones of furnace*

Item	Preheating zone	Calcining zone	Cooling zone
Average zone temperature ° Fahr	1,023	1,433	914
Outside temperature do	64	64	64
Temperature difference do	959	1,369	850
Outside area square feet	36	42.8	26.6
Radiation and convection B. t. u. per minute	535	738	348
Transfer number	0.93	0.76	0.92

These figures are reasonably concordant. One would expect higher transfer numbers in the top and bottom zones because both the roof and bottom are thin. The figure for the center of the calcining section is probably good for the condition of a 9-inch fire-brick lining.

For the rabble arms, which are cooled by air, a similar calculation showed the average temperature difference between inside and

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[8] Pratt, A. D., The utilization of waste heat for steam-generating purposes: Trans. Am. Soc. Mech. Eng., vol. 38, 1916, p. 599.

outside of the arms was 760° F. As the heat transfer through the arms was 656 B. t. u. per minute and the total cross-sectional area through which this transfer took place was approximately 15.45 square feet, the transfer number was 3.35.

OTHER HEAT TRANSFER TESTS

Since this work was done, one of us, in cooperation with the Pacific Foundry Co., has tested the heat transfer in a 7-foot rabble arm mounted in a special testing furnace. The transfer number ranged from 3.8, when the mass velocity (pounds per second per square foot of cross section of the path of flow) of the air was 1, to 10 when the mass velocity was 5. In practice, the usual mass velocity of the air is about 2, which would make the transfer number about 5.8. This figure is for a clean rabble arm and in practice it will be reduced about 50 per cent by the accumulation of dust on the arm.

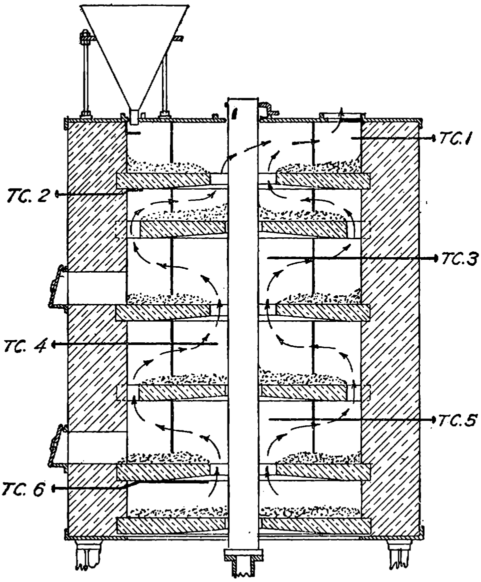

FIGURE 17.—Imaginary cylinders and course of gases through the furnace. Numbers show position of thermocouples

VELOCITIES OF GASES

Gas velocities are of much importance to the furnace designer. We therefore give a rough approximation of the velocities in various parts of the furnace during run 28. As Figure 17 shows, we are interested in the velocities of the gases through the various ports and over the surfaces of the charge being calcined; therefore, we have imagined cylinders concentric with the furnace walls and midway between them and the central ports and have calculated the velocities of the gases past these cylinders. The gas velocities are tabulated in Table 24.

TABLE 24.—*Gas velocities in Herreshoff furnace, run 28*

	Feet per minute
Through ports:	
From hearth 4 to 3	1,024
From hearth 5 to 4	780
Through imaginary cylinder:	
Hearth 3	161
Hearth 4	164
Hearth 5	166
Calcining zone	164
Hearth 1	143
Hearth 2	404
Preheating zone	274

DATA ON RUN 29 AND RUNS 3 AND 4

Run 29 followed run 28 immediately, so that the data are probably representative of the conditions that exist when a thermal steady state has been approached. The feed and the rate of firing, however, were increased to see how much the capacity could be increased. Runs 3 and 4 were made under parallel conditions; this resulted in some unburned gases in the combustion gases and rendered the calculation of the heat balances more difficult and less reliable because assumptions had to be made. However, the general results compare favorably with those of run 28, and are of interest. The chief data for run 29, with those of runs 3 and 4 given for comparison, appear in Table 25.

TABLE 25.—*Principal data of runs 3, 4, and 29*

		Run 29	Runs 3 and 4
Average temperatures:			
Hearth 1	° Fahr.	518	562
Hearth 2	do.	1,154	1,156
Hearth 3	do.	1,348	1,460
Hearth 4	do.	1,450	1,572
Hearth 5	do.	1,530	1,602
Furnace	do.	1,153	1,235
Calcine leaving hearth 5	do.	1,172	----------
Calcine leaving hearth 6	do.	906	----------
Room	do.	64	64
Air from rabble arms	do.	710	778
Gases in lower stack	do.	712	700
Flow of fuel gas	cubic feet per minute	18.65	16
Pressure of fuel gas	inches of water	3.9	6.23
Temperature of fuel gas	°Fahr.	57	----------
Pressure of air to burners	pounds per square inch	15.7	13
Draft	inches of water	0.233	1.645
Speed of rabble arms	r. p. m.	1.645	----------
Approximate time of material in furnace	minutes	30	30
Weight of feed	pounds per minute	5.69	5.5
Weight of calcine	do.	2.21	2.09
Ignition loss determination of calcine	per cent CO_2	9.26	5.3
CO_2 in stack gases	per cent	16	19.95
O_2+CO in stack gases	do.	10.4	8.37
Weight of CO_2 from material	pounds per minute	1.867	1.804
Weight of flue dust	do.	1.582	1.58
Proportion of total oxides (solid) lost in flue dust	per cent	30.9	31.4

Use of the same type of calculations as in run 28 gave the heat balances in Tables 26 and 27:

TABLE 26.—*Heat balance of run 29*

Item	Input, B. t. u.	Output, B. t. u.	Per cent of total
Heat in gas burned (71 per cent of methane unburned)	7,100		
Heat of decomposition		2,195	30.9
Sensible heat in stack gas		2,091	29.4
Sensible heat in flue dust		250	3.5
Sensible heat in calcine		496	7.0
Radiation and convection loss, by difference		2,068	29.2
	7,100	7,100	100.0

Calculating the transfer numbers in the various parts of the furnace for run 29 gives the following results:

Heat transfer number in preheating zone	B. t. u.	25.2
Heat transfer number in calcining zone	do	12.9

Gas velocities in the furnace for run 29 are somewhat similar to those for run 28—1,474 feet per minute in the ports between hearths 4 and 3, 1,160 feet per minute in the ports from hearths 5 to 4, 259 feet per minute through the imaginary cylinders in the calcining zone, and 386 feet per minute through the imaginary cylinders in the preheating zone.

TABLE 27.—*Heat balance of runs 3 and 4*

Item	Input, B. t. u.	Output, B. t. u.	Per cent of total
Heat in fuel gas burned	6,740		
Heat of decomposition		2,310	34.3
Sensible heat in stack gases		1,631	24.2
Sensible heat in stack dust		275	4.1
Sensible heat in calcine		520	7.7
Radiation losses (by difference)		2,004	29.7
	6,740	6,740	100.0

HEAT TRANSFER

From runs 3 and 4 data are available for calculating the transfer number of the preheating zone only. The result is 23.7 B. t. u., which compares well with the corresponding figure for run 29. In these two runs, an excess of air was avoided and the combustible in the gases passing up the stack was 29 per cent in run 29 and 22.3 per cent in runs 3 and 4. However, the thermal efficiency of the fuel that was burned was 30.9 per cent in run 29, and 34.3 per cent in runs 3 and 4; whereas in run 28, where no unburned fuel went up the flue, the thermal efficiency was only 22.6 per cent. Distinction should be made between the capacity of this furnace as a calciner and as a fuel burner. In commercial practice, the latter will usually be the ruling consideration; that is, the furnace will be operated at a capacity that gives good economy of fuel.

DATA ON RUN 8

Run 8, like run 28, was made at low speed, but about one-third of the heat was introduced by the use of coal that was blown into the furnace and dropped on the charge in hearth 3. This coal was not completely consumed, and part of its distillation products went up the stack unburned. The thermal efficiency was 24.4 per cent, which is much like that of run 28, 22.6 per cent. The heat transfer numbers, 10.5 for the preheating zone and 29.1 for the calcining zone, indicate a possible advantage from doing part of the calcining with coal burned with the magnesite on the hearths. However, this point was not definitely established and was dropped due to difficulty in getting all the coal to burn.

GENERAL DISCUSSION

A résumé of the data from the foregoing heat balances and calculations is given in Table 28.

TABLE 28.—*Résumé of data on heat balances of Herreshoff furnace*

Run No.	Material	Rate of feed	Calcine	Flue-dust loss	Stack gases	Surplus air	Fuel furnished	Fuel burned	Fuel unburned	Stack gas		Calcine sensible heat	Radiation and convection losses	Thermal efficiency	Transfer numbers			Maximum gas velocity
										Sensible heat	Latent heat				Heating zone	Calcining zone	Average	
		Pounds per minute	*Pounds per minute*	*Per cent*	*Pounds per minute*	*Per cent*	*B. t. u. per minute*	*B. t. u. per minute*	*Per cent*	*B. t. u.*	*B. t. u.*	*B. t. u.*	*B. t. u.*	*Per cent*				*Feet per minute*
28	M-45	2. 414	0. 93	26. 6	8. 50	113	4, 710	4, 710	0. 0	1, 514	499	164	1, 855	22. 6	9. 9	11. 85	11. 1	1, 024
29	M-45	5. 69	2. 21	30. 9	12. 65	120	10, 000	7, 100	29. 0	2, 091	747	496	2, 068	30. 9	25. 2	12. 9	17. 7	1, 474
3+4	M-33	5. 5	2. 09	31. 4	9. 88	60	8, 690	6, 740	22. 3	1, 631	709	520	2, 004	34. 3	23. 7	----------	----------	1, 202
8	M-33	2. 52	. 98	29. 5	7. 09	70	4, 970	4, 442	10. 7	1, 045	390	303	1, 910	23. 5	10. 5	29. 1	21. 8	874

RECOVERABLE LOSS

Attention is called to the fact that most of the loss in flue dust is recoverable; part of the dust settles in the flues and the remainder can be almost entirely recovered by the use of Cottrell precipitators. In the design of large furnaces of this type, however, it will be well to provide means of reducing to a minimum the origin of dust within the furnace. The Northwest Magnesite Co. utilizes these electrical precipitators at its dead-burning plant in Chewelah, Wash.

INFLUENCE OF RATE OF COMBUSTION

Comparison of the transfer numbers immediately shows that the transfer of heat was higher in the tests where the rate of the furnace was increased, and the velocity of the gases and the speed of rabbling were higher. In the laboratory-size furnace used, the higher rate of combustion caused much of the fuel to escape into the flues unburned; in a larger furnace where the travel of the gases through the hot zones would be much longer, and the time for complete combustion correspondingly increased, it is probable that this loss of unburned fuel would be eliminated and high heat-transfer numbers obtained with a good utilization of fuel. The thermal efficiency is also higher in those tests where the furnace was operated at higher capacity, when efficiency is based on fuel actually burned.

EFFECT OF ADDING COAL TO CHARGE

Run 8 is of interest on account of the high transfer number for the calcining zone, where coal was introduced to provide part of the heat. In a small furnace, because of the loss of unconsumed gases, it was impossible to obtain all the heat value of the coal, but better conditions may be expected in a larger furnace. This method of "duplex" firing deserves further attention. In a few tests the gas firing was reduced after the furnace was in thermal equilibrium; the idea was to eliminate gas or other external firing entirely, but the furnace always cooled when only coal was introduced on the charge and the fire finally went out.

CONCLUSIONS ON FURNACE DESIGN

From the experience gained in these tests the following criteria were deduced for the design of plastic magnesia calcining furnaces:

1. In any given furnace, arrange for complete combustion of the greatest possible amount of fuel with the least possible amount of excess air, and provide facilities for passing through all the magnesite that will be burned by this fuel.
2. Use as high a frequency of rabbling as the capacity of the furnace and the spacing of the rabbling teeth will permit. Quick

rabbling prevents overheating of the particles on the surface of the bed of magnesite and continually turns up cool material which can absorb heat better than the hot. Speed of rabbling is the most important single factor in obtaining high rates of heat transfer.

3. The stack gases should pass through a Cottrell precipitator to collect the dust and return it to the furnace; then no dust will actually pass up the stack. To reduce the formation of dust within the furnace to the practicable minimum is desirable.

THERMAL EFFICIENCY AND CAPACITY OF COMMERCIAL FURNACE

When this report was prepared no commercial furnace of the Herreshoff type had been constructed for calcining magnesite, but since then the Santa Cruz Portland Cement Co., of San Francisco, has constructed a commercial-size plant for testing out the Pike three-stage process for burning Portland cement, in which a Herreshoff-type furnace of special design is employed, for calcining the raw cement mix before clinkering. Although the calcining of magnesite and of cement mix differ in some important details, it is expected that operating data from this new cement-burning plant will serve to check our conclusions and form a basis of design for the Herreshoff-type calciner for magnesite.

From the unit figures collected in this work, calculations were made for a commercial-size 10-hearth Herreshoff furnace. These calculations were based on the following general figures for the small and the large furnace.

The chief dimensions of the experimental furnace were as follows:

Dimensions of laboratory-size furnace

Height	feet	5.4
Circumference	do	14.1
Area of shell	square feet	72.2
Area of bottom	do	16.6
Net area of hearths with outside drop	do	16.5
Net area of hearths with inside drop	do	19.5
Total hearth area	do	36.0

The principal dimensions of the assumed commercial furnace having 10 hearths, with the roof functioning as a drying hearth, were as follows:

Dimensions of proposed commercial furnace

Height	feet	30.0
Outside diameter	do	18.6
Superficial area, shell and bottom	square feet	2,027.0
Superficial area, combustion chambers	do	1,408.0
Hearths		11
Total net hearth area	square feet	1,886.0

In runs 3 and 4 the weight of calcine produced daily per square foot of hearth area was 83.7 pounds. If this figure is used for the commercial furnace—an assumption that is justifiable if the same frequency of rabbling is used, and since it is possible to use an ample amount of combustion space—the capacity of the commercial furnace should be 79 tons per 24-hour day.

Calculations based on the heat losses per unit of exposed furnace area and on the assumptions that there will be five preheating hearths, that the calcine will be discharged at a temperature of 600° F., and that coal of a heating value of 12,750 B. t. u. per pound will be used for firing with 50 per cent surplus air, show that the temperature of the gases entering the stack will be about 700° F. The weight of coal needed is deduced from the following equation which sums up all the mathematical operations necessary.

$$WC = Hr + Hc + Hl + (W \times A + W + G) \times (T - t) \times s + fW \text{ in which—}$$

W=weight of coal in pounds per minute.
C=calorific value of coal=12,750 B. t. u. per pound.
Hr=heat of calcination=108,500 B. t. u. per minute.
Hc=sensible heat in hot calcine=15,700 B. t. u. per minute.
Hl=heat lost by radiation=17,800 B. t. u. per minute.
A=air used per pound of coal=15 pounds.
G=weight of CO_2 gas from charge per minute=87 pounds.
T=temperature of stack=700° F.
t=temperature of atmosphere=60° F.
s=specific heat of stack gases=0.25.
f=latent heat in stack gases per pound of coal=463 B. t. u.

Solving the above equation to the weight of coal used per minute gives 16.05 pound; and for 1 ton of calcined magnesia gives 292 pounds or 3,720,000 B. t. u.

This calculated amount of fuel needed for the Herreshoff furnace should be compared with the fuel consumptions of various commercial plastic magnesia calcining kilns, the data of which have been assembled in Table 29. The figures show that the Herreshoff furnace compares favorably with the best stack furnaces and that slack coal can be used in it instead of the coke that is necessary for them. Stack furnaces are the most efficient calciners, but for high efficiency the feed must be in coarse lumps and the fuel must be coke. Many of the coarse lumps, when properly burned at the centers, are overburned on the outside. Stack kilns also suffer from the disadvantage of having small capacities per unit.

TABLE 29.—*Fuel used in calcining magnesite in various types of kilns*

Date	Calciner	Location	Magnesia	Kiln		Daily capacity	Fuel		Output	Size of feed	Authority
				Kind	Size		Kind	Amount			
						Tons			*B. t. u. per ton*		
1917	American Magnesite Co.	Porterville, Calif.	Plastic	Rotary	6 by 73 feet	50	Oil	1.75 barrels	10,700,000	1 inch	Stevenson.[a]
1920	do	do	do	do	do	50	do	1.5 barrels	9,200,000	do	C. S. Maltby.
1918	White Rock Mines	Rutherford, Calif.	Dead burned	Stack	4½ by 25 feet	5	Coke	335 pounds	4,200,000	8 to 1 inches	W. E. Balcom.
1918	Mineral Products Co.	Patterson, Calif.	Plastic	Stack	6½ by 22 feet	10	do	340 pounds	4,250,000	do	R. D. Pike.
1920	C. S. Maltby	Livermore, Calif.	do	Stack	5 by 20 feet	10	Oil	1 barrel	6,100,000	do	C. S. Maltby.
1917	Northwest Magnesite Co.	Chewelah, Wash.	Dead burned	Rotary	7½ by 45 feet 7 by 80 feet	60	do	1.57 barrels	9,600,000	Through 2-inch mesh.	R. B. Rodgers.
1920	do	do	do	do	do	60	Powdered coal.	778 pounds	9,889,000	8-mesh	R. D. Pike.
1920	Tulare Mining Co.	Porterville, Calif.	Plastic	Stack		18	Oil	1 barrel	6,100,000	?	Delaney and Gillespie.
1922	C. S. Maltby	Livermore, Calif.	do	Scott		22	do	0.92 barrel	5,600,000	1½ inches	Riddell and Schuette.

[a] Superintendent, American Magnesite Co.

SCOTT FURNACE

The data on the Scott furnace have been taken from a paper recently published.[9] The Scott furnace, which has no moving parts, is an adaptation of the model used in the metallurgy of quicksilver, and can calcine fine material as well as coarse. It consists of a stack with inclined shelves alternating on opposite sides with passages around the end so that the flue gases pass under the shelves and over the magnesite. The only thing that has to be watched is the calcining temperature. The furnace is a good example of how a tried and proved method of furnacing materials can be adapted to a new process requiring similar conditions. Although the Scott furnace probably can be adapted to do the same work as the Herreshoff, it can not be built in such large units. Small producers will probably find it more advantageous than the Herreshoff. Credit is due C. S. Maltby for being the first to use the Scott furnace for calcining magnesite.

