HYDRATION OF MAGNESIA IN DOLOMITIC HYDRATED LIMES AND PUTTIES

By Lansing S. Wells and Kenneth Taylor

ABSTRACT

Heat-of-solution and ignition-loss methods have been developed for determining the degree of hydration of magnesia in hydrated dolomitic limes and in hydrated dolomitic lime putties. The rate of hydration of magnesia in such limes has been studied when the limes were aged as putties at different temperatures, when subjected to steam hydration at various temperatures and pressures, and when exposed to different relative humidities. In the six commercial hydrates studied, 70 to 90 percent of¹ the magnesia was still unhydrated after the customary 1 day of soaking. From 2 to 4 months were required to hydrate 95 percent of the magnesia when the limes were soaked at room temperature, but the rate of hydration was much more rapid at higher temperatures.

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I. INTRODUCTION

Since plasters and mortars are continuously subjected to changing atmospheric conditions, expansions and contractions are constantly going on. These movements, except those caused by changes in temperature, may be ascribed almost wholly to the cementitious material.

A study of the durability of mortars or plasters therefore involves a consideration of the properties of the cementitious materials, especially those related to volume changes. Such changes are often the result of chemical reactions. The hydration of the constituents of limes is attended by marked expansion. If the hydration occurs prior to the setting and hardening of a plaster or mortar the danger of any subsequent expansion from this source is eliminated.

Calcium oxide, CaO, unless "dead burned", reacts so rapidly with water to form calcium hydroxide, $Ca(OH)_2$, that hydration is completed in a short time. Chemical analysis of high-calcium hydrated limes as commercially produced indicates that the combined water is almost sufficient for complete hydration. On the other hand, the magnesia, MgO, of dolomitic limes (which contain CaO and MgO in nearly equimolecular proportions) hydrates slowly. Chemical analysis of commercial dolomitic hydrated limes indicates that ordinarily only 55 to 65 percent of the water required for complete hydration is present. Some additional hydration occurs during the customary 1 day of soaking prior to their use, but just how much is not known. If the exposure conditions are such that no further hydration takes place in the hardened mortar or plaster, or if hydration is extremely slow, no damaging expansion is likely to result. However, the rates of hydration under various conditions are not known. In fact, but little work has been done on this subject, and no satisfactory method prior to this investigation had been developed for determining the extent of hydration of magnesia in dolomitic lime putties. The development of such a method is essential to the study not only of the rates of hydration of dolomitic limes but also to the possible correlation of the hydration with attending expansion. Furthermore, such a method would be useful in determining the time required to completely hydrate the limes either on the job or at the plant. It should prove useful for manufacturers in ascertaining the relationship of temperature and time of burning of limes to their rates of hydration.

An investigation was undertaken, therefore, with the primary objects of developing a satisfactory method of measuring the degree of hydration of magnesia in dolomitic hydrated limes and putties and of studying the rate of hydration under various conditions.

II. METHODS OF DETERMINING THE DEGREE OF HYDRATION OF MAGNESIA

In 1927 Richardson [1] [1] described a thermochemical method of analysis for determining the degree of hydration of magnesia and calcium oxide in commercially hydrated dolomitic limes. The method was based upon the fact that the two hydroxides have appreciably different dissociation temperatures. Thus the percentages of magnesia and calcium oxide hydrated could be calculated from the weight loss

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[1] Figures in brackets here and elsewhere throughout the text refer to references at the end of this paper.

when the temperature was raised just high enough to decompose, first, the magnesium hydroxide and then the calcium hydroxide. By this method, Richardson analyzed 10 representative commercial dolomitic hydrates, and concluded that in such limes the calcium oxide is largely hydrated, while the magnesia is only slightly hydrated. He also determined the additional amount of magnesia hydrated when one of these limes was soaked (as putty) for 24 hours at room temperature. However, as the lime putty was oven-dried at 110° C, he could not be certain that a substantial amount of this hydration did not take place during the drying.

By a similar method, Fox and Mathers [2] determined the amount of hydrated magnesia in nine dolomitic hydrated limes, and also the additional magnesia hydrated upon soaking these limes at room temperature for 12 hours. The putties were oven-dried at 105° C, and here again it is probable that an appreciable hydration of magnesia took place during the drying period. The data given by Fox and Mathers showed that from 2.8 to 14.3 percent of the total magnesia was hydrated at the start and that from 9.1 to 18.1 percent of additional magnesia hydrated during the soaking and drying periods.