PHYSICAL PROPERTIES OF CHEWELAH MAGNESIA MADE IN HERRESHOFF FURNACE

Hundreds of tests were made of the physical properties of the plastic magnesia produced during the calcining tests of magnesites from Washington and from California. Some of these tests are reported later in this bulletin. A few are reported here because they show how the physical properties of cements made with the plastic magnesia are affected by conditions of burning. The incompleteness of burning is frequently indicated by the percentage of undecomposed magnesium carbonate in the plastic magnesia. This percentage can be computed from the percentage of carbon dioxide remaining in the calcine. In Figure 18 the physical properties and some of the chemical properties of various samples of burned Chewelah magnesite (samples M—45 and M—46) are plotted as functions of the residual carbon dioxide in the magnesite.

IGNITION LOSS

As the total ignition loss of a sample of burned magnesite includes the carbon dioxide and the combined water, the oblique lines at the bottom of Figure 18 represent these two components of the ignition loss. Much of this water is taken up from the air by the material during incidental handling after burning, although great care was taken to minimize the duration of exposure to air.

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[9] Riddell, W. C., and Schuette, C. N., The production of caustic calcined magnesite in the Scott furnace: Eng. and Min. Jour. Press., vol. 114, 1922, pp. 981–984.

EFFICIENCY

The main point brought out by this set of curves is that the highest tensile strengths are those of samples burned to leave 3 to 4 per cent of carbon dioxide in the plastic magnesia. The lightest burned samples show the fastest setting time. The expansion after setting is greatest for the samples burned at higher temperatures and to a very low percentage of carbon dioxide. The content of free lime increased with the completeness of burning, probably because of the higher temperatures involved.

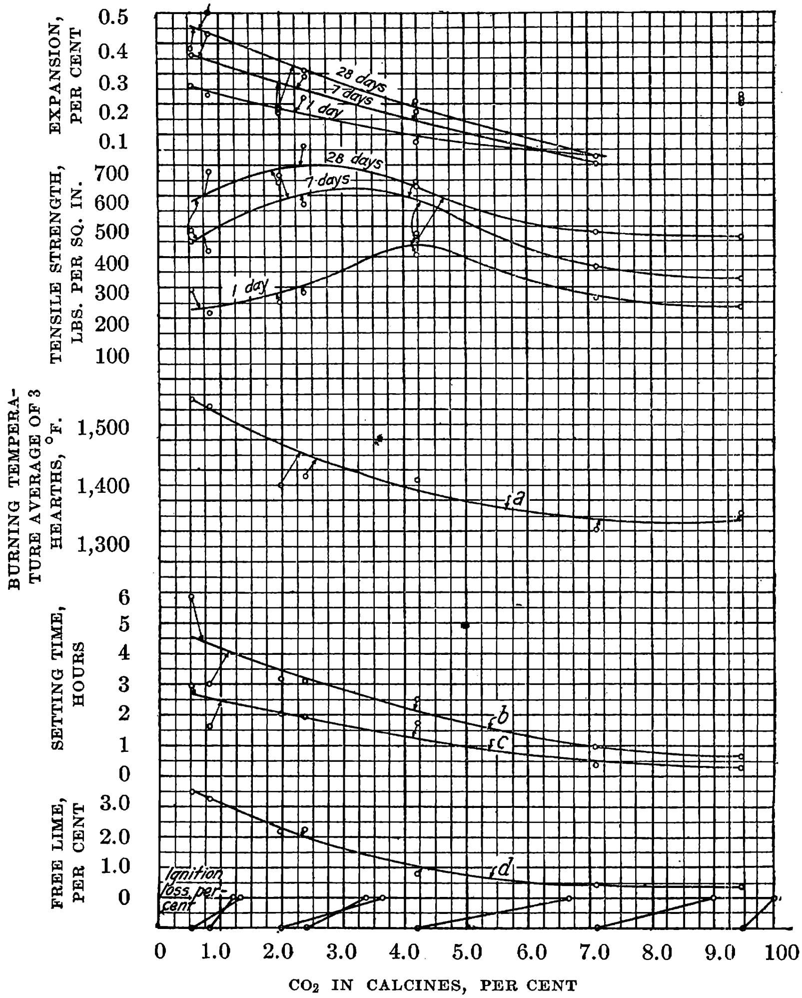

FIG. 18.—Samples of Chewelah magnesite burned in Herreshoff furnace, tested under the same conditions. Physical properties of cements plotted as a function of the carbon-dioxide content: *a*, burning temperature, ° F.; *b*, final set; *c*, initial set; *d*, free lime

In general, the physical properties of the Sorel cements made from these samples of plastic magnesia compare favorably with those of cements made with magnesia from the cryptocrystalline (amorphous) magnesites, California and foreign, which are now the sole source of plastic magnesia and have been regarded as the only magnesites suitable for its manufacture. Consequently the belief that crystalline magnesites are not adapted to the production of plastic magnesia has no foundation.

METHODS OF JUDGING QUALITY OF PLASTIC MAGNESIA

Plastic magnesia is used almost entirely in the preparation of cements for flooring or for stucco, and experience has demonstrated that the best way to judge its quality is to prepare characteristic mortars, allow them to harden, and then test the physical properties of the mixes. As for Portland cement, these physical tests are of far more value than any chemical tests. When our work was done no standard specifications for testing or judging plastic magnesia existed, but the United States Bureau of Standards was testing various mixes for flooring or stucco, and the Dow Chemical Co., of Midland, Mich., was developing tests for magnesia mortars. Both have given us valuable help. Their representatives, and representatives of the Bureau of Mines and of the Northwest Magnesite Co. have held several conferences with representatives of the main users of plastic magnesia to make preliminary drafts of methods for testing in the hope that the American Society for Testing Materials would ultimately take up the problem and adopt a standard procedure. Our tests and methods are therefore probably as near standard as they could be made at the time. Since then we have learned much about proper procedure and have discovered the causes of many discrepancies due to unforeseen variables. Seaton,[10] of the Dow Chemical Co., has published a good paper on the testing of magnesium cements, to which the reader is referred.

GROUPING OF TESTS

We have divided the tests into two groups—chemical and physical. Attention is called to the possibility that two samples of identical chemical analysis may show widely different physical properties and action. The heat treatment of the mineral and the conditions under which the treated material is stored affect remarkably the physical properties of magnesium oxychloride cements.

CHEMICAL TESTS

The three chemical constituents of plastic magnesia that are of most interest are free lime, carbon dioxide, and water. The content of silica is of subsidiary interest; that of iron is of indirect interest as

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[10] Seaton, Max. Y., Plastic magnesite and oxychloride cements: Chem and Met. Eng., vol. 25, 1921, pp. 233–236.

bearing on color and the care required in burning to prevent the formation of inert magnesia (periclase).

About 4 per cent of Fe_2O_3 in calcined Chewelah magnesite gives a deep buff color; whereas the white-burning magnesites contain only a trace of iron. In general, small amounts of certain impurities are permissible; but large amounts have bad effects on the magnesia. Silica tends to flux the magnesia, forming a magnesium silicate; but the allowable percentage depends more on the physical condition of the silica than on the ratio of silica to magnesia content. Coarse particles of silica do little harm. Intimately blended silica is most likely to cause trouble. The best way to judge its effect is to heat a sample of the magnesite through the ordinary range of temperature and time used for good magnesites and to test the product by physical methods.

FREE LIME

Free lime is important. The permissible upper limit for free lime is unknown, but too much will yield magnesium oxychloride cements of poor quality. When we first undertook this research it was commonly supposed that all lime was objectionable; but like the research laboratory of the Dow Chemical Co., we found that the only objectionable form was free lime, and that all lime present as calcium carbonate was inert. In fact, marble chips are often used as inert material for commercial aggregates. In general, although one may look with suspicion on any plastic magnesia containing more than about 4 per cent of free lime, we know that many of the samples we tested showed good physical properties with a much higher content.

CARBON DIOXIDE

The content of carbon dioxide is important mainly as an index of the previous heat treatment of the magnesia, and, to some extent, as an index of the length of time or the conditions of storage. A magnesia containing no carbon dioxide has probably been heated too highly and has been transformed in whole or in part to the crystalline variety, called periclase, which is unsuitable for making oxychloride cements. Burning until the CO_2 content is 2 to 5 per cent will usually give a product that will make a cement of fair physical properties. Higher percentages of carbon dioxide are due either to insufficient burning or to storage under conditions that permitted absorption of carbon dioxide and moisture. Too high a content of CO_2 may cause the plastic magnesia to be of inferior quality, whereas storage effects are frequently of great value, as will be seen in the chapter on "Exposure of plastic magnesia."

WATER

The water content of a sample of plastic magnesia is more or less of an index of the storage conditions. As mentioned above, storage permits a plastic magnesia to take up water and carbon dioxide, thus changing its physical properties. One of the most noteworthy changes is the increased setting time of a cement aggregate.

Water content is determined by observing the ignition loss of a sample and assuming this loss to represent water and carbon dioxide. From a seperate determination of carbon dioxide the water content can be estimated.

Below appear the average chemical analyses of two sets of shipments of commercial plastic magnesia received by the Dow Chemical Co. in 1920.

TABLE 30.—*Average analyses of commercial plastic magnesia*

	Average 25, first quarter	Average 75, second, third, fourth quarters	Maximum	Minimum
	Per cent	*Per cent*	*Per cent*	*Per cent*
Ignition loss	5.0	7.5	24.6	2.7
Silica	6.0	6.1	17.0	.9
Iron and aluminum oxides	1.0	1.1	4.8	.3
Carbon dioxide	2.5	2.8	5.8	.6
Calcium oxide	3.5	4.7	6.5	1.6
Magnesium oxide	84.5	80.2	89.0	67.0

Our methods of analyzing samples of plastic magnesia are given in detail in the following pages.

NECESSARY CHEMICAL DETERMINATION

COKE AND COAL

Coal and coke are present in some samples of plastic magnesia, especially those from certain types of kilns, and, although they are rarely mentioned in specifications, we found it necessary to determine them roughly. Two grams of coarse calcine as received from the furnace was treated with hydrochloric acid to dissolve magnesia, lime, etc., leaving carbon and some silica. The resulting solution was poured on a filter mat of prepared asbestos in a Gooch crucible, washed, dried, and weighed. After ignition the weight was again determined and the loss in weight called carbon.

IGNITION LOSS

For the determination of ignition loss to control furnace operation 2 grams of calcine was placed in a porcelain crucible, burned in an electric muffle at 1,000° C. for 30 minutes, cooled in a desiccator, and weighed. Magnesites high in silica require the use of platinum crucibles because they stick to an ordinary crucible. During the removal of the crucible from the furnace and cooling in the desiccator, the sample tends to take up water, therefore it is wise to cool and weigh it in covered crucibles. Most of the ignition loss in samples of freshly burned plastic magnesia that have been properly protected from the air is due to carbon dioxide.

WATER

After the carbon dioxide content is subtracted from the ignition loss, the remainder is called water.

CARBON DIOXIDE

An ordinary combustion train was tested for direct determination of carbon dioxide and water, but was found too slow. The use of the Penfield tube, as described by Hillebrand,[11] was found more advisable. Full particulars can be found in the original description. The form we used is shown in Plate VII (p. 70.) It consists of a decomposing vessel, a reservoir for strong acid, and a measuring burette with appropriate gas connections and thermometers for measuring the temperature. A quantity of the material to be tested, ranging from 0.5 to 2.0 grams according to its CO_2 content, is weighed into the test tube shown in the upper left corner of the apparatus. The test tube is then attached to the apparatus, strong acid is forced over into it from the large reservoir situated between the burette and the test tube, and a free flame is applied to the test tube. After all the CO_2 has been evolved and has passed over into the burette, the temperature of the gas and acid is brought down to the temperature of the burette by use of an external condenser around the test tube. The remaining acid is forced over into the acid reservoir and the number of cubic centimeters of CO_2 read off on the burette and converted into grams. Our results by this method have been very satisfactory. Combustion-tube absorption checks have shown that the sum of water and carbon dioxide is usually a little higher than the ignition loss.

FREE LIME

When the World War made possible the utilization of American magnesites for plastic magnesia it was believed that many of them would be unsuitable for this purpose because of their high

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[11] Hillebrand, W. F., The analysis of silicate and carbonate rocks: U. S. Geol. Survey Bull. 700, 1919, p. 77.

lime content. Lime in certain forms had proved injurious to magnesian cements, therefore all magnesites containing lime were thought unsuitable. Our own work and that of others, notably the research laboratory of the Dow Chemical Co., has practically proved that the injurious form of lime is CaO or free lime, whereas calcium carbonate does not injure the cements. It is, therefore, necessary to distinguish between the total calcium oxide content and the free calcium oxide content of a sample. For the determination of free lime two methods are available—one originated by us and the other that used by the Dow Chemical Co.

BUREAU METHOD OF DETERMINING FREE LIME

Since our work was completed, Seaton, Hill, and Stewart[12] of the Dow laboratory, have published the results of tests made both by their own and by our methods, but these do not alter our conclusions.

Our own method involves leaching a sample of plastic magnesia with water free from dissolved carbon dioxide, and is based upon the fact that calcium carbonate is so slightly soluble in water that its solubility can not be measured by ordinary analytical laboratory methods, whereas calcium oxide is soluble to the extent of 0.176 gram per 100 c. c. of water at 20° C. According to various authorities magnesium oxide is soluble to the extent of only 0.008 to 0.012 gram per liter of water, the latter figure probably being the best at 18° C. This method has already been described by L. H. Duschak.[13]

DESCRIPTION

Briefly the procedure was to place a 1 to 2 gram sample in a closed graduated flask with 200 c. c. of distilled carbon dioxide-free water, and allow it to stand for a fixed time, usually overnight, with occasional shaking if possible. The liquid was then filtered, and 100 c. c. was titrated with standard hydrochloric acid solution, and phenolphthalein as an indicator. All the alkalinity was assumed to be due to dissolved calcium oxide. The method yielded good results with ordinary magnesites, but, when high-line magnesites were used a slight correction was necessary because of the solubility of magnesium oxide in the large amount of water needed to dissolve all the lime. The following Table 31 gives the results of a series of tests in which the lime in the extract was determined by oxalate precipitation instead of by acid titration; from this

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[12] Seaton, Max. Y., Hill, C. R., and Stewart, L. C., Action of lime in magnesium oxychloride cements: Chem. and Met. Eng., vol. 25, 1921, pp. 270–274.

[13] Duschak, L. H., Extraction of calcium oxide from calcined magnesite: Chem. and Met. Eng., vol. 23, 1920, p. 628.

table the errors are calculated. The solubility figures of magnesium hydroxide can also be used for calculating the errors.

TABLE 31.—*Lime determination by oxalate precipitation*

Weight of sample per 100 c. c. of solution	Sample number and CaO determination						Error, mean CaO
	M-13		M-18		M-25		
	Found	Error	Found	Error	Found	Error	
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
2 grams	1.13	0.03	0.67	0.06	0.69	0.10	0.06
1 gram	1.13	.03	.76	.15	.75	.16	.11
0.5 gram	1.27	.17	.91	.30	.86	.27	.25
0.25 gram	1.49	.39	1.32	.71	1.27	.68	.59
0.1 gram	2.34	1.24	2.62	2.01	2.21	1.62	1.62
True CaO content	1.10		.61		.59		

The error involved when less than 0.5 gram of the sample is used per 100 c. c. of water is doubtless too large. However, for comparison the errors were calculated from the known solubility of magnesium hydroxide on the assumption that it is not much affected by the solubility of calcium hydroxide. These calculated errors and the observed mean errors from the above table are tabulated as follows:

TABLE 32.—*Tabulation of calculated and observed mean errors in the determination of lime*

Weight of sample per 100 c. c. of solution	Error in CaO determination	
	Observed	Calculated
	Per cent	*Per cent*
2 grams	0.06	0.07
1 gram	.11	.14
0.5 gram	.25	.28
0.33 gram		.42
0.25 gram	.59	.56
0.1 gram	1.62	1.40

The above values may be applied as a correction to be subtracted from the calculated percentage of CaO according to the weight of the sample used per 100 c. c. of water. Different samples of magnesia may be expected to show some variation in behavior, since the rate of hydration of the magnesium oxide and the rate of solution of the hydroxide formed will differ according to the temperature of calcination of the magnesite and the impurities present in it. For practical purposes, however, by using one-half gram or more per 100 c. c. of water, it is believed that results may be obtained accurate to 0.1 per cent CaO.

DOW CHEMICAL CO. METHOD OF DETERMINING FREE LIME

The method used by the Dow Chemical Co. is similar to that used by us. The difference is that a solution containing 0.5 per cent $MgCl_2.6H_2O$ is used instead of water and the lime in solution is determined by the oxalate method. It has been suggested that calcium carbonate might be hydrolyzed both by water and by magnesium chloride solution but to a different extent, so that results by the two methods might not agree. To test this we made several tests in parallel and to magnify the effect used a 1 per cent magnesium chloride solution, occasionally shaking it for 16 hours. Tabulation of the comparative results follows:

TABLE 33.—*Comparative results in determination of free CaO*

Substance	Method	
	Dow	Bureau of Mines
	Per cent	*Per cent*
Precipitated $CaCO_3$	0.15	0.16
Sample M–57 crude	.00	.04
Sample M–57 calcined	.47	.54

The sample of crude M–57 had been ground thoroughly in an agate mortar and contained a large proportion of minus 200-mesh material. Some of the precipitated calcium carbonate was boiled in distilled water free of carbon dioxide and the lime in solution determined by the oxalate method. The result expressed in terms of free CaO was 0.11 per cent as compared with 0.16 per cent given above. The difference is within the experimental error of the procedure.

The above tests led to the conclusion that there is no essential difference in the behavior of calcium carbonate under either method and the error due to the solubility of the calcium carbonate was not greater than the other experimental errors.

ULTIMATE ANALYSIS OF MAGNESITE

The ultimate analysis of a sample of magnesite or of calcined magnesia has little practical importance, but is occasionally of interest. It is much like that of a sample of limestone or of dolomite. One of us authors has already published a well-tested rapid method[14] which we have used on both crude and calcined products.

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[14] Riddell, W. C., Analysis of magnesite: Min. and Sci. Press, vol. 120, 1920, p. 943.