Campbell [3] used an ignition-loss method in determining the degree of hydration of magnesia (prepared from magnesite) soaked for various periods. Hydration was considered complete when the ignition loss (of the dried material) did not increase on further soaking. The results were expressed as percentage of total hydration, no distinction being made between the calcium oxide (about 4 percent on an ignited basis) and the magnesia. In his first experiments, the putties were dried for 1 day in a vacuum desiccator over concentrated sulphuric acid, and then oven-dried overnight at 102 to 105° C. He found, however, that the prolonged oven-drying decomposed some of the magnesium hydroxide, and so thereafter dried to constant weight in the desiccator. This usually required 7 or 8 days.

Since the determination of the degree of hydration of lime putties by the above methods involved uncertainties, as in drying, or required long drying periods, it seemed desirable to attack the problem in some other way. If, for example, the degree of hydration could be measured by determining the heats of solution of the putties in an acid, the accuracy of drying would not enter into the calculations. This method is possible since the hydration of a lime is attended by a decrease in its heat of solution. If the bulk of the unhydrated material is made up of one constituent, such as MgO, the problem of determining the extent of hydration by the heat-of-solution method is greatly simplified. Previous investigations have indicated that the unhydrated material is largely magnesia. The truth of this observation can be further tested by comparing observed heats of solution of dolomitic hydrated limes (or putties) with those calculated on the assumption that the lime, CaO, is completely hydrated to $Ca(OH)_2$ and that the magnesia is but partially hydrated. An agreement between the observed and calculated values would verify the assumption, provided there were a substantial difference in the heats of hydration of lime and magnesia.

In order to calculate the heat of solution of a hydrated dolomitic lime, it is necessary to know the heats of solution of the compounds which make up such a material. For practical calculations, these

may be considered as usually being calcium hydroxide, calcium oxide, calcium carbonate, magnesium hydroxide, and magnesium oxide. Iron and aluminum oxides and silica are also present, but usually in small amounts. If these are uncombined with the calcium or magnesium oxides, their heats of solution are very low; if combined, the heats of solution of the resulting compounds are roughly of the same order of magnitude as those of calcium and magnesium hydroxides, and are therefore largely compensated for. Disregarding these constituents does not, therefore, introduce any great error when their sum does not exceed 1 or 2 percent. Although some of the carbon dioxide may be combined with the magnesia, it seems probable that it is mainly combined with the calcium oxide, since the latter is much more active, and since calcium carbonate has a higher dissociation temperature than magnesium carbonate. At any rate, the carbonates have low heats of solution, and the error introduced by this assumption is necessarily small when there is not more than 2 or 3 percent of carbon dioxide present.

III. HEATS OF SOLUTION OF CaO, Ca(OH)$_2$, CaCO$_3$, MgO, AND Mg(OH)$_2$

Although the heats of solution of the above compounds had been determined by other investigators, it was necessary to redetermine these values. The heat of solution of a material in an acid varies with the concentration of the acid, the volume of acid per unit weight of material dissolved, the temperature at which the determination is made, and, in some instances, with the manner in which the sample has been prepared. Therefore, in comparing the observed heats of solution of limes with those calculated from the heats of solution of their constituents, it is important that the heats of solution of the limes and of the constituents be made under similar conditions.

The determinations of the heats of solution were made by means of an isothermal calorimeter [4] similar to the one used to test the Boulder Dam cements. The determinations were made at 25° C, using 640 g of 2 N hydrochloric acid and a sample of approximately 1.5 g.

The calcium carbonate used was of analytical reagent quality. An analysis showed that it was completely soluble in hydrochloric acid, free of chlorides, sulphates, and silicates, and contained only traces of iron and aluminum oxides. The ignition loss was 43.93 percent (theoretical, 43.97 percent).

The calcium oxide was prepared from the above calcium carbonate by igniting a sample for about 4 hours over a Meker burner just prior to each determination of the heat of solution. The ignition temperature was found to be 1,050 to 1,100° C, which roughly approximates the temperature at which dolomitic limes are burned.