PHYSICAL TESTS

STRENGTH

The chief physical properties of magnesium oxychloride cements which we have investigated are tensile strength, cross-bending strength, expansion, and setting time. Many other physical properties should be investigated, and the Dow Chemical Co. has made an extensive series of practical tests, including water-resistance and wearing tests, and has called attention to the need of an "activity" test. Since very little literature exists on methods of testing plastic magnesia for oxychloride cements, we have given our report in detail.

COLOR

Plastic magnesia is usually white to buff, although it is sometimes highly colored by oxides of iron. Since many of the uses to which plastic magnesia is now put call for the addition of coloring matter to the mix, the color is not as important as it might appear to be at first. Floors or stucco of white magnesia are glaring to the eye and soon show dirt and stains. At present the trade still prefers white plastic magnesia, but as the demand increases the deep buff Chewelah magnesites can be utilized as scratch coats for stucco when the slight color which they impart would make them undesirable for a finish coat.

GRINDING

Calcined magnesite must be ground rather finely to prepare it for use in cements. Some of the best samples of commercial plastic magnesia obtainable contained about 70 per cent of material which would pass a 200-mesh sieve (Tyler standard). Grinding to this fineness has been found to be necessary. Max. Y. Seaton, of the Dow Chemical Co., claims that the highest tensile strength he has ever obtained in a test bar of oxychloride cement was 1,500 pounds per square inch from a briquet made with plastic magnesia only 9 per cent of which would not pass a 300-mesh screen. Microscopic examination of various bricks had shown him that large pieces of plastic magnesia would not react immediately with the magnesium chloride solution, although they did so later. Cracks developed in the big grains that functioned as centers of weakness because they were softer than the remaining material. Fine grinding is essential to develop maximum strength. However, there are many purposes for which a strong cement is not needed.

The laboratory was equipped with two ball-mill grinding machines. One was a porcelain pebble-mill (Abbe jar mill) carrying a

25-pound pebble load and is shown in Plate VIII, *A*. In one-half hour it would grind 8 pounds of calcined Chewelah magnesite so that 70 per cent of it would pass a 200-mesh screen. The second mill could carry a load of 420 pounds of pebbles revolving at 30 r. p. m., and could grind 160 pounds of Chewelah magnesite to 200-mesh fineness in 1¼ hours; this mill was made by the Patterson Foundry & Machine Co. and is shown in Plate VIII, *B*, with the screen for catching the pebbles when a charge was dumped. The ground material was always passed over a 30-mesh screen to remove chips and small pieces of pebbles.

These pebble mills worked very well on Chewelah crystalline magnesite, but when California cryptocrystalline material was ground the charge packed in the mill. To conduct tests fairly the material which packed in had first to be chiseled out and then ground, screened, and returned to grinding. Air-separation mills, such as the Raymond roller mill, or burr stones, can grind the California material better.

SCREENING

Our practice has followed that of the Bureau of Standards, which consists in shaking the material by hand when on a 100 or 200 mesh screen until as much as possible has passed through the screen. The Dow Chemical Co. makes screen analyses by placing its screens on the Tyler Rotap screen shaker for one hour. We find hand shaking most reliable. Table 34 gives average screen analyses of many samples of commercial plastic magnesia bought by the Dow Chemical Co. in 1920.

TABLE 34.—*Average screen analyses of commercial plastic magnesia*

Passing—	Average 25	Average 75	Maximum	Minimum
	Per cent	*Per cent*	*Per cent*	*Per cent*
100 mesh	94.5	93.5	100	60
150 mesh	85.7	75.3	99	43
200 mesh	75.7	57.7	98	22
275 mesh	41.7	22.9	90	4

STORAGE OF SAMPLES OF PLASTIC MAGNESIA

All samples of plastic magnesia, before or after grinding, should be kept in air-tight containers to avoid the possibility of their taking up carbon dioxide and water vapor. We have used large carbide cans for large batches and 10-pound friction-top tin cans for smaller samples.

STORAGE OF TEST PIECES

At first we stored our test bars and briquets in a small cupboard, but the effect of the temperature and humidity of the atmosphere in the storage cupboard on the properties of the test pieces soon became evident. Therefore a constant-temperature cabinet, as shown in Plate IX, *A* and *B*, had to be devised. The cabinet was heated by electric lamps on the bottom of a 6-inch galvanized-iron pipe which passed upward through the center of the cabinet. The temperature was controlled by a toluene thermostat in the top of the cabinet and was maintained at 25° C. A pan of 50 per cent sulphuric acid was kept in the bottom to control the humidity, which was kept at 50 to 60 per cent. In the galvanized pipe a propeller driven by an outside motor caused the air to circulate over the lamps, up the pipe, past the thermostat, and down through the shelves of the cabinet to the bottom again. The variation of temperature between the top and bottom of the cabinet was never more than 2°. A recording hydrograph closely controlled the humidity of the air in the cabinet. As soon as the cabinet was put in commission, the reproductibility of test results improved greatly.

Many weak briquets, which before had broken under a pressure of 350 pounds per square inch or less, showed a breaking strength of 800 to 1,000 pounds after one night's storage at 95° C. If the test pieces were stored at 95° C. and then returned for a week to the 25° C. cabinet, they reverted to their lower breaking strengths. Therefore storage conditions are of utmost importance when the qualities of test pieces are judged.

We also found it of advantage to put the molds for the test pieces into the cabinet as soon as they were filled with the mortar; the pieces were removed from the molds next morning and returned to the cabinet.

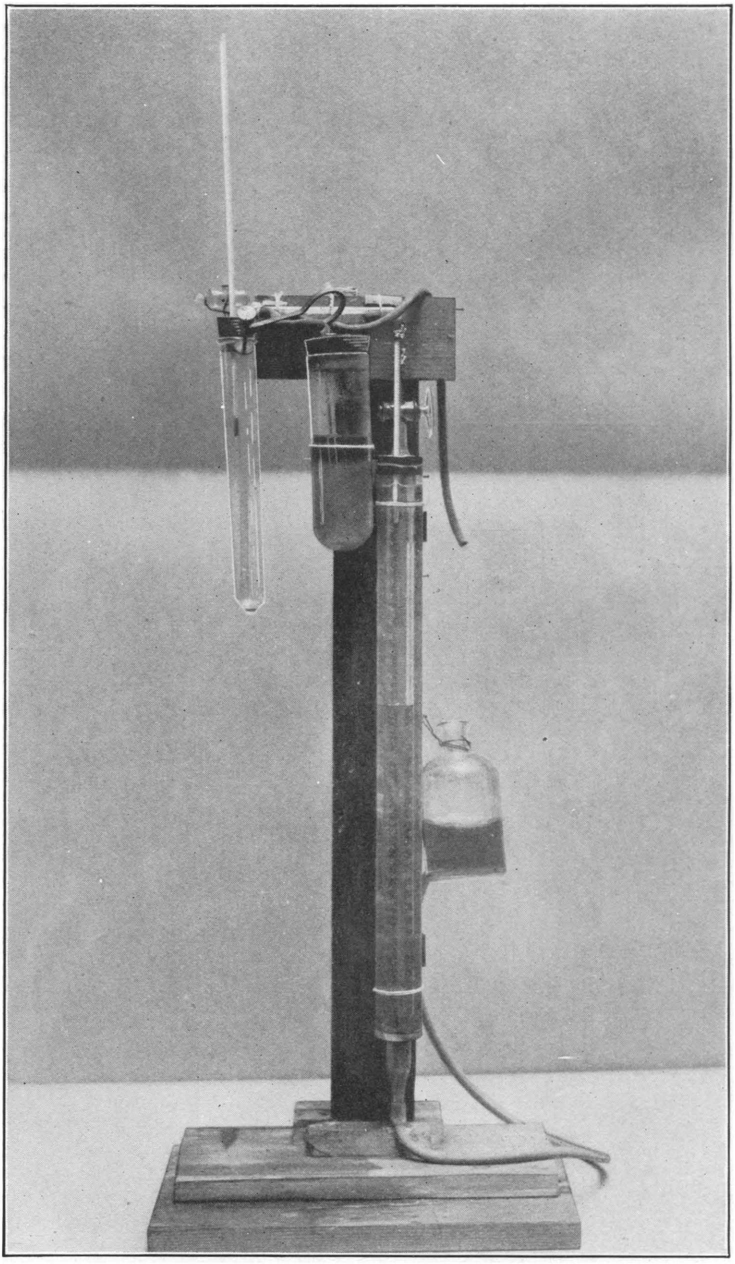
MIXING MORTAR FOR TEST PIECES

STANDARD STUCCO

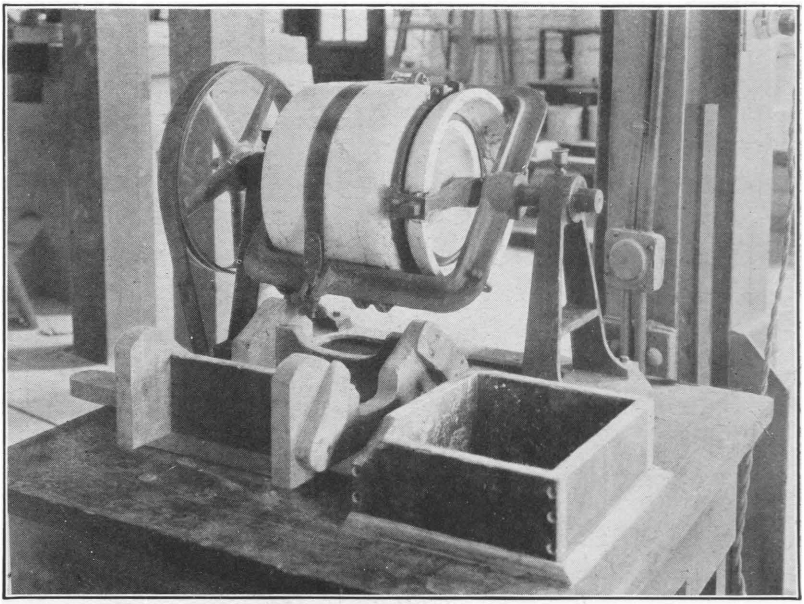
Many different formulas for mixing magnesium oxychloride cement mortars have been used, but after much testing we decided that the standard stucco mix of the Dow Chemical Co. was one of the most reliable and easy to follow. It consists of—

1 part plastic magnesite (12.5 per cent).
2 parts silex (25 per cent).
5 parts standard Ottawa testing sand (62.5 per cent).

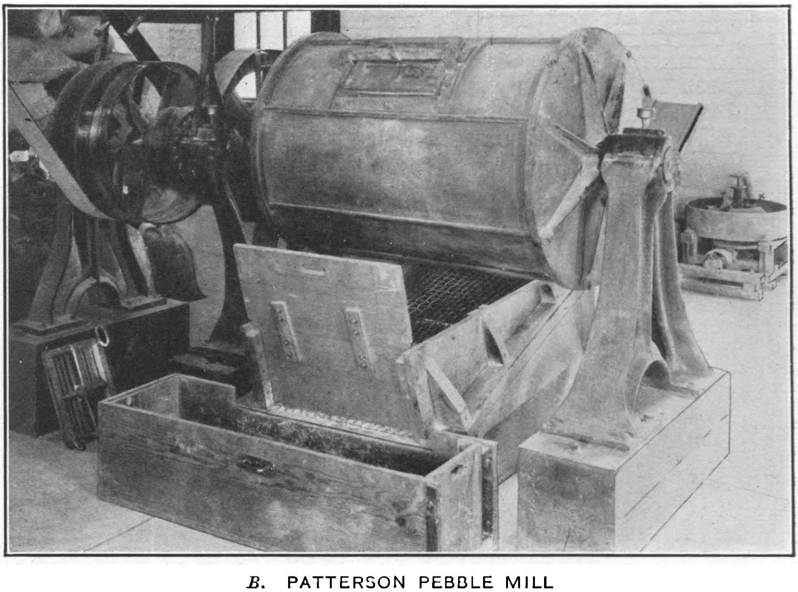
Silex is finely ground silica, 95 per cent of which will pass a 200-mesh screen. The standard Ottawa testing sand is the material formerly so widely used in testing Portland cement and is a silica sand very uniform in size of grains.



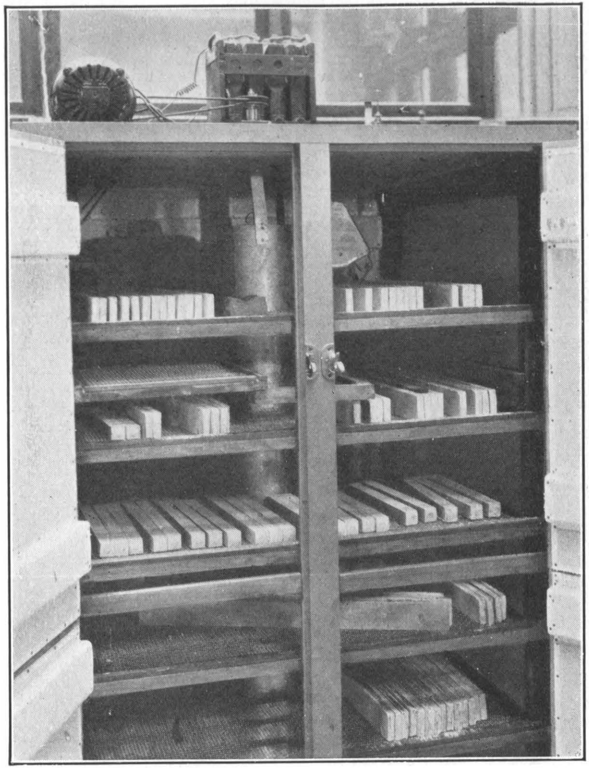
PENFIELD TUBE FOR DETERMINATION OF CARBON DIOXIDE



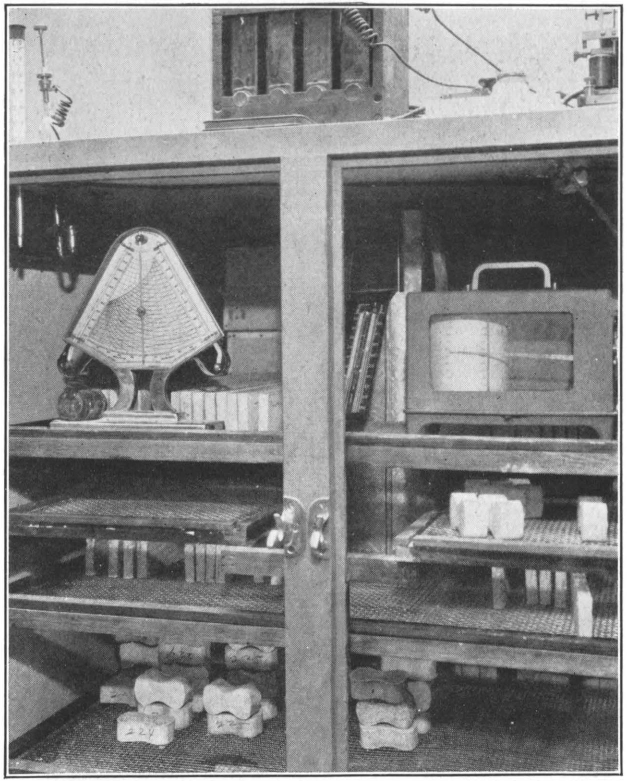
A. ABBE JAR MILL



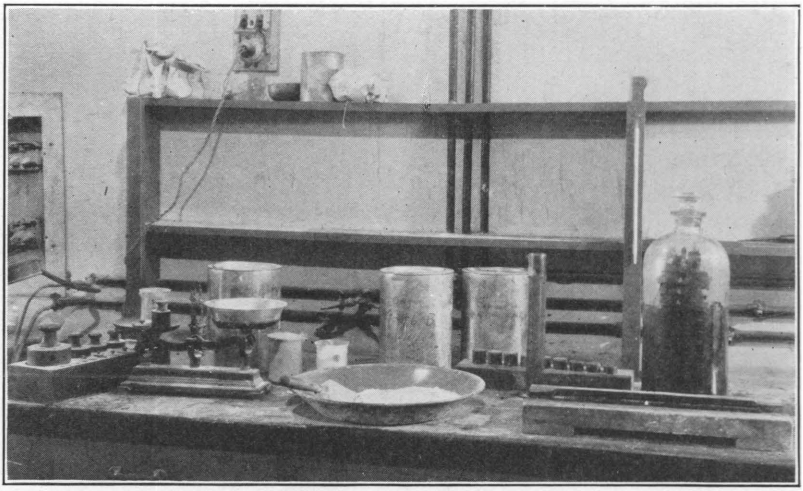
B. PATTERSON PEBBLE MILL



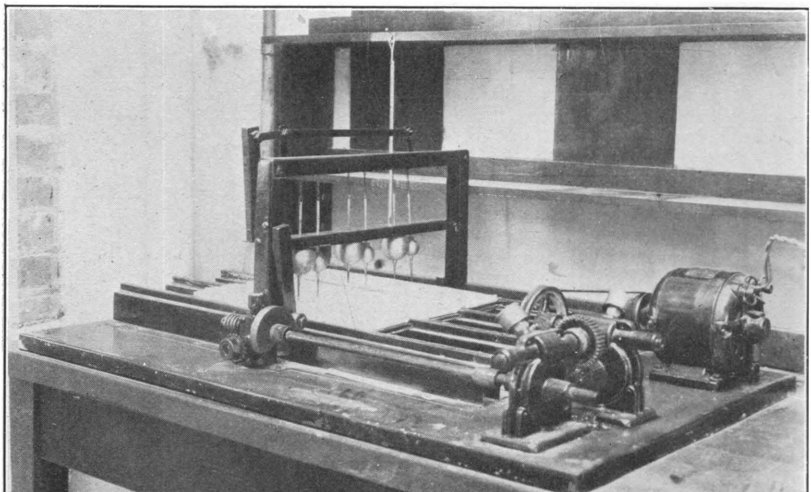
A. INTERIOR OF CONSTANT-TEMPERATURE CABINET, SHOWING CROSS-BENDING AND EXPANSION TEST BARS



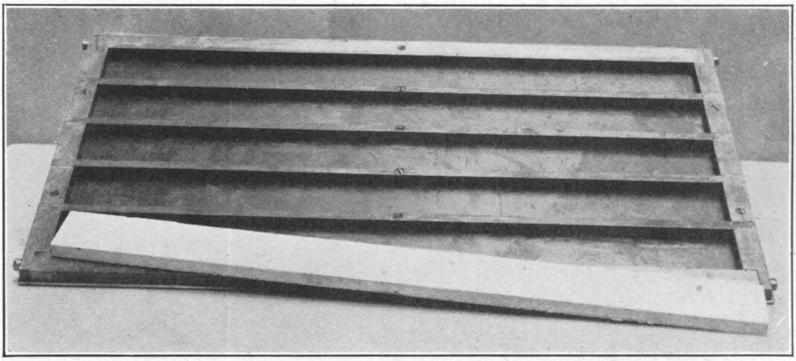
B. RECORDING HYDROGRAPH IN INTERIOR OF CONSTANT-TEMPERATURE CABINET



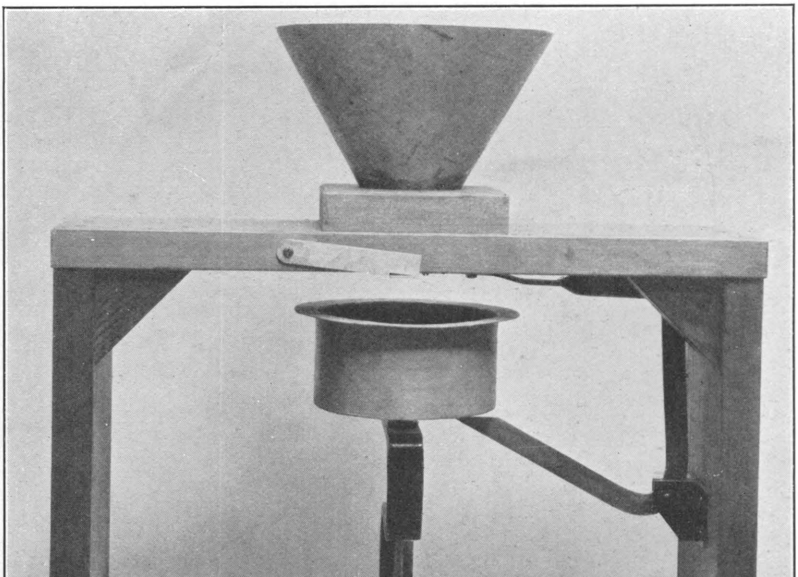
A. MIXING DESK AND EQUIPMENT



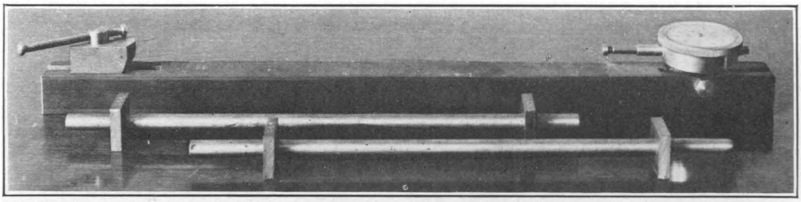
B. HILL AUTOMATIC SETTING-TIME APPARATUS



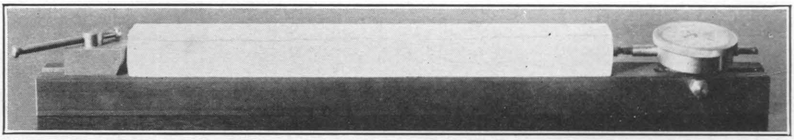
A. MOLDS FOR PREPARING SLABS FOR CROSS-BENDING TESTS



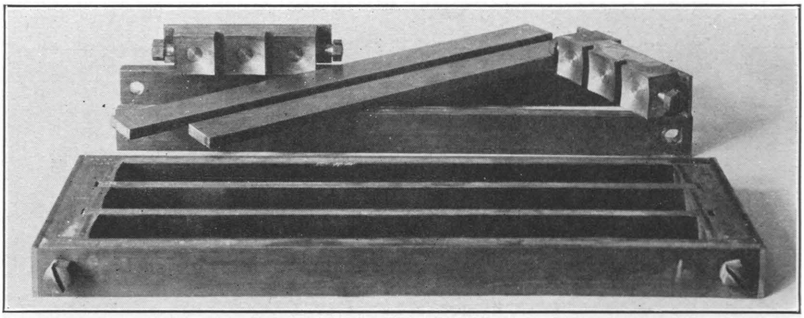
B. CROSS-BENDING MACHINE FOR MEASURING MODULUS OF RUPTURE



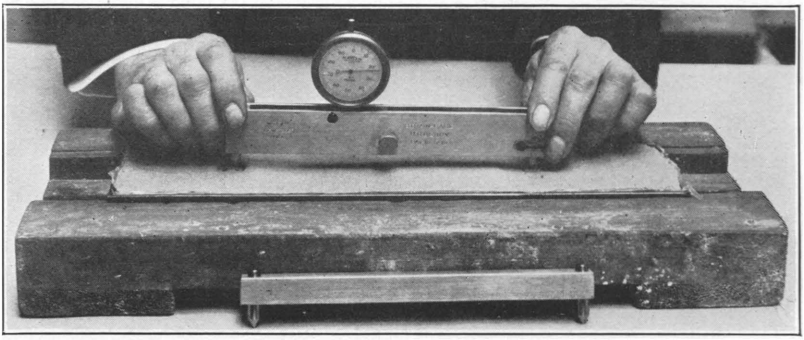
A. EXTENSOMETER



B. EXTENSOMETER WITH TEST BAR IN POSITION FOR MEASURING



C. MOLDS FOR MAKING EXPANSION-TEST BARS



D. BERRY STRAIN GAUGE

This stucco mix conforms generally with the principles of concrete mixing—that the voids of the sand are filled by the silica and the voids of the silica are filled with magnesia. The only difference from concrete mixing is that no coarse materials are used. It must be remembered that all of the magnesia is active in forming cement, whereas all Portland cement contains a high percentage of coarse inert material. The silex in the above stucco mix is, in a way, a substitute for the inert material in ordinary Portland cement. One advantage in using the above mix for testing is that the small percentage of magnesium oxide makes the resultant mortar particularly sensitive to the properties of the magnesium oxide itself. A lean mortar will serve to detect variations in magnesium oxide that would not be disclosed by a richer mix.

FLOORING MIXES

The Dow Chemical Co. uses a standard flooring mix of the following composition:

5 parts calcined magnesite
5 parts silex
1 part wood fiber, medium
1 part talc
1 part red iron oxide

mixed with 1.18 specific gravity magnesium chloride solution.

The other widely used mix is the standard flooring formula used by the Bureau of Standards and by the Dow Chemical Co., consisting of—

5 parts plastic magnesia (50 per cent)
3 parts silex (30 per cent)
2 parts asbestos (20 per cent)

The difficulty of preparing shredded asbestos is the principal objection to this formula. The tests of expansion of the mix during setting and later are erratic, probably because part of the internal changes in volume may be cushioned by the asbestos. The easy reproductibility of the stucco mix encouraged us to do most of our work with it rather than with the flooring mix.

EQUIPMENT

Our mixing desk and equipment are shown in Plate X, *A*. A scale with weights, friction-top cans with the various materials to be used, a pan with mixing trowel, a graduate to measure out the magnesium chloride solution, and the molds into which the mortar is put to form test bars constitute the principal apparatus. The "consistence" measuring weights described below are very important.

We used a magnesium chloride solution of about 1.19 specific gravity at ordinary temperatures, corresponding to 560 grams of commercial fused magnesium chloride per liter. The Dow Chemical Co. has also used solutions of this specific gravity, but more recently has tested solutions of 1.22 specific gravity. In its Magnesium Chloride Service Bulletin No. 5 the Dow company discusses at length the effect of the strength of this solution on the physical properties of the cements formed.

The dry ingredients are first mixed thoroughly in the mixing pan; then the magnesium chloride is added and stirred in until the mortar reaches normal consistence.

NORMAL CONSISTENCE OF MAGNESIUM OXYCHLORIDE MORTAR

A method of measuring a good standard consistence of mortar was invented by Max. Y. Seaton of the Dow Chemical Co. and found useful by us. Round brass rods are so cut that each weighs 250 grams, but they differ in diameter by one-sixteenth-inch steps. The mortar is so mixed that one of the series from fourteen-sixteenths to eighteen-sixteenths inch diameter will just barely fail to sink into the mortar. When a stucco mix is made the endeavor is to get a mortar of No. 16 consistence, one that will barely support a sixteen-sixteenths inch rod. Seaton recommends a No. 13 consistence for laboratory briquets. We noticed some variation in the amount of magnesium chloride solution of 1.19 specific gravity needed for making a mix of standard consistence with 1 kg. of dry stucco mix. It ranged from 140 to 195 c. c. of the solution and although the different materials partly accounted for it, we were unable to find any definite ruling factor that would cause the variations in the amount of solution necessary. As a rule, about 150 c. c. of solution per kilogram of dry mix was enough.

QUANTITIES OF MORTAR FOR TEST MOLDS

After the mortar had been mixed to the proper consistence as quickly as possible, it was transferred to the molds and put in the storage cabinet to set; setting-time pats of the mix were placed in the setting-time measuring machine described on a later page. Table 35 shows the quantities of mix required to fill the various molds described later in this paper:

TABLE 35.—*Quantities of mix required to fill molds*

Test	MgO 1 part	Silex 2 parts	Std. sand 5 parts	Total weight	Mold dimensions
	Grams	*Grams*	*Grams*	*Grams*	*Inches*
Setting time, 1 pat	125	250	625	1,000	15 by 3⅝ by ½.
Tensile strength, 12 briquets	250	500	1,225	2,000	Regular cement molds.
Tensile strength, 18 briquets	375	750	1,975	3,000	Briquet molds.
Expansion bars, 3 bars	187	375	938	1,500	3(11½ by 1 by 1).
Cross bending, 5 bars	500	1,000	2,500	4,000	5(24 by 2 by ½).

From this table it can be calculated that 40 grams of dry mix is required to fill 1 cubic inch of mold space, or 2.44 grams per cubic centimeter.

SETTING-TIME TESTS

HILL SETTING-TIME MACHINE

For measuring the times of initial and final set of various magnesium-oxychloride-cement mortars we used the Hill automatic setting-time machine shown in Plate X, *B*. This machine consists of a motor-driven device for raising and lowering the standard Gilmore needles for measuring the setting time of Portland cement and a mechanism for moving forward a long pat of the mortar while the needles are raised. When the lighter Gilmore needle failed to penetrate the mortar, the elapsed time was considered the period for initial set, and when the heavier one failed to penetrate, the final set was considered to have taken place. The lighter needle is one-twelfth inch in diameter and has a weight of one-fourth pound; the heavier is one twenty-fourth inch in diameter and is weighted with 1 pound. The Hill machine we used had three pairs of needles and could be used to test three samples of mortar at once.

A small electric motor through reduction gearing actuates a cam that causes the needles to rise and fall periodically; simultaneously the motor causes the platen carrying the pat of mortar to move forward by means of a rack. Our machine dropped the needles once in eight minutes and the platen moved forward 2.57 centimeters per hour. The indentations due to the needles were therefore spaced every 0.34 centimeter along the test pats.

PROCEDURE

The platens were greased and a layer of oiled paper was put on them to prevent sticking of the mortar when it was laid on and smoothed out. The time required for mixing the mortar and for placing the pat on the machine was carefully noted in order that the time when initial set showed could be calculated from the rate of travel of the machine. The operator was thus free for other work. The 342 experiments were performed at room temperatures, varying from 55° to 75° F. Pats one-half inch thick were used throughout the investigation.

To practical workers the importance of the initial and final setting times can not be emphasized too strongly. The mortar must be placed before the initial set occurs, hence too quick setting is not desired. On the other hand, the final set must occur within a reasonable time, as rain can wash off stucco that has not hardened.

Any troweling and finishing must be done between the time of initial and final set, therefore a reasonably prompt time of set is important when floors are being made. A great many considerations—the past history of the plastic magnesia, the temperature at the time of setting, the humidity and strength of magnesium chloride solution used, and the proportions of the mix—affect the setting time.

Our study of the effect of storage conditions on the physical properties of magnesian cements is discussed on page 94. In general we found that, during exposure to the air, plastic magnesia took up moisture and carbon dioxide, lengthening the initial and final setting times markedly, although other physical properties were usually benefited. We therefore recommend storage as a method for securing any desired time of set for a definite kind of plastic magnesia.

INFLUENCE OF OTHER FACTORS

The Dow Chemical Co., in its Magnesium Chloride Service Bulletin No. 2, has given the effects of other factors. Temperature is very important—at 160° F. setting takes place in only 25 per cent of the time necessary at 70° F., whereas at 20° F. setting requires 480 per cent of the time needed at 70° F. The strength of the magnesium chloride solution used has a marked effect—the more dilute the solution the more rapid the setting time, and the denser the solution the longer the setting time—although the effect of temperature is even more important. Humidity does not affect the initial set very much, but if high does delay the final set somewhat. A mortar thinned with too much magnesium chloride solution will require less than the normal setting time, whereas dry mortar takes longer to set. If the percentage of magnesia in the dry mix is increased, the setting time is decreased.

TENSILE-STRENGTH TESTS

Briquets used for these tests were shaped like those used in testing the tensile strength of Portland cement. Some of the briquets are visible in the storage cabinet shown in Plate IX, *B*. We used ordinary cement molds, greased with a heavy cup grease to minimize sticking, and cleaned them between tests with a wire scratch brush. After these molds were filled with mortar they were put in the cabinet overnight; the briquets were then removed from the molds and replaced in the cabinet. A Fairbanks testing machine was used and the load was applied at the standard rate—600 pounds per minute. Four bricks were broken at 24 hours, at 7 days, and at 28 days, and the remainder held for longer-time tests. A great many briquets showed a distinct rise in strength after the 28 days.

GENERAL CONCLUSIONS

In general, materials which impart high tensile strength are regarded as satisfactory aggregates unless other physical properties are undesirable, such as expansion or water resistance. By measuring the tensile strengths of briquets made with different aggregates the Dow Chemical Co. has been able to work out formulas which demand a minimum amount of plastic magnesia or of magesium chloride solution and to test various sands, silexes, and other raw materials. The company found, as we did, that the tensile strength of a briquet depends upon the temperature and humidity at which it has been stored, and that high tensile strength results from storage at higher temperatures and lower humidities. The bricks should be stored with air spaces all around them so that they can dry out uniformly. Plastic magnesias vary greatly in tensile strength when made into mortars, depending upon previous heat treatment and storage conditions as well as inherent impurities.

COMPRESSIVE STRENGTH

The compressive strength of magnesia cements in still relatively unimportant. The Dow Chemical Co. has made some tests and concluded that the compressive strength of ordinary stucco mixes averages about five and one-half times that of the tensile strength and that the compressive strength of the ordinary flooring mix averages about four times the tensile-strength values.

CROSS-BENDING TEST

The cross-bending test was devised by the Dow Chemical Co. primarily for testing stucco, and our apparatus was built according to plans and specifications it supplied. The shapes used in these tests approximate those of the material used in practice more than do the briquets used in testing tensile strength. The tests, moreover, demonstrate the superiority of magnesian-cement stucco over Portland-cement stucco. Both have a modulus of elasticity of about 3,000,000, but when plastered on a wall magnesian mortor develops a tensile strength of about 500 pounds per square inch, whereas Portland-cement mortor develops a strength of only about 100 pounds. The modulus of elasticity for average floorings is about 1,000,000; they would therefore be deflected three times as much by the same load as would a stucco.

The slabs tested measure 24 inches by 2 inches by ½ inch, and thus resemble somewhat the flat slabs of stucco on the side of a building ing. The molds for making these slabs are shown in Plate XI, *A*, and the machine for breaking them in Plate XI, *B*. A 20-inch span of a slab is loaded gradually at the center by a bar on which is mounted a pan for catching a stream of shot falling from a funnel overhead. When the bar (see Plate XI, *B*) breaks the stream of shot is automatically cut off; the weight of shot that broke the bar is noted and the strength calculated.

We did not make many tests, but the modulus of rupture for various magnesites in the average stucco mixture ranged from a minimum of 482 to as much as 1,899, with about 1,000 as a safe average for all bars which were seven days or more old, and 800 for bars only one day old.

EXPANSION AND CONTRACTION TESTS

In magnesium oxychloride cements several kinds of expansion and contraction must be considered: First, that due to temperature changes, which is usually small or negligible when compared with the other changes; second, the effects of internal structure changes during setting, usually at a maximum just after the "final set"; third, changes in volume from ageing and storage conditions, due especially to alterations in moisture content that result from varying humidity, rain, or other causes. Most of the trouble with commercial stuccos and floorings has probably been due to unfavorable changes in volume and much work is needed to bring these under control.

To measure expansion we have used two instruments, an extensometer (Pl. XII, *A*) and a Berry strain gage (Pl. XII, *D*); the latter proved satisfactorily accurate and easy to manipulate. Plate XII, *B*, shows a test bar in position to be measured. The molds for making expansion test bars are shown in Plate XII, *C*. The test bars were 1 inch square and 11.5 inches (about 300 mm.) long (Pl. XII, *B*).

The two cylindrical bars—one 300 mm. and the other 304 mm. long—shown in Plate XII, *A*, are made of invar and used for setting the gage at zero. A test bar was inserted and measured and twice reset and remeasured. The average of the three readings was taken, and three bars were measured for each condition. The final figure was therefore the average of nine readings. The gage reads to 0.01 mm. and the expansion or contraction in millimeters, divided by 300, gives the percentage expansion or contraction.

The bars were made up in the morning, usually between 8 and 10 o'clock; and if the material set quickly enough, they could be taken from the mold and the initial reference measurement made immediately after the final set and before the end of the day. Measurements were then made in 24 hours, 7 days, and 28 days, respectively.

The above method gives no information on the expansion or contraction between initial and final sets. For this purpose the Dow Chemical Co. has adopted the Berry strain gage shown in Plate

XII, *D*, and tested by us. This gage measures to 0.0001 inch. Small pieces of galvanized iron with punch marks at intervals are set into the mortar as soon as it is placed in the mold and the distance between the marks measured. Usually the pieces were set into the slab by the bar shown in Plate XII, *D*, in order that all tests would start with the guiding punch marks the same distance apart (8 inches). The points are placed in position just before initial set, and measurements with the gage are begun as soon as the gage no longer shows signs of "creep," which is immediately after the initial set. The Dow Chemical Co. claims that stuccoes which contract as much as 0.03 per cent during setting are almost sure to crack.