The calcium hydroxide was also prepared from this sample of calcium carbonate. The carbonate was ignited for several hours in a muffle furnace at 950° C and then immediately hydrated in the autoclave for 2 hours at 125-lb/in.^{2} steam pressure. After the hydroxide had been oven-dried for 1 hour at 105° C, it had an ignition loss of 24.32 percent (theoretical, 24.32 percent).

The source of both the magnesium hydroxide and the magnesium oxide was a sample of magnesium oxide of analytical reagent quality. Before being used, this sample was extracted with water to remove

any water-soluble substances with which it might be contaminated. An analysis then showed that it was completely soluble in hydrochloric acid, free of chlorides and sulphates, and contained only traces of silica, iron oxide, and aluminum oxide.

In the preparation of the magnesium hydroxide the above oxide was ignited in a muffle furnace for several hours at 850° C and then hydrated and dried as in the preparation of calcium hydroxide. The ignition loss was 31.05 percent (theoretical, 30.88 percent).

The magnesium oxide used in determinations of the heat of solution was obtained by igniting a sample of the above prepared magnesium hydroxide for about 4 hours over a Meker burner just prior to each determination (ignition temperature, 1,050 to 1,100° C).

In determining the heat of solution of calcium carbonate, the carbonate was mixed with an equal weight of a hydrated dolomitic lime (heat of solution previously determined) and the mixture compressed into tablets. By this procedure, a too rapid effervescence of carbon dioxide was prevented. The heat of solution of the calcium carbonate was readily computed since the value for the dolomitic lime was known. In the case of calcium carbonate, determinations were made in 2 N hydrochloric acid, both saturated and unsaturated with carbon dioxide. With the other materials, the acid was not saturated with carbon dioxide. The results of determinations of the heats of solution of these various compounds are shown in table 1.

TABLE 1.—*Heats of solution (in 2 N hydrochloric acid at 25° C) of the principal compounds in hydrated dolomitic limes*

Determination	Heat of solution (cal/g)					
	CaO	Ca(OH)$_2$	MgO	Mg(OH)$_2$	a CaCO$_3$	b CaCO$_3$
1	833.4	556.4	890.5	666.5	59.5	104.6
2	834.9	557.5	891.2	667.5	58.8	105.4
3	833.3	557.2	889.8	667.8		
4			891.3	666.6		
Average	833.9	557.0	890.7	667.1	59.2	105.0

	Heat of solution (cal/mole)					
Average	46,760	31,230	35,910	26,900	3,320	5,780

a Acid saturated with CO$_2$.
b Acid not saturated with CO$_2$.

Table 1 shows that the heat of solution of calcium carbonate is less in the acid which has been saturated with carbon dioxide. In this case, substantially all of the carbon dioxide formed in the reaction escapes as a gas. When the acid has not been previously saturated, a part of the carbon dioxide formed goes into solution and the remainder escapes as a gas. The larger value, 105 cal/g, was used in all calculations since the heats of solution of the dolomitic limes were determined in acid not saturated with carbon dioxide. Obviously, the heat of solution of calcium carbonate in hydrochloric acid not saturated with carbon dioxide will vary, since if a small sample of calcium carbonate is taken, nearly all of the carbon dioxide formed may dissolve, while if a larger sample is taken, a smaller proportionate part may go into solution. However, since the limes tested contained

only small amounts of carbon dioxide, and the heat of solution of the carbonate is, in any case, low compared with that of the principal constituents, the error introduced by using the approximate value of 105 cal/g should not be appreciable.

The approximate heat of hydration may be obtained by subtracting the heat of solution of the hydrated from that of the unhydrated material. Table 1 shows that the molar heats of hydration of calcium oxide (approximately 15.53 Cal) and of magnesium oxide (approximately 9.01 Cal) differ markedly. (To obtain the exact heat of hydration from heat-of-solution data it is necessary to make several minor corrections which are not significant in this work.)

It should be understood that the data of table 1 apply only to materials prepared as described above. Giauque and Archibald [5] have reported an appreciably higher heat of hydration for magnesium oxide prepared by decomposing magnesium hydroxide at 300° C. It has been found in this laboratory that the heat of hydration of magnesium oxide varies appreciably with the temperature and time of ignition prior to a determination. However, the calcium oxide and magnesium oxide, for which data are given in this paper, were ignited at temperatures roughly approximating those at which dolomitic limes are burned in practice. It is planned to present, in a later paper, data showing the variation of the heat of hydration of magnesia with the ignition temperature, and also the corrected heat of hydration values for the calcium and magnesium oxides ignited as described above.