CHANGES IN VOLUME

Expansion frequently takes place while the mortar is setting and may cause serious buckling of floors or stucco. For practical purposes it is important to know the changes in volume that take place after the material can no longer adjust itself to stresses by internal flow after the final set. Therefore the figures computed with the aid of the extensometer and used in some of the tables of this bulletin are those of greatest importance. The expansion or contraction of any particular magnesite varies greatly according to the conditions under which test bars are stored. For example, in dry air the bars may contract and in moist air they may expand an equal amount. Some stuccoes have been known to expand as much as 2 per cent after repeated wetting. On that account use of the constant-temperature storage cabinet with its atmosphere of 50 per cent humidity was absolutely necessary in order to get reproducible measurements. Extensive research is necessary on the changes of volume of magnesian cements with varying conditions.

The Dow Chemical Co. has noted that minimum changes in volume occur when mortars are made up with a magnesium chloride solution of about 1.19 specific gravity. The burning conditions of the magnesite and the chemical composition of the plastic magnesia that results from burning or from storage both affect the contraction or expansion remarkably. Our observations on the changes in plastic magnesia due to exposure are given on page 94. The measurements are recorded as "Percentage expansion," which is given a negative value when contraction took place. In general, the fresh samples of plastic magnesia gave cements whose seven-day expansion was positive, but after exposure to the atmosphere for varying periods of time it gave mortars that had a negative expansion (contraction). To prepare mortars that have no change in volume may be possible, but probabilities are against it, as test pieces stored in atmospheres of different humidity would give different sets of figures. The state of dampness of a sample of magnesium oxychloride cement is probably the greatest single influence on the change in volume.

WATER-RESISTANCE TESTS

For practical purposes the Dow Chemical Co. has developed a special rain test for stuccoes. A panel of stucco is sprayed for various periods of time and its properties are then studied. One surprising effect is that when sprayed with water equivalent to about a year's rainfall, many stuccoes lose at least half of their chlorine content, but still retain their strength. This agrees with the theory that magnesium oxychloride cement is not an oxychloride—that the magnesium chloride merely assists the hydration of the magnesium oxide. The most resistant materials are those in which the aggregate has been proportioned to give a minimum of voids in the mortar.

REPRODUCIBILITY OF PHYSICAL TESTS

When we found that it was difficult to produce mortars of the same consistence with the same amounts of solutions on the same dry mixes at different times, we undertook a series of tests on the reproducibility of results. Table 36 gives tensile tests of three different magnesias over about three months. The same materials were kept in tight storage cans and mixed up into mortars on the dates given in the table. Possibly the personal factor in the mixing of the mortars by hand is a disturbing element because the later tests are shown to be more nearly reproducible. The table is presented mainly to show the variations that are met in testing the physical properties of plastic magnesia by the methods described above.

TABLE 36.—*Reproducibility of results, tensile strength*

Sample No.	Date	Consistence No.	$MgCl_2$ solution	Tensile strength		
				1 day	7 days	28 days
			C. c.	*Lb. per. sq. in.*	*Lb. per sq. in.*	*Lb. per sq. in.*
M-45-A	Oct. 11, 1920	14	190	203	349	459
	Dec. 2, 1920	14	157	210	434	550
	Dec. 8, 1920	14	156	293	486	450
	Jan. 19, 1921	14	155	160	420	576
	Jan. 24, 1921	14	155	261	519	864
	Jan. 27, 1921	14	155	230	476	769
M-37	Sept. 24, 1920	16	180	277	271	468
	Jan. 19, 1921	18	152	460	498	572
	Jan. 24, 1921	15	152	414	545	706
	Jan. 27, 1921	15	152	469	566	706
M-22	Sept. 2, 1920		160	374		366
	Oct. 27, 1920	14	160	286	298	330
	Feb. 4, 1921	17	151	392	455	574
	Feb. 11, 1921	18	151	407	549	648

Fortunately it was possible to arrange for the making of simultaneous tests of the same materials by our laboratory at Berkeley, Calif., and that of the Dow Chemical Co., at Midland, Mich. Results of tests of five samples are tabulated in Table 37; they indicate that at Berkeley the experimenters almost invariably used more magnesium chloride solution per gram of plastic magnesia in the mix. The setting times at Berkeley were also uniformly less than at Midland. The tensile-strength figures agree fairly well, although the Berkeley results are somewhat lower than those at Midland; the same is true for the modulus of rupture. The greatest disagreement comes in the expansion tests, although there are many excellent checks, and both series of figures fall in about the same order when one magnesia is compared with another. Inasmuch as the industry is yet in an experimental stage, the agreement of results is all that could be expected.

SPECIFIC GRAVITY

We have determined the specific gravity of a number of samples of commercial plastic magnesia. Other things being equal, the oxide that has the lower apparent specific gravity seems to give the better results. The true specific gravity, as determined in the Le Chatelier flask, varies from 2.87 to 3.25. Of these two samples the one that had the smaller specific gravity weighed 38.2 pounds per cubic foot and the other 48.4 pounds, which shows that the bulk weight of ground plastic magnesia increases somewhat faster than the true specific gravity.

Table 37.—*Comparison of results on Chewelah magnesite* [a]

Sample No.	Burned at—		MgCl$_2$ solution per gram of MgO	Setting time		Tensile strength			Modulus of rupture	Expansion		
	Temperature	Size lump		Initial	Final	1 day	7 days	30 days		1 day	7 days	30 days
	° C.	*Inch*	*C. c.*	*H. m.*	*H. m.*	*Lbs. per sq. in.*	*Lbs. per sq. in.*	*Lbs. per sq. in.*		*Per cent*	*Per cent*	*Per cent*
45-9-A	738	⅛	1.40	-- 30	1 45	222	362	520	1260	−0.03	−0.04	−0.06
			1.48	-- 20	-- 55	264	369	480	1027	+.03	----------	+.03
45-9-B	751	⅛	1.50	-- 15	-- 45	250	368	522	1248	+.02	+.06	−.10
			1.62	-- 15	-- 40	232	329	465	911	+.23	+.20	+.22
45-8	779	⅛	1.42	2 15	3 00	351	527	638	1500	+.09	+.09	+.09
			1.54	1 40	2 30	476	453	629	1268	+.08	+.18	+.22
46-B	782	½	1.45	2 30	4 00	282	885	835	1620	+.19	+.30	+.30
			1.51	1 55	3 05	284	570	762	1571	+.22	+.29	+.31
46-A	845	½	1.50	3 00	4 30	185	638	663	1458	+.18	+.53	+.54
			1.51	1 40	3 00	219	420	679	1365	+.23	+.43	+.50

[a] Upper figures, Dow Chemical Co.; lower figures, Pacific experiment station, Bureau of Mines.

RECARBONATING FREE LIME IN BURNED MAGNESIA AND DOLOMITE

As noted earlier in this bulletin, experiments performed during this investigation established the fact that free or active lime had deleterious effects on the properties of magnesian cements. The active lime seemed to be free calcium oxide liberated during burning or easily hydrolyzed calcium silicates likewise formed during burning. A recent publication by Seaton, Hill, and Stewart,[15] of the Dow Chemical Co. laboratory, makes it unnecessary for us to present data to support this conclusion, as they investigated the subject more thoroughly than we did and proved quite definitely that the effect of these forms of active lime is likely to be harmful. They also found that, under some conditions freshly precipitated calcium carbonate can also prove injurious. The relationship between active lime and the physical properties of magnesian cements is evident only when average results are considered, because certain disturbing factors frequently allow a rather high lime mix to develop good physical properties or a low lime material to fall below expectations. Therefore, although active lime is not always a sure indication of poor quality in the plastic magnesia, it is to be regarded with suspicion.

We believed that if the free-lime content of a plastic magnesia could be reduced by converting it to the carbonate, the physical properties of the cements made from the magnesia should be improved. In fact, we thought that dolomite might be calcined at the temperature necessary for liberating most of the magnesium oxide and that any calcium oxide freed simultaneously might be recarbonated if the material were treated at lower temperatures with gas that contained carbon dioxide.

BASIC PRINCIPLES

The thermal decomposition curves of magnesium and calcium carbonates, given in Figure 19, present the data on calcium carbonate collected by Johnston and mentioned on page 12, and the corresponding data by Marc and Simek on magnesium carbonate. The carefully determined equilibrium curves of Marc and Simek gave 402° C. as the temperature at which magnesium carbonate has a dissocia-

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[15] Seaton, Max. Y., Hill, C. R., and Stewart, L. C., Action of lime in magnesium oxychloride cements: Chem. and Met. Eng., vol. 25, 1921, pp. 270–274.

tion pressure of 1 atmosphere. All other investigators find that about 575° C. is the temperature at which any reasonable speed of decomposition can be obtained. Our own work has shown that magnesium carbonate does not recarbonate appreciably at temperatures above 402° C., although at this temperature we were able to get about 4.6 per cent recarbonation in 16 hours.

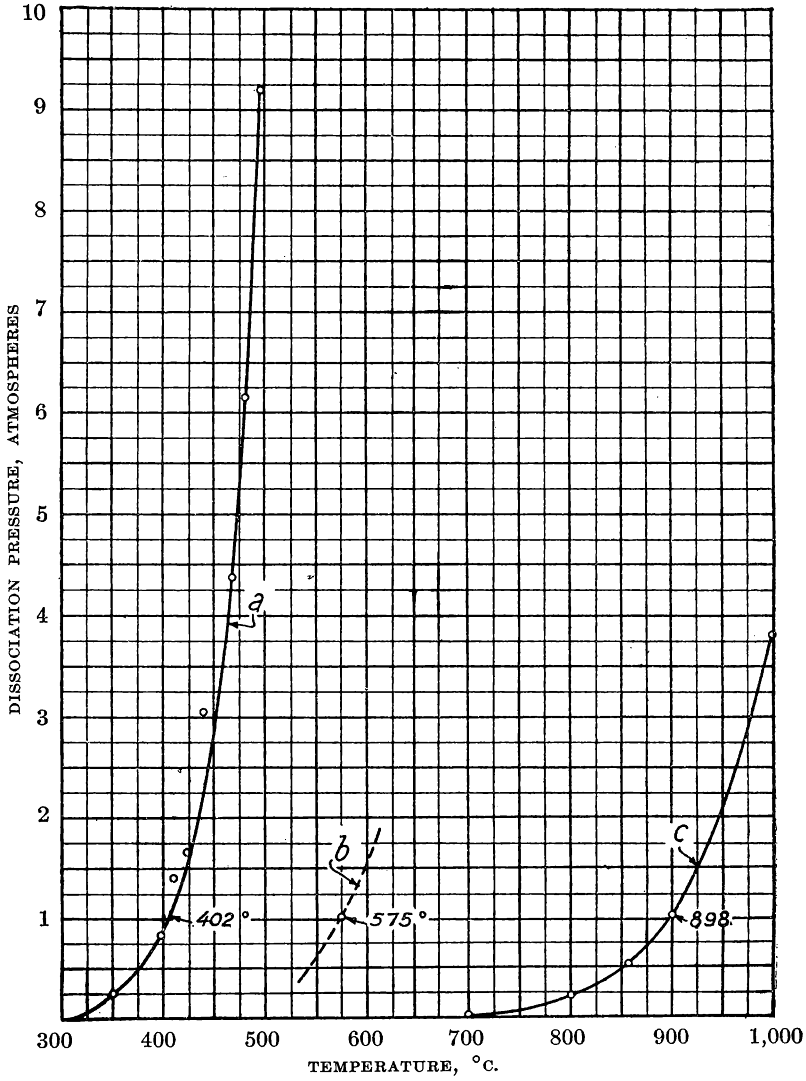

FIGURE 19.—Thermal decomposition of magnesium and calcium carbonates: *a*, Magnesium carbonate (Marc and Simek) of questionable value; *b*, magnesium carbonate, showing dissociation temperature for rapid heating, determined by the Bureau of Mines; *c*, calcium carbonate (Johnston)

On the other hand, calcium carbonate, according to its curve, should form by recarbonation of CaO at all temperatures under about 700° C. and at 800° C. the necessary pressure of carbon dioxide need be only about 0.24 atmosphere. Thus at the latter temperature a 24 per cent CO_2 flue gas from the calcining of magnesite would be enough to form calcium carbonate. At 850° C. one-half atmosphere pressure of carbon dioxide gas is needed. Fairly satisfactory plastic magnesia can be formed from magnesite at 750° C.; the pressure of CO_2 needed to prevent decomposition of the calcium carbonate present is about 5 per cent—a proportion that is easily attainable. Dolomite must be heated above 800° C. and preferably to about 900° C. to decompose the magnesium carbonate it contains, necessitating a rather high pressure of carbon dioxide. Conditions for calcining dolomite without making free lime are most easily attained by heating it in a retort without the access of flue gases.

CONTROL OF TEMPERATURE

We therefore conclude that careful control of the maximum temperature to which ordinary magnesites are subjected will prevent the liberation of free lime from the calcium carbonate present in the magnesite during burning. However, we thought that perhaps the best way to insure the absence of objectionable proportions of free lime would be to let the calcined material cool slightly and then to treat it with flue gases at temperatures between about 500° and 700° C., the safe operating range indicated in Figure 19, in which only calcium carbonate should be recarbonated. Practically all the successful experiments described in the following pages were carried out within this range of temperature. This principle was followed when burned dolomites were recarbonated so that only their magnesium oxide content was free, the calcium carbonate acting only as a filler or diluent and the magnesium oxide being in favorable condition to react with water and magnesium chloride to form magnesian cements.

INFLUENCE OF WATER VAPOR

The presence of water vapor in the recarbonation gases is also important. Hedvall[16] has shown that dry calcium oxide and dry carbon dioxide do not react. However, if the combustion gases from the ordinary calcination of the raw material are used for recarbonation, plenty of water vapor is present.

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[16] Hedvall, J. Arvid, Concerning the formation and decomposition temperatures of carbonates of calcium, barium, strontium, and magnesium at a pressure of one atmosphere: Ztscht. anorg. Chem., Bd. 98, 1916, p. 47.

This method of recarbonating free lime in plastic burned magnesia and dolomite was made the subject of a patent assigned to the Northwest Magnesite Co.[17]

ALLOWABLE AMOUNTS OF FREE LIME

Specifications of the associations of flooring manufacturers have frequently named about 3.5 to 4 per cent of CaO, indicated by chemical analysis, as the upper limit allowable in plastic magnesia. Our work and that of the Dow laboratory have shown that this limit should apply only to the free CaO and not to the total, since the $CaCO_3$ normally has no effect and we have been able to make excellent cements from properly treated dolomite. The Berkeley and the Dow methods of determining free lime (p. 65) are recommended as the proper test. However, we have made satisfactory cements with more than 4 per cent of free lime and believe the whole question deserves further investigation. For example, a high-lime sample from the Chewelah quarries containing 8 per cent free lime gave good tests, whereas that much free lime in the cryptocrystalline magnesites of California would almost certainly cause trouble.

Our work has shown that the free-lime content in most of the magnesites tested can be reduced much below 1 per cent by recarbonation. We were surprised to find that the physical properties of some of them were benefited very little and that those of some were even injured. Conditions under which the original magnesite was burned are far more important. However, for burned dolomites the effect has been marked; frequently the recarbonated material has contained less than 1 per cent of free lime and almost never over 2 per cent—well within the ordinary limits demanded by specifications for plastic magnesia.

EARLY EXPERIMENTS

Our first work was the treatment of small amounts of plastic magnesia samples in combustion tubes at temperatures from room temperature to 150° C. Under these conditions the magnesia absorbed as much water and carbon dioxide as did the lime, and little benefit was noticed from the free-lime content. We also tried turning a stream of damp carbon dioxide gas into the ball mill in which a sample of plastic magnesia was being reduced to the size necessary for use in cements. This method was likewise of little value and we then concluded that the material must be held at temperatures above the dissociation temperature of magnesium carbonate to recarbonate free lime only.

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[17] Pike, R. D., Method of treating magnesite. U. S. Patent 1,449,696, March 27, 1923.

FINAL EXPERIMENTS

With this in mind we used the horizontal electrically heated tube furnace employed in the earlier calcining experiments on magnesite which had internal dimensions 4 by 60 inches and could be rotated through a wide range of speeds. Carbon dioxide gas or mixtures of air and carbon dioxide were introduced at one end and allowed to escape from the other. The ends were plugged so that a batch of material could be placed in the furnace, heated to the necessary temperature and then treated with the carbonating gases for any time desired. We found in general that the rate of recarbonation increased as the temperature rose and that temperatures of 500 to 700° C. were quite satisfactory, as will be seen later.

The ends of the furnace were about 50° C. cooler than the middle where the thermocouple was placed; and in consequence a part of the material was not heated to the indicated temperatures; it must therefore be assumed that the average effective temperature in the furnace was 10° to 20° C. cooler than that given in our tables.

Most of our experiments were with a California dolomite and a Washington magnesite, although we made a few tests of other materials.

RECARBONATING CALCINED DOLOMITE

Owens Lake dolomite from the California Alkali Co., Cartago, Calif., was tested. It had the following analysis:

Analysis of Owens Lake dolomite

	Per cent
Insoluble	0.55
Iron oxide (Fe_2O_3)	.00
Silica (Al_2O_3)	.15
Lime (CaO)	30.40
Magnesia (MgO)	22.86
Ignition loss	46.04
	100.00

This dolomite was burned at temperatures up to 900° C. to make plastic magnesia, then recarbonated in the electrically heated rotating-tube furnace. In some experiments the CO_2 used was pure in others it was made into a 30 per cent mixture with air. The mixture was passed through a wash bottle to provide water vapor and the flow was measured with flowmeters. The experiments with mixed gas suffered because of heavy dust losses.

PRELIMINARY TESTS

The input of electrical current for heating the furnace was followed, and it was quite easy to observe any chemical reaction of the carbon dioxide on the solid material as heat was liberated; then the temperature either rose or the electrical input would have to be dropped to keep the temperature constant. We finally decided that we could obtain the best results by putting the sample of burned dolomite into the furnace, then raising the electric energy input to the point necessary for maintaining the desired temperature of the experiment. Next the stream of carbon dioxide was admitted and the temperature allowed to rise and finally fall when the reaction was over.

RECARBONATION TESTS

After these preliminary tests five recarbonation tests of the calcined Owens Lake dolomite were made. The results are tabulated in Table 38. In test G–7 only was a 30 per cent CO_2 gas used, all other tests being made with pure gas. The percentage efficiency of absorption of the carbon dioxide was as high in this test as in the others. The test at 200° C. showed that recarbonation was too slow at this temperature. In test G–8 the material was ground to pass a 30-mesh instead of a 4-mesh screen, the size used in all the other tests. This resulted in a higher rate of recarbonation, as shown by the rise in furnace temperature during the reaction.

TABLE 38.—*Recarbonation of calcined Owens Lake dolomite*[a]

Test	Size	Air	CO_2	Carbon dioxide gas—				Temperature		Final material	
				Added	Absorbed	For CaO	Efficiency	Start	Rise	Ignition loss	Free CaO
	Mesh	*Liters per minute*	*Liters per minute*	*Pounds*	*Pounds*	*Pounds*	*Per cent*	° *C.*	° *C.*	*Per cent*	*Per cent*
G–4	−4		5. 00	2. 025	1. 32	1. 28	65	400	115	30. 65	1. 05
G–5	−4		4. 95	2. 00	1. 23	1. 34	62	500	90	30. 80	. 33
G–6	−4		5. 10	2. 065				200	0	23. 10	9. 00
G–7	−4	10. 66	4. 98	2. 02	1. 23	1. 33	61	500	72	30. 80	. 52
G–8	−30		4. 90	1. 985	1. 15	1. 33	58	500	140	30. 20	. 50

[a] Material, M–48–B, 10 pounds to each charge, 100 minutes to each test. Original showed by analysis: 22.6 per cent ignition loss, 17.5 per cent free lime, and 1.16 per cent moisture.

CHANGES DUE TO CALCINATION

The material first used, which contained a high percentage of free lime, showed some difference between the amount indicated by analysis (12.5 per cent) and the amount which we calculated was present (17.5 per cent). However, free lime in the material last used was well within the limits ordinarily met in magnesites of satisfactory grade. The original material was worthless for making oxychloride cements, whereas some of our materials showed desirable characteristics after recarbonation. Table 39 shows the physical properties of oxychloride cements made up with the original material and two of the recarbonated dolomites.

TABLE 39.—*Physical tests of recarbonated dolomitic oxychloride cements*

Sample	Mixture	Gaging liquid	Consistency	Ratio $\frac{MgCl_2}{MgO}$	Setting time		Tensile strength			Expansion		
					Initial	Final	1 day	7 days	28 days	1 day	7 days	28 days
					Hours	*Hours*	*Lbs. per sq. in.*	*Lbs. per sq. in.*	*Lbs. per sq. in.*	*Per cent*	*Per cent*	*Per cent*
Original	1-2-5	$MgCl_2$	14	1.21	10.85	+31.9	None.	None.	None.	(?)	(?)	(?)
Do	2-1-5	do	14	.75	10.85	+31.9	30	38	None.	−0.69	−0.74	(?)
G-5	1-2-5	do	16	.88	4.03	5.7	140	127	124	+.14	−.05	+1.13
Do	1-2-5	50 per cent $CaCl_2$	16	.88	3.84	6.12	86	103	68	+.09	+.32	----------
G-8	2-1-5	$MgCl_2$	14	.50	1.70	2.96	286	381	345	+.41	+.62	+.63
Do	3-0-5	do	15	.349	2.11	3.3	379	569	589	+.25	+.38	+.38

The original calcined dolomite proved worthless for use in oxychloride cements, undoubtedly because of the high percentage of free lime it contained. Likewise, when calcium chloride was substituted for half of the magnesium chloride in the gaging liquid, the cement briquets were inferior in strength and expansion and failed completely when allowed to stand over seven days.

EFFECT OF $CaCl_2$

This effect of calcium chloride is of much interest, for it gives us additional insight into the reason why free lime is undesirable in plastic magnesia. When free lime can act on magnesium chloride solution, the following reaction occurs:

$MgCl_2+Ca(OH)_2=CaCl_2+Mg(OH)_2$[18]

indicating that calcium chloride is formed and that magnesium chloride is destroyed; and, if enough free lime is present, the concentration of the magnesium chloride solution will be so cut down that oxychloride cements will not form. Oxychloride cements can be made with calcium chloride; they set like magnesium oxychloride cements, but they deteriorate with time, until after 28 days very few of the briquets have any mechanical strength whatever. On the other hand, most magnesian cements improve with age. Therefore every effort should be made to convert lime to an insoluble unreactive condition so that it will not react with the magnesium chloride solutions.

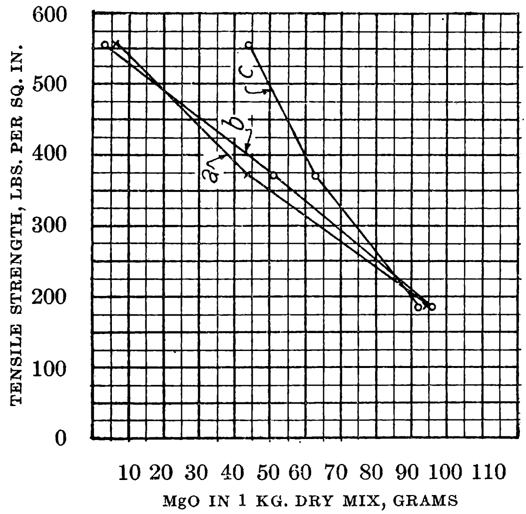

Figure 20.—Relation between tensile strength and MgO content of briquets of recarbonated calcined dolomite: *a*, 7 days; *b*, 28 days; *c*, 1 day.

PROPORTIONING OF MIXES

By proper proportioning of mixes it was possible to get cements of good physical properties. Since about 70 per cent of the recarbonated dolomite is inert material, the amount of silex ordinarily

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[18] Shaw, J. B., and Bole, G. A., New developments in oxychloride stucco and flooring: Jour. Am. Cer. Soc., vol. 5, 1922, p. 315.

used in briquets made with pure magnesia should be reduced. The ordinary 1–2–5 mix used for stucco contains 1 part of plastic magnesia, 2 parts of finely ground silica (silex), and 5 parts of standard testing sand. We found that by leaving out the silex and using a 3–0–5 mix with recarbonated dolomite and standard sand, excellent cements were made which were, indeed, more satisfactory than the standard 1–2–5 mixes prepared with 85 per cent plastic magnesia. It is, therefore, well to refer to the actual MgO content as a criterion. Figure 20 shows the relation between the MgO content and the tensile strength of briquets we made from recarbonated calcined dolomite. None of the mixes we made had received the maximum useful proportion of MgO. The curves in Figure 21 are even more interesting because they show the relation between the age of the briquets and the tensile strength for various mixes. A progressive change in the shape of the curves from the 1–2–5 mix to the 3–0–5 mix is noticeable; it is probably connected with the change in the ratio of $MgCl_2$ to MgO. On that account, the curves in Figure 22 were prepared to show the effect of this ratio on the tensile strength and the change in volume of the briquets. There is at least a smooth relation in the tensile strength curves, but the expansion curves are difficult to interpret.

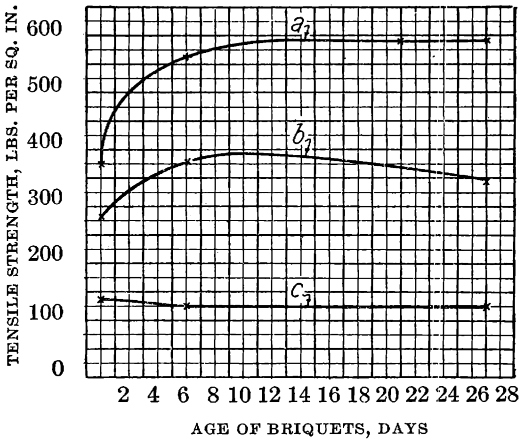

FIGURE 21.—Relation of tensile strength to age of dolomite oxychloride briquets, different mixes: *a*, 3–0–5 mix; *b*, 2–1–5 mix; *c*, 1–2–5 mix

SETTING TIME OF MIXES

One peculiarity of recarbonated dolomites is their setting time. Although plastic magnesia takes up water and carbon dioxide when exposed to the atmosphere, with a corresponding increase in setting time, and recarbonation at the temperatures at which the dolomites were recarbonated also increases the setting time of the magnesites to some extent, these dolomites all have rather low setting times in comparison; this action could not be satisfactorily explained. Possibly the recarbonation of lime in a calcined dolomite caused it to "swell" and displace the MgO molecules from the space lattice in which they occurred, thus allowing greater activity of this MgO than with normal MgO. On the other hand in a plastic magnesia this swelling from the presence of small amounts of lime would not occur, but a little of the magnesium oxide on the surfaces of the particles is undoubtedly recarbonated, and reduces the effective activity of the magnesia. In the dolomite the increased activity due to the disruption of the crystal form by recarbonation must outweigh the decreased activity due to the surface carbonation of the particles of magnesia.

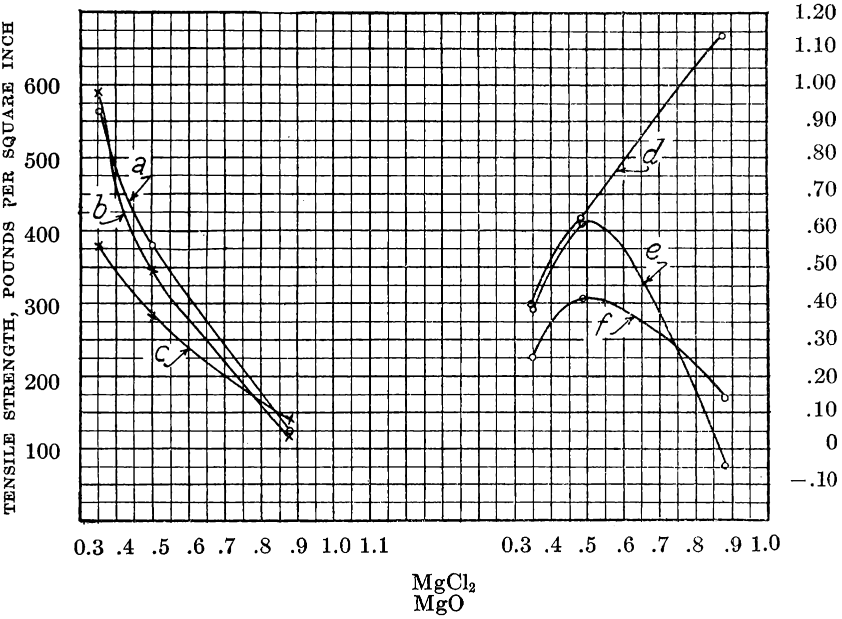

FIGURE 22.—Effect of ratio $MgCl_2$: MgO on tensile strength and expansion of dolomitic oxychloride cement briquets: *a*, Tensile strength after 7 days; *b*, after 28 days; *c*, after 24 hours; *d*, expansion after 28 days; *e*, after 7 days; *f*, after 24 hours

We made physical tests of one dolomite only, but later tests by Bole and Shaw mentioned on page 24 showed that many other dolomites produced satisfactory cements when calcined so that all the calcium remained in the material as carbonate. However, certain dolomites—particularly those that contain silica, iron, and alumina—must be tested carefully to determine the effects of recarbonation when some of these constituents have caused slagging or sintering.

RECARBONATING CHEWELAH MAGNESIA

Several samples of plastic magnesia made from Chewelah magnesite, chosen because of their varying contents of free lime, were tested for recarbonation for the same length of time and in the same apparatus as that used for the dolomite. Free lime was added to a few of the samples to test the effect of lime that was definitely known to be free. The results of these recarbonating tests appear in Table 40.

TABLE 40.—*Recarbonation of calcined Chewelah magnesite*

Test	Material	CaO added	Size	Temperatures		CO^2 efficiency	Free lime		Carbonated	
				Start	Rise		Original	Final	CaO	MgO
		Per cent	*Mesh*	° *C*	° *C*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
G-9	M-29-A		82 per cent −200	500	2	14. 27	1. 24	0. 28	79. 0	0. 50
G-10	M-45-A		−4	500	32	35. 1	4. 31	. 49	88. 2	. 22
G-11	do		70 per cent −200	500	49	35. 1	4. 12	. 49	87. 9	. 33
G-18	M-45-B		−4	500	25	35. 1	2. 70	. 47	82. 6	1. 53
G-19	M-46-A		−2	500	30	40. 6	3. 23	. 44	86. 8	1. 64
G-20	M-29-A	3	70 per cent −200	500	35	24. 1	3. 56	. 61	82. 9	
G-28	do	3	−30	503	37	18. 7	3. 62	. 83	77. 0	
G-22	M-45-A		71 per cent −200	600	40	26. 3	3. 48	. 55	84. 2	. 11
G-23	do		76 per cent −200	300	5	12. 1	3. 48	3. 31	4. 9	1. 06
G-31	do		−4	400	12	20. 0	3. 48	1. 51	56. 6	. 33
G-26	M-29-B		−30	500		8. 8	. 58	. 33	43. 1	

CONCLUSIONS

The following conclusions may be drawn from the figures in Table 40:

1. A temperature of 300° C. is not high enough for satisfactory recarbonation of the free lime, and some of the magnesia is inclined to recarbonate at that temperature.
2. A temperature of 400° C. is somewhat low, but 500° to 600° C. is satisfactory with respect to speed and efficiency of gas absorption and carbonation of the free lime.
3. Free lime added to the magnesia is carbonated like the free lime originally present.
4. Fairly coarse material is as efficiently carbonated as that which is finely ground.
5. At 500° to 600° C. the free lime in the recarbonated material should not amount to 1 per cent, obtained with a gas efficiency of over 30 per cent.

In order to compare the physical tests of recarbonated plastic magnesia with those of ordinary material, Table 41 has been prepared to give five parallel pairs of tests of some of the materials whose recarbonation data are presented in Table 40. These tests are chosen from a great number to illustrate the facts discovered. All were made up into the regular 1–2–5 stucco mix for tests, magnesium chloride solution of 1.19 specific gravity being used and the $MgCl_2$ to MgO ratio determined from the known MgO content of the various samples.

TABLE 41.—*Physical tests of recarbonated Chewelah magnesia*

Material	Carbonation test No.	Consistence	Ratio $MgCl_2$ to MgO	Setting time		Tensile strength			Expansion		
				Initial	Final	1 day	7 days	28 days	1 day	7 days	28 days
				Hour	*Hour*	*Lb. per sq. in.*	*Lb. per sq. in.*	*Lb. per sq. in.*	*Per cent*	*Per cent*	*Per cent*
M-45-A	--------	14	0.393	--------	--------	166	542	629	0.31	0.48	0.45
	G-11	14	.393	4.2	6.0	150	497	632	.16	.18	.24
M-46-B	--------	14	.395	1.9	3.1	284	570	762	.22	.29	.31
	G-33	14	.395	3.1	4.5	279	560	780	.15	.29	.27
M-45-8	--------	14	.402	1.7	2.5	576	643	459	.07	.16	.20
	G-27	15	.437	1.6	2.3	495	661	589	.08	.03	.05
M-45-7B	--------	15	.414	1.4	2.8	390	496	366	.15	.18	.22
	G-18	15	.414	3.6	4.8	393	429	395	.10	.32	.31
M-29-B	--------	14	.390	.09	.42	352	398	376	.02	.12	.12
	G-26	14	.382	.10	.48	352	419	392	.04	.37	.05

EFFECTS OF RECARBONATION

Inspection of this table shows that recarbonation has the most marked effect on the setting time, which increased quite uniformly in every test for every sample but one. The greatest effects on setting time were noted in the materials that contained the most free lime.

The tensile strength of the 28-day briquets and often that of briquets not exposed so long also increased quite uniformly, although some other minor variable is involved here.

When we examined our records, we noted that recarbonation tended to show greater improvement in lightly burned materials that contained a small amount of free lime, a fact contrary to expectations based on the previously reported favorable tests of dolomites. This fact may indicate that even small amounts of free lime could be recarbonated to advantage, although recarbonation generally seems to reduce expansion, it is evident that other more important factors determine what the expansion of a mortar shall be.

The chemical improvement due to recarbonation has been conclusively demonstrated; but the physical changes in the magnesites tested, unlike those in the dolomite, are seldom important enough to establish recarbonation as a commercially valuable process. The increase in tensile strength is quite definite, but does not warrant much extra expense for recarbonation. If the calcined material can be recarbonated in the flue gases from the burning kiln with little extra cost of power or labor it might be worth while to recarbonate all the calcined material—except when a quick-setting plastic magnesia is desired.

TESTS OF IMPURE MAGNESITES

Several samples of plastic magnesia made from magnesites containing high amounts of silica were tested after recarbonation. The results were erratic. The lime always tended to form silicates that would react with the magnesium chloride solution to liberate the lime again, and these silicates were not affected by the recarbonation. The results on these impure magnesites were therefore conflicting and indefinite.

GENERAL CONCLUSION

Recarbonation of free lime in burned dolomite or plastic magnesia, in order that these materials will yield satisfactory magnesian cements, has proved of great value for dolomites, but of doubtful value for magnesites, although they are benefited to some extent. The results of the work on dolomites in the United States is quite interesting.

The big centers of consumption of plastic magnesia are in the Eastern States, whereas the only producing districts of the country are in California and possibly Washington. This condition makes plastic magnesia delivered in the East decidedly expensive. On the other hand, large supplies of good dolomite are available in the East and our tests have shown that recarbonated dolomite makes very satisfactory stuccoes. Dolomite does not contain enough magnesia for flooring cements, which usually require over 40 per cent MgO. However, since 80 per cent of the plastic magnesia sold is used for stucco, recarbonated calcined dolomite could satisfactorily supply most of the demand for plastic magnesia.

Research undertaken to show the suitability of Chewelah crystalline magnesite for the manufacture of plastic magnesia, while accomplishing its purpose definitely and satisfactorily, incidentally discovered a process for using dolomite in magnesian mortars which may well prove commercially important. This discovery indicates a use for vast deposits of pure dolomite near eastern consuming centers and may revolutionize the magnesian mortar industry.

EFFECT OF EXPOSURE ON PLASTIC MAGNESIA

EXPOSURE TO WATER

Plastic magnesia is not as strongly inclined to slake as plastic or caustic lime, but takes up moisture and carbon dioxide from the air slowly. A great deal of water can be poured over a load of plastic magnesia without the properties being visibly affected, provided the magnesia does not soak too long. However, experience in Germany as reported by Verwey,[19] shows that burned magnesite damaged by water has lost most of its value for industrial purposes. Magnesite has been observed to gain weight during shipment and consequently to become lower in magnesium oxide. Just how much ordinary exposure in handling would affect the properties of the plastic magnesia was not known. Some of the American manufacturers of flooring have noticed that in general a certain amount of "aging" improves the quality of plastic magnesia, making a floor tougher and more elastic, although the cement is slower in setting.