IV. COMPARISON OF THE OBSERVED AND CALCULATED HEATS OF SOLUTION OF HYDRATED DOLOMITIC LIMES, AND THE DEGREE OF HYDRATION OF MAGNESIA IN THESE LIMES

Having determined the heats of solution of the compounds in hydrated dolomitic limes, it was now possible to compare the calculated and observed heats of solution of several of these limes and thereby test the assumption that the calcium oxide was completely hydrated.

The limes, the analyses of which are given in table 2, were obtained from four different manufacturers. The first six were received as dry hydrates. Lime 7 was obtained as the ground limestone and burned in this laboratory. A comparison was made of the calculated and experimental heats of solution of these limes first, as they were received from the manufacturer, and second, after they had been hydrated in the autoclave for 2 hours at 120-lb/in.² steam pressure. The limes were considered to be completely hydrated by this autoclave treatment. Lime 3, which was representative of the group, showed no further hydration, as measured by ignition loss, after 1 hour in the autoclave at this pressure.

TABLE 2.—*Chemical analyses of dolomitic limes*

(Lines 1 to 6, inclusive, hydrated limes; line 7, quicklime)

Constituent	Amount of constituents in limes						
	1	2	3	4	5	6	7
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
CaO	48.1	46.3	47.8	48.1	47.2	48.1	54.6
MgO	33.9	32.4	33.3	33.6	33.0	33.7	38.7
SiO$_2$				0.2	0.2	1.2	4.7
R$_2$O$_3$				.4	.3	0.7	2.2
H$_2$O, extraneous ^{a}	0.2	0.4	0.1	.4	.3	.4	0.0
H$_2$O, combined	16.6	16.9	17.3	16.0	16.4	15.8	.0
CO$_2$	0.6	3.2	1.3	1.2	2.6	0.3	.1
Total	99.4	99.2	99.8	99.9	100.0	100.2	100.3

^{a} Obtained as loss on drying 1 hour at 105° C.

The method used in calculating the heats of solution will be illustrated with lime 3. It is assumed that the calcium oxide is completely hydrated, provided of course that there is sufficient water available, and that only water present in excess of this amount goes to hydrate the magnesia. Also, it is assumed that all of the carbon dioxide is combined with the calcium oxide. The small amounts of iron and aluminum oxides and silica are ignored. The distribution of the compounds which enter into the calculation of the heat of solution of a gram of this lime is, therefore, as follows:

Calcium oxide in carbonate _____ 0. 016 g.
Calcium oxide in hydrate _____ . 462 g.
Magnesium oxide in hydrate _____ . 056 g.
Magnesium oxide _____ . 277 g.

The heat of solution of each of these components is now calculated.

$$0. 016 \times 105. 0 \text{ cal} = 1. 7 \text{ cal.}$$
$$. 462 \times 557. 0 \text{ cal} = 257. 3 \text{ cal.}$$
$$. 056 \times 667. 1 \text{ cal} = 37. 4 \text{ cal.}$$
$$. 277 \times 890. 7 \text{ cal} = 246. 7 \text{ cal.}$$

Total = 543. 1 cal.

It is desirable to express the heat of solution, not in calories per gram but in calories per gram of ignited material. From the analysis (table 2) it is seen that 1 g of lime 3, upon ignition gives 0.813 g. Therefore, 543.1 is divided by 0.813, giving a heat of solution 668.0 cal/g of ignited material.

Calculations for the completely hydrated lime are made as follows. The heats of solution which were computed for the components of the lime at the start are again used, with the exception that the 0.277 g of free magnesia is now calculated as hydrated.

$$0.016 \times 105.0 \text{ cal} = 1.7 \text{ cal.}$$
$$.462 \times 557.0 \text{ cal} = 257.3 \text{ cal.}$$
$$.056 \times 667.1 \text{ cal} = 37.4 \text{ cal.}$$
$$.277 \times 667.1 \text{ cal} = 184.8 \text{ cal.}$$

Total = 481.2 cal.