EXPOSURE TO AIR

We therefore undertook to determine the effect of exposure in order to ascertain what might occur during storage and whether the changes that take place would demand special storage facilities. Exposure conditions were purposely accelerated by placing samples of finished plastic magnesia (calcined and finely ground) in thin 1.5 to 2 inch layers on the bottoms of shallow pans and mixing the material thoroughly once a day, 6 days a week, for 60 days.

A rack was built on which were placed galvanized iron pans 3 inches deep and 36 inches square, as shown in Plate XIII, *A*. Plate XIII, *B*, shows the method of turning over the magnesia daily. Enough material for making complete physical and chemical tests was withdrawn from time to time. Material was tested after intervals of 7, 28, and 60 days. After the tests were completed and the results had been plotted, it was seen that tests should also have been made at the end of 3 days and that the 7-day tests were somewhat out of harmony with the others. However, as some difficulty was experienced in preparing the briquets and bars at the time of the 7-day tests, the curves were drawn without reference to those 7-day

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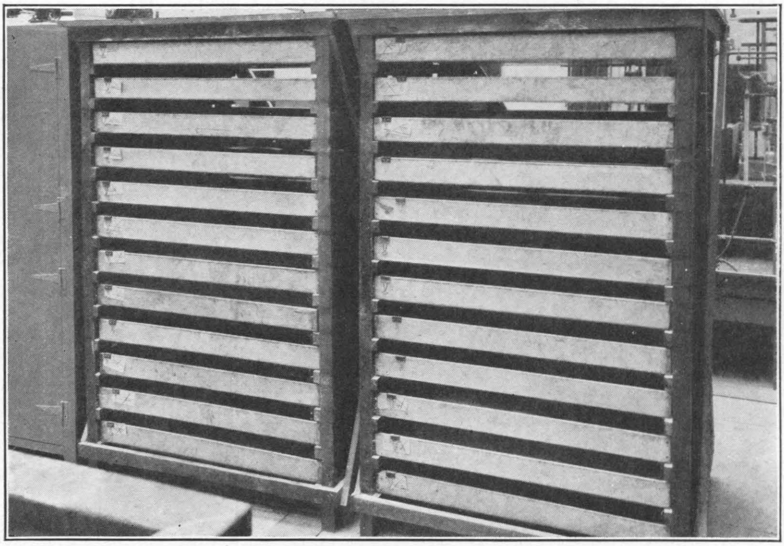
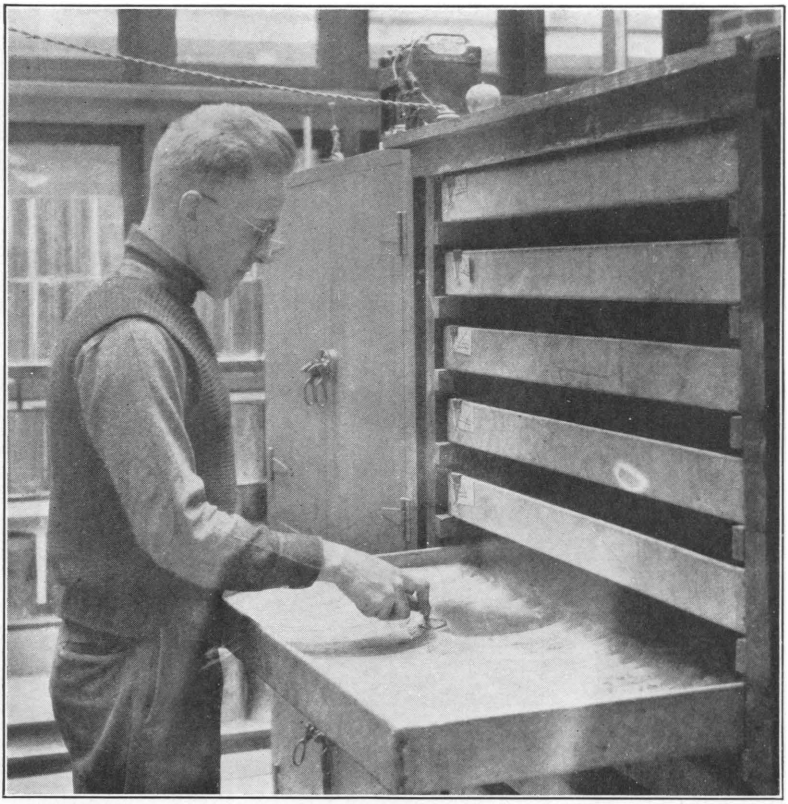
[19] Verwey, A., Über die Probenahme und die Beurteilung von calciniertem Magnesit: Chem. Ztg., Jahre. 37, 1913, p. 813.



A. RACK WITH PANS FOR EXPOSING SAMPLES OF PLASTIC MAGNESIA TO THE AIR



B. METHOD OF TURNING OVER PLASTIC MAGNESIA DURING EXPOSURE

tests that gave results far below the other tests. We believe that weathering slows down the development of strength, so that the tensile strength tests of chief interest are those made after 28 days.

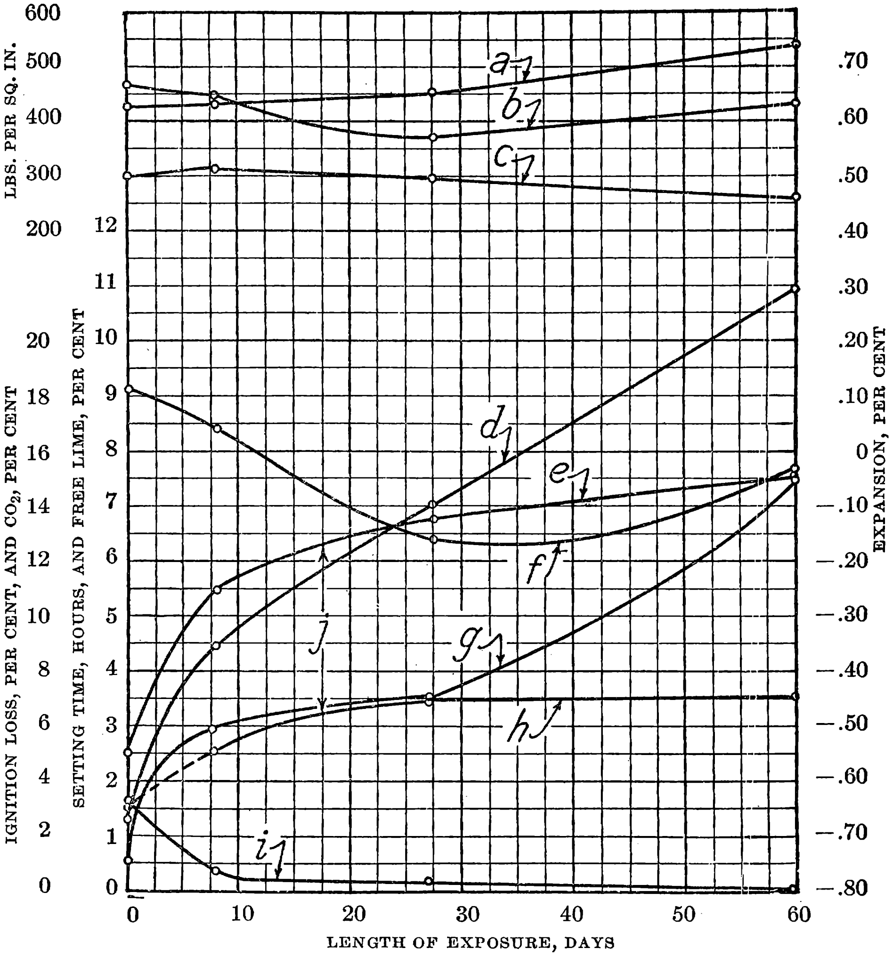


FIGURE 23.—Exposure tests of plastic magnesia from crystalline magnesite. Source, Chewelah, Wash. Sample, M–33. Calcined in Herreshoff furnace, Berkeley laboratory, Bureau of Mines. Curves give chemical properties of material after exposure to laboratory air in a thin bed turned over daily, and physical properties of cements made from the exposed magnesia: *a*, Tensile strength, 28 days; *b*, tensile strength, 7 days; *c*, tensile strength, 1 day; *d*, final set, hours; *e*, ignition loss, per cent; *f*, per cent expansion, 7 days; *g*, initial set, hours; *h*, carbon dioxide, per cent; *i*, free lime, per cent. (Fineness: +100 mesh, 8.72 per cent; +200 mesh, 30.68 per cent; —200 mesh, 69.32 per cent)

The complete data for 5 out of 8 of these tests are presented as curves in Figures 23 to 27. These curves show the percentage of carbon dioxide, the total ignition loss (carbon dioxide and moisture), the percentage of free lime, the time of initial set and final set of cements made with the plastic magnesia, the expansion 7 days

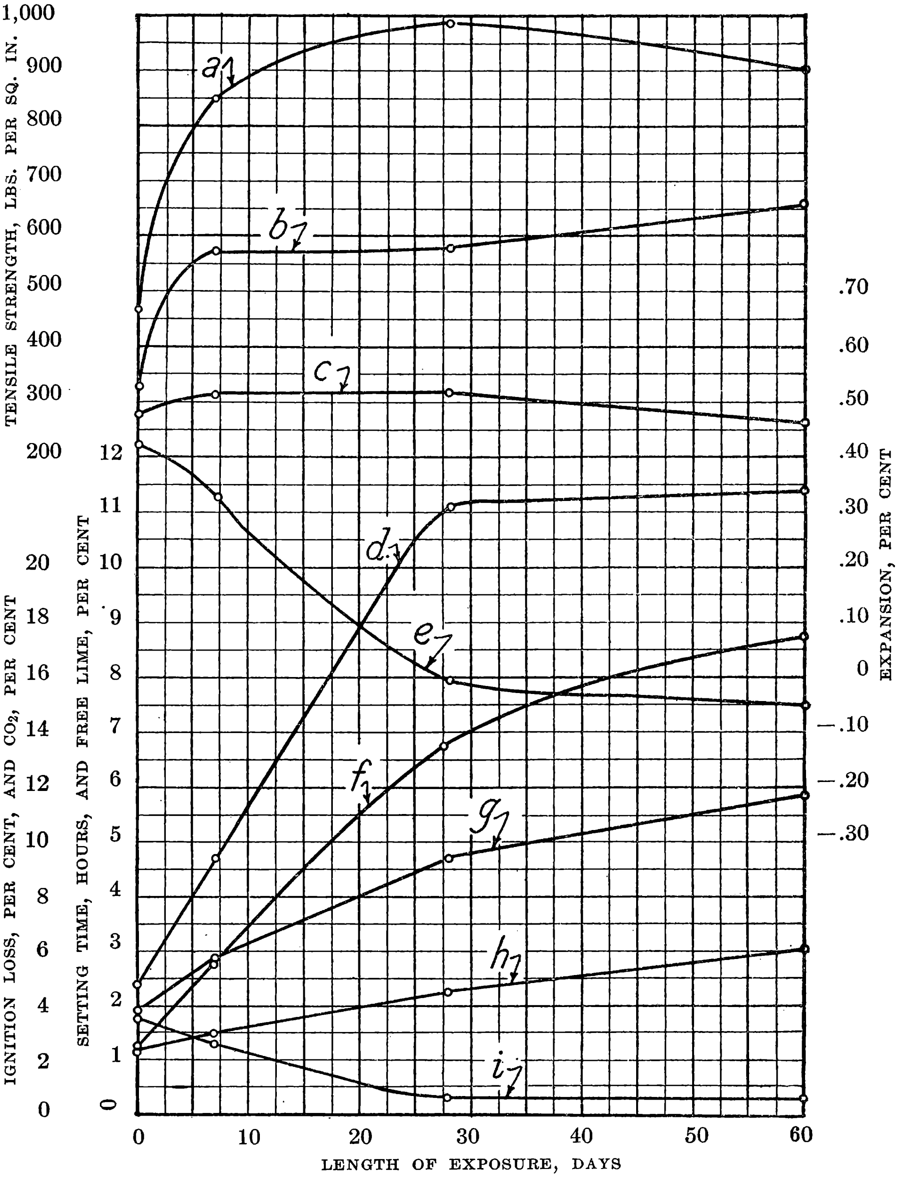


FIGURE 24.—Exposure tests of plastic magnesia from crystalline magnesite. Source, Chewelah, Wash. Sample M–45–B. Calcined in Herreshoff furnace, Berkeley laboratory, Bureau of Mines. Curves give chemical properties of material after exposure to laboratory air in a thin bed turned over daily, and physical properties of cements made from the exposed plastic magnesia: *a*, Tensile strength, 28 days; *b*, tensile strength, 7 days; *c*, tensile strength, 1 day; *d*, final set, hours; *e*, expansion, per cent; *f*, initial set, hours; *g*, ignition loss, per cent; *h*, carbon dioxide, per cent; *i*, free lime, per cent. (Fineness: +100 mesh, 2.30 per cent; +200 mesh, 12.46 per cent; —200 mesh, 87.54 per cent)

after the cement was mixed, and the tensile strengths 1, 7, and 28 days after the mixing of the cements. In spite of the fact that these curves represent a great deal of work, they leave much to be desired.

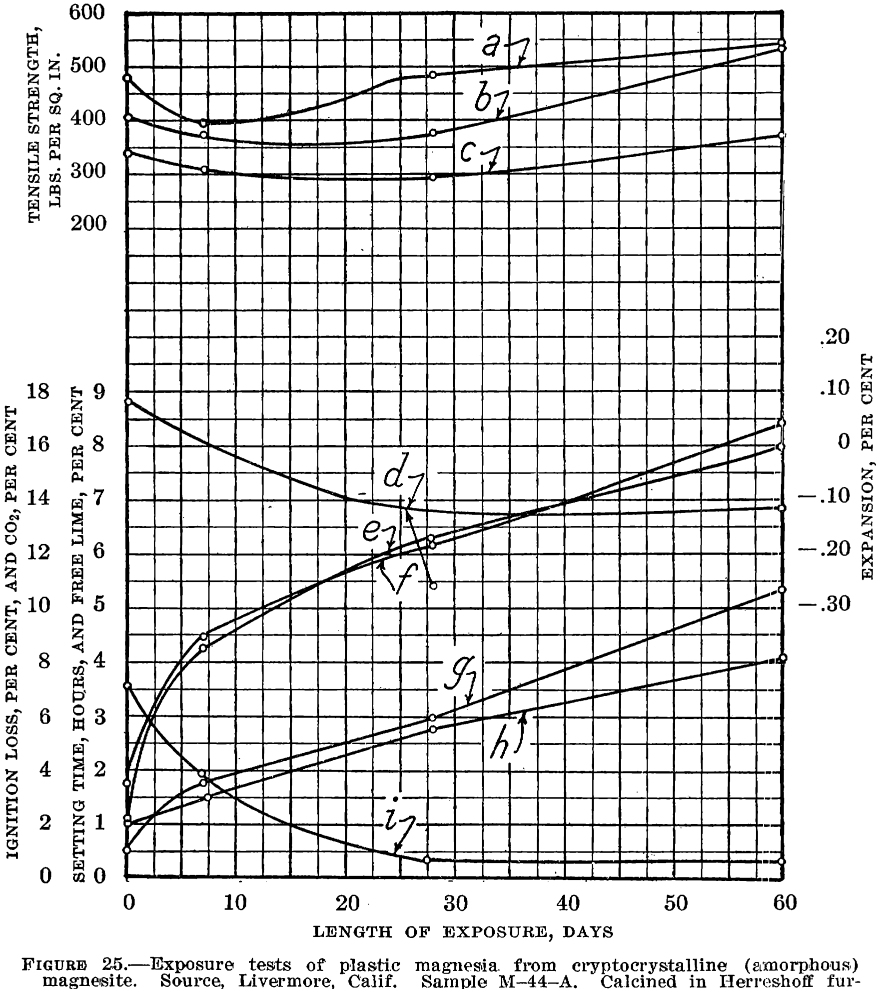


FIGURE 25.—Exposure tests of plastic magnesia from cryptocrystalline (amorphous) magnesite. Source, Livermore, Calif. Sample M–44–A. Calcined in Herreshoff furnace, Berkeley laboratory, Bureau of Mines. Curves give chemical properties of material exposed to laboratory air in a thin bed turned over daily, and physical properties of cements made from the exposed plastic magnesia: *a*, Tensile strength, 28 days; *b*, tensile strength, 7 days; *c*, tensile strength, 1 day; *d*, expansion, 7 days; *e*, ignition loss, per cent; *f*, final set, hours; *g*, initial set, hours; *h*, carbon dioxide, per cent; *i*, free lime, per cent. (Fineness: +100 mesh, 14.58 per cent; +200 mesh, 43.18 per cent; −200 mesh, 57.80 per cent)

The five samples tested represent crystalline and microcrystalline magnesites furnaced in different ways. The crystalline material came from Chewelah, Wash., and the microcrystalline or amorphous material from Livermore, Calif. In general the two different kinds of magnesite give a series of closely comparable products.

CONCLUSIONS ON EXPOSURE

The general conclusions on the effects of exposure are as follows:

1. Exposure of plastic magnesia to contact with the atmosphere for 60 days, under conditions permitting rapid absorption of carbon dioxide and moisture, causes much absorption of these two compounds, and the absorption continues beyond 60 days.

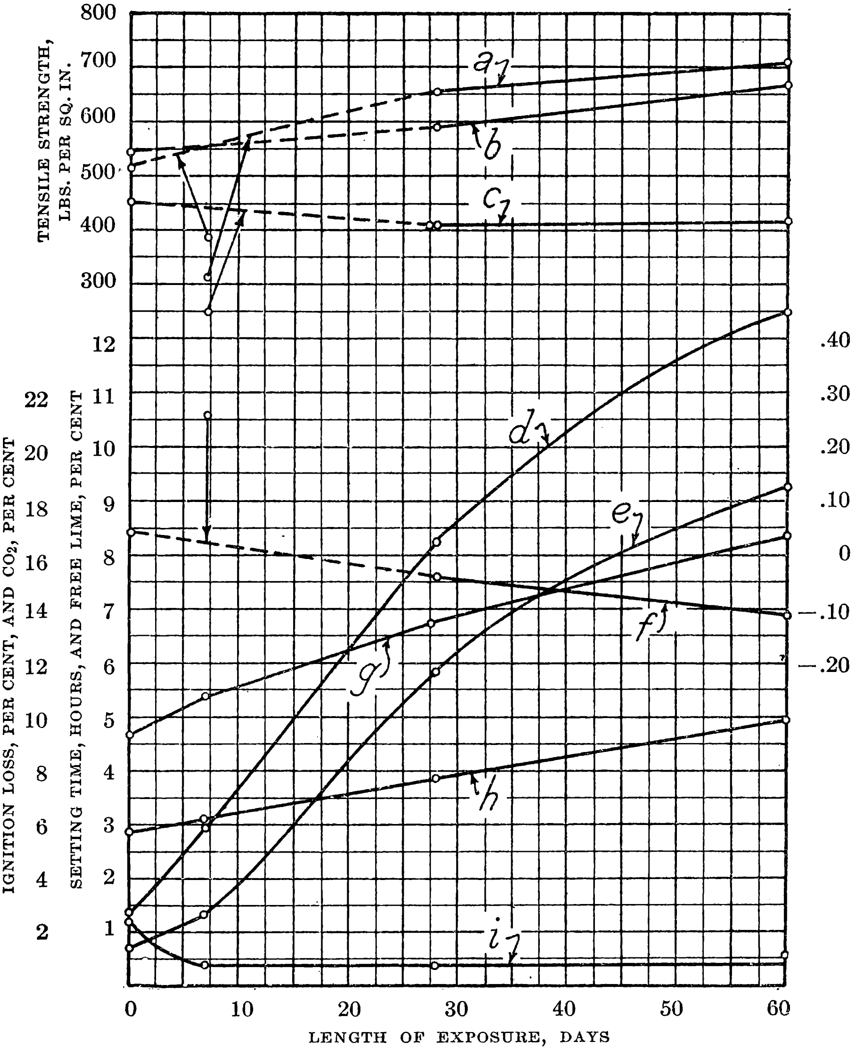


FIGURE 26.—Exposure tests of plastic magnesia from cryptocrystalline (amorphous) magnesite. Source, Livermore, Calif. Sample M–51. Calcined in commercial Scott furnace. Curves give chemical properties of material after exposure to laboratory air in a thin bed turned over daily, and physical properties of cements made from the exposed plastic magnesia: *a*, Tensile strength, 28 days; *b*, tensile strength, 7 days; *c*, tensile strength, 1 day; *d*, final set, hours; *e*, initial set, hours; *f*, per cent expansion, 7 days; *g*, ignition loss, per cent; *h*, carbon dioxide, per cent; *i*, free lime, per cent. (Fineness: +100 mesh, 36.60 per cent; +200 mesh, 52.94 per cent; —200 mesh, 47.06 per cent.)

2. The percentage of "free lime" diminishes steadily with exposure to the air, evidently because more or less lime is carbonized in preference to the magnesia.

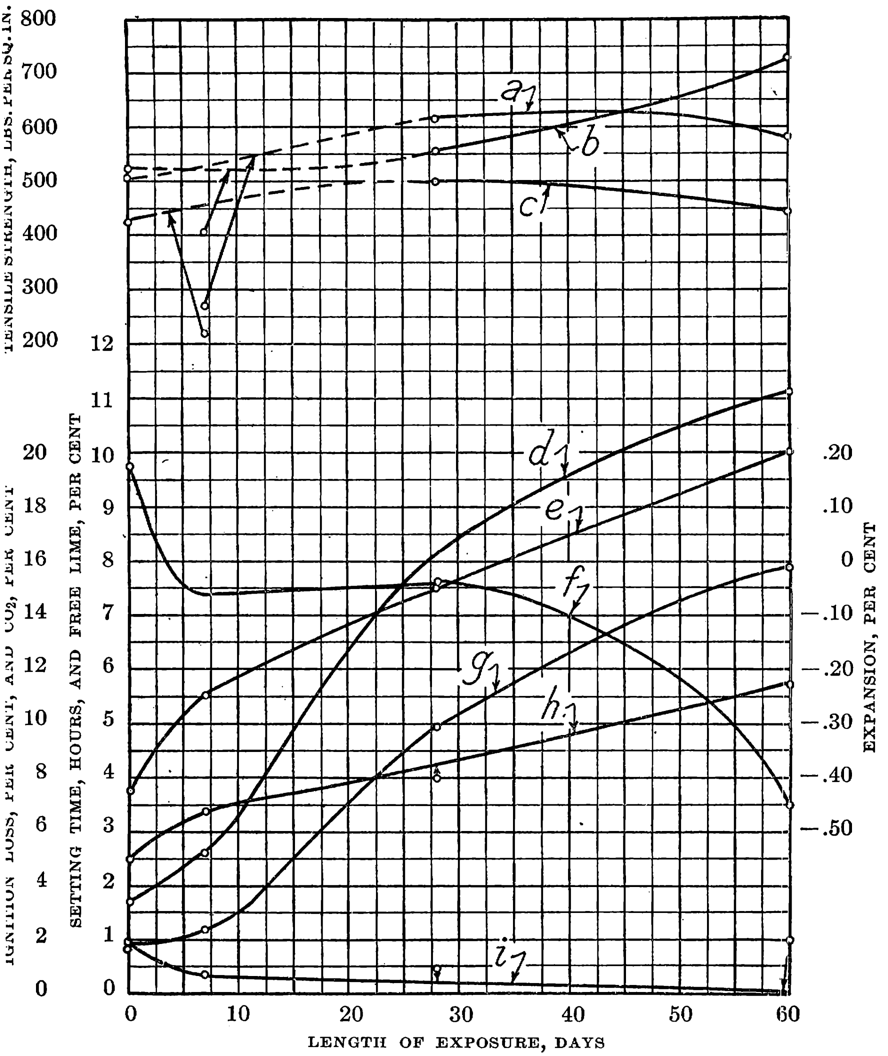


FIGURE 27.—Exposure tests of plastic magnesia from cryptocrystalline (amorphous) magnesite. Source, Livermore, Calif. Sample M–52. Calcined in commercial stack furnace. Curves give chemical properties of material exposed to laboratory air in a thin bed turned over daily, and physical properties of cements made from the exposed plastic magnesia: *a*, Tensile strength, 7 days; *b*, tensile strength, 28 days; *c*, tensile strength, 1 day; *d*, final set, hours; *e*, ignition loss, per cent; *f*, expansion per cent, 7 days; *g*, initial set, hours; *h*, carbon dioxide, per cent; *i*, free lime, per cent. (Fineness: +100 mesh, 11.02 per cent; +200 mesh, 35.62 per cent; —200 mesh, 65.64 per cent.

3. Exposure of plastic magnesia increases the time necessary for the initial and final set of cements made from it, and the curves indi-

cate that still longer exposure would increase the time. This is one of the most positive effects observed.

4. In general exposure increases the tensile strengths of magnesian cements, although some briquets (during the earlier days of exposure and while freshly made) showed less tensile strength than the original freshly burned magnesite. However, with only one exception the tensile strength of 28-day briquets (made from material exposed to the atmosphere for 60 days) was increased noticeably.

5. Cements made from exposed material expanded less. Each mortar made from unexposed material showed expansion after 7 days and each mortar made from the material weathered for 60 days showed contraction.

SUMMARY

If care is taken not to lengthen the setting time beyond practical limits the other physical properties are improved by exposing plastic magnesia to the atmosphere. Just how many months of storage in barrels or in sacks would be equivalent to the various periods of exposure given our material is difficult to determine; and of course this time would vary with the tightness of the barrels or sacks and the method of piling them. It would probably take several years of storage in loose containers before the plastic magnesia could alter as much as it did in 60 days in these accelerated tests. As mentioned above, any changes that take place, with the possible exception of lengthening the time of setting too much are desirable.

EFFECTS OF EXPOSURE

The marked change in setting time caused by exposure suggests that when a definite time of set is specified material might be deliberately exposed in thin layers until it acquires the desired characteristic and then be packed for shipment. This procedure promises to be a valuable method of control, and it is recommended that large-scale tests on exposure be undertaken by interested operators.

A few tests of accelerated exposure to carbon dioxide and moisture were made by exposing small lots of plastic magnesia, lime, calcined dolomite, and other materials to atmospheres enriched with moisture and carbon dioxide under various temperatures up to that of steam. Duration of treatment ranged up to 60 hours and all materials showed great increases in weight. However, no physical tests of the end products were made. We have little doubt that proper methods of processing plastic magnesia would give desirable products in much less time than was required for the main series of tests above reported.

EFFECTS OF STANDING

Another feature to be considered was the effect of long standing on the composition of a magnesium oxychloride mortar. A 2-inch cube of such a mortar, molded on December 6, 1909 (12 years before the following test was made), and left standing in air during that time, was given for the experiment by Prof. A. C. Alvarez, of the department of civil engineering, University of California. The composition of the original mortar had been as follows:

Composition of mortar

Magnesia (from Red Mountain, Calif.)	1 part
Monterey sand	4 parts
$MgCl_2$ solution (sp. gr. 1.23)	13 per cent

A chemical analysis, made by W. C. Riddell, of the final block of material follows:

Analysis of aged magnesium oxychloride mortar

ANALYSIS	Per cent	CALCULATED	Per cent
Insoluble	62.85	Insoluble	62.8
Chlorine (Cl)	2.98	Magnesium chloride ($MgCl_2$)	4.0
Alumina, iron oxide (Al_2O_3, Fe_2O_3)	Trace.	Magnesium carbonate ($MgCO_3$)	4.6
Lime (CaO)	0.84	Calcium carbonate ($CaCO_3$)	1.5
Magnesia (MgO)	15.00	Magnesia (MgO)	11.8
Water, below 110° C	5.65	Water, below 110° C	5.6
Water, above 110° C	9.00	Combined water	9.0
Carbon dioxide (CO_2)	3.10	Total	99.3
Total	99.42		

The particular point to be noted in this analysis is the small amount of carbonate in the material after long exposure to the atmosphere. However, few of the present uses of magnesia for stucco or flooring contemplate the use of cement much more than one-half inch thick and the behavior of this 2-inch cube merely shows the slowness of the changes in thick layers.

BEHAVIOR OF SILICA DURING THE BURNING OF MAGNESIA

In order to determine the value of siliceous magnesite, a number of tests were arranged, because it was suspected that silica might combine with magnesia during the burning of the material and form silicates of magnesium which might be inert or even might be deleterious to the cements made from the magnesia. The sample chosen was No. M–57, supplied by the Nevada Magnesite Co. from a deposit in the valley of the Muddy River, near St. Thomas, in southern Nevada. When first discovered this deposit was thought to be one of the best yet uncovered in the United States. One sample was sent to the Dow Chemical Co. laboratory and another to the Bureau of Mines laboratory in Berkeley for determination of the possibility of making plastic and dead-burned magnesia from it. The tests for the latter purpose are not being given here.

COMPOSITION OF SAMPLE

The sample we received had the following ultimate analysis:

Composition of siliceous magnesite from St. Thomas, Nev.

Substance	Per cent	Remarks
nsoluble	12. 2	True silica=11.1 per cent. Insoluble on CO_2—H_2O free basis=21.6 per cent.
Alumina (Al_2O_3)	. 4	
Ferric oxide (Fe_2O_3)	. 7	
Calcium oxide (CaO)	6. 0	Equivalent to 10.6 per cent CaO on the CO_2—H_2O free basis.
Magnesia (MgO) (by difference)	37. 3	
Carbon dioxide (CO_2)	39. 2	Equivalent to 36.0 per cent magnesia.
Water, below 110° C	2. 15	
Water, above 110° C	1. 9	Ignition loss determined=43.4 per cent.
	100. 0	

This analysis does not show enough carbon dioxide to satisfy the magnesium oxide in the ore and neglects the lime entirely. Consequently one must assume that some of the magnesia or the lime is combined with silica. Careful microscopic examination of a similar sample by Prof. Austin F. Rogers, of Stanford University, showed no calcium carbonate as such, and he concluded that the substance f present must be isomorphous with magnesium carbonate. In fact, he found that none of the particles of what appeared to be magnesium carbonate were free of lime.

The analysis of the sample sent the Dow Chemical Co. was similar:

Composition of silicious magnesite from St. Thomas, Calif.

Substance	Per cent	Remarks
Insoluble	11. 25	True silica=9.85 per cent; insoluble MgO=0.84 per cent.
Alumina and ferric oxide (Al_2O_3, Fe_2O_3)	1. 53	
Calcium oxide (CaO)	6. 55	
Magnesium oxide (MgO)	38. 47	
Carbon dioxide (CO_2)	38. 61	
Water, below 105° C	1. 20	
Water, above 105° C	2. 39	
	100. 00	

The insoluble in this sample was also determined by the Portland cement method, which involves treatment of the weighed sample with hydrochloric acid, followed by removal of any silica (liberated from silicates) by means of sodium carbonate solution. This gave a "Portland cement insoluble" of 2.25 per cent and corroborates to some extent the deduction that part of the lime and magnesia must be combined in the material as silicates. Reversal of the order in which sodium carbonate and hydrochloric acid were applied showed that the acid had actually decomposed some silicates and liberated hydrated silica, which was dissolved by the sodium carbonate. Recalculation of the Dow analysis was then made, on the assumption that all the carbon dioxide was combined with the magnesia, with the following result:

Recalculated analysis

	Per cent
Moisture	1. 2
Magnesium carbonate and basic magnesium carbonate	79. 2
Silicates of lime, magnesia, alumina, and iron	19. 6

EFFECTS OF TEMPERATURE AND DURATION OF BURNING

Since the lime content of both samples was high, it was also thought best to determine the effect of the time and temperature of calcination on the lime as well as the silica. We placed small weighed samples in silica crucibles and heated them to various temperatures, each for a definite time. We analyzed them for soluble and insoluble silicates and also for free lime by the Berkeley method (use of excess distilled water to dissolve CaO, with correction for solubility of magnesium oxide). Temperatures were determined by a thermocouple and are accurate to ±10° C. The results are given in Table 42.

TABLE 42.—*Plastic calcination of siliceous magnesite*

Temperature	Time	Silica			Free lime
		Insoluble, 1-4 HCl	Soluble, 1-4 HCl	Total	
	Hours	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Raw material		11.8	0.4	12.2	
500 °C	12	23.0	.7	23.7	0.7
600 °C	4	22.0	.8	22.8	1.4
700 °C	4	18.6	5.3	23.9	2.6
700 °C	4	18.3	5.7	24.0	2.2
800 °C	4	8.05	13.75	21.8	.7
900 °C	4	4.7	16.6	21.3	.2
1,000 °C	1	10.5	10.1	20.6	.14

This table shows that calcining below 800° C. renders some of the lime in this magnesite soluble, either through the formation of calcium oxide from the carbonate or through the formation of a silicate which is easily hydrolyzed by water. At 800° C. and above, the increase in soluble silica and the decrease in free lime point to the formation of silicates that are unaffected by water. Since the free lime formed at lower temperatures should affect the physical properties of the plastic magnesia, tests were run to determine the qualities of plastic magnesia made from this magnesite; these tests are reported on page 92. At higher temperatures the free lime is removed by its combination into a difficultly hydrolyzed silicate, although long-time standing in contact with water may liberate the lime. This fact would be indicated in the physical properties of test pieces that are stored for some time. However, if heating to 1,000° C. could be carried on without overburning the magnesia, the resulting product ought to have better physical properties than the product burned at lower temperatures. Unfortunately the time was too short to carry out such a test, and since the properties of the material made at lower temperatures were not promising, the matter was dropped. Very poor finished products resulted from the tests made at higher temperatures.

Tests similar to ours were made in the laboratory of the Dow Chemical Co. with similar results. The company also made a series of time tests at 725° C. which showed that the amount of free lime increased up to the end of two hours and then fell off appreciably. The maximum content of free lime, as determined by the Berkeley method, was 2.25 per cent after two hours of heating at 725° C., which corresponds to our figures of 2.6 and 2.2 per cent after 4 hours of heating at 700° C. The amount of "Portland cement insoluble" in the Dow sample likewise went through a maximum during the time tests; this maximum was 1.3 per cent at the end of about 1.25 hours. Our tests were not so conducted as to give an opportunity for checking this effect. A similar time series at 600° C., investigated for free lime only, showed no such effect; the free lime increased during the whole test up to 22 hours.

LARGE-SCALE BURNING TESTS

Several burning tests were made in the Herreshoff furnace, using the Nevada magnesite as raw material. The furnace was brought into good thermal equilibrium before the tests were started, and the temperatures on the various hearths during the test were very uniform. The feed was held steadily at 2.4 to 2.5 pounds per minute, and the duration of the tests was three to six hours.

The average hearth temperatures and other data of these two tests are as follows.

Test No.	Hearth numbers and temperatures						Ignition loss
	1	2	3	4	5	6	
	° C.	*° C.*	*° C.*	*° C.*	*° C.*	*° C.*	*Per cent*
M-57-A	281	569	773	818	863	550	0.
M-57-B	284	583	727	753	768	513	1.

These materials, when ground so that 74 per cent passed a 200-mesh screen, were made up into standard test shapes and the following data on their physical properties were collected:

Sample No.	Chloride per gram	Setting time		Tensile strength			Modulus of rupture, 14 days	Expansion percentage		
		Initial	Final	1 day	7 days	30 days		1 day	7 days	30 days
	C. c.	*Hours*	*Hours*	*Pounds*	*Pounds*	*Pounds*		*Per cent*	*Per cent*	*Per cen*
M-57-A	1.49	8.98	14.12	47	169	175	0	−0.06	+0.11	+0.1
M-57-B	1.98	1.75	3.59	408	394	248	952	+.02	−.05	−.0

The setting times of these two materials were rather high as compared to those of plastic magnesia made from purer magnesite A good fresh plastic magnesia will have an initial setting time of about one-half hour. Exposure of these samples to the action of the air increased their setting time enormously, M-57-A taking nearly 28 hours to reach final set.

The tensile strengths of both fell off with time, which seems to indicate the slow hydrolysis of a silicate in the material with consequent increasing deleterious effect due to lime. The first materia gave a cross-bending bar that was too weak for a modulus of rupture test after 14 days and the modulus for the other sample was rather low. The expansion figures of the first material, which was burned at the higher temperature, were bad; but those of the second material were quite satisfactory.

On the whole, the physical properties ofmortars made from plastic magnesia burned at a maximum temperature of 768° and 863° C. were unsatisfactory, indicating increasing deterioration with age of the mortar and also poorer qualities from burning at the higher temperature. This behavior is ascribed to the formation of calcium and magnesium silicates which slowly hydrolyze and finally disrupt the cement.

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