The hydration of 0.277 g of magnesia requires 0.124 g of water. As the lime at the start contained 0.1 percent of extraneous water, a gram of this lime upon complete hydration should produce 1+ (.124—.001), or 1.123 g. Therefore, 481.2 cal is the heat of solution of 1.123 g of the completely hydrated lime. The heat of solution of 1 g is 481.2÷1.123, or 428.5 cal. Before the heat of solution can be expressed in calories per gram of ignited material, it is necessary to compute the ignition loss of the completely hydrated lime. The ignition loss at the start was 18.7 percent and 0.123 g of water was added to each gram of the lime upon complete hydration. The ignition loss therefore becomes 0.187+.123/1.123, or 27.6 percent. A gram of the completely hydrated lime should therefore produce 0.724 g of ignited material, and the heat of solution, on an ignited basis, should be 428.5÷.724, or 591.9 cal/g.

Similar calculations were made for all of these limes. The observed and calculated heats of solution are compared in table 3. The observed values are the average of two determinations which differed by a maximum of 2.1 cal/g.

An extremely close agreement between the observed and calculated values could not be expected, since besides the calorimetric work, there were several possible sources of slight error. Mainly, these were: uncertainty as to the distribution of the carbon dioxide, the chemical analysis, and the presence of iron and aluminum oxides and silica. In the case of the six hydrated limes, which contained relatively small amounts of impurities, it would seem that an agreement within 3 to 4 cal/g should be obtained. Deviations somewhat larger than this in the first two limes indicate the possibility of a small fraction of the calcium oxide being unhydrated. If it is assumed that the combined water is equally divided between the calcium oxide and magnesia, then the calculated heat of solution of lime 3, for example, becomes 695.6 cal. This is 26.9 cal higher than the observed value. At least for the practical purpose of following the hydration of magnesia, it would seem therefore, that one is justified in assuming the complete hydration of calcium oxide in such limes.

Table 4 shows the degree of hydration of magnesia in the six commercially hydrated dolomitic limes as received from the manufacturer. The values were calculated from the chemical analyses, the calcium oxide being considered as completely hydrated.

TABLE 3.—Comparison of the observed and calculated heats of solution of dolomitic limes

Condition		Heats of solution of limes						
		1	2	3	4	5	6	7
As received	observed	cal/g 682.5	cal/g 648.0	cal/g 668.7	cal/g 670.1	cal/g 652.9	cal/g 672.3	cal/g 792.8
	calculated	677.1	643.4	668.0	673.4	657.4	673.1	797.5
	difference	−5.4	−4.6	−0.7	+3.3	+4.5	+0.8	+4.7
Completely hydrated	observed	593.6	570.6	590.2	587.8	576.4	587.7	567.4
	calculated	594.0	572.5	591.9	589.0	580.3	585.6	560.2
	difference	+0.4	+1.9	+1.7	+1.2	+3.9	−2.1	−7.2

TABLE 4.—*Degree of hydration of magnesia in hydrated dolomitic limes as receiv from the manufacturer*

Magnesian constituents	Amount of magnesian constituents in limes					
	1	2	3	4	5	6
MgO, hydrated	% 3.1	% 7.4	% 5.6	% 2.5	% 5.1	% 1.1
MgO, unhydrated	30.8	25.0	27.7	31.1	27.9	32.4
Total MgO	33.9	32.4	33.3	33.6	33.0	33.5
$\frac{\text{MgO, hydrated}}{\text{Total MgO}} \times 100$	9.1	22.8	16.8	7.4	15.5	3.3

V. CALCULATIONS INVOLVED IN THE DETERMINATION OF THE DEGREE OF HYDRATION OF MAGNESIA IN DOLOMITIC LIME PUTTIES BY THE HEAT-OF-SOLUTION METHOD

Lime 3 will be used to illustrate the method of calculation. Table 4 shows that this lime, as received from the manufacturer, contained 33.3 percent of total magnesia and 5.6 percent of magnesia in the hydrated form. The percentage of the total magnesia which was hydrated was therefore 0.056÷.333, or 16.8. The experimental heat of solution of this lime as received was 668.7 cal/g and after complete hydration in the autoclave, 590.2 cal/g, a decrease of 78.5 cal/g. A change of 78.5 cal in the heat of solution is due to the hydration of 100.0−16.8, or 83.2 percent of the magnesia. Since the heat of solution is determined on an ignited basis, the change in the heat of solution is directly proportional to the percentage of magnesia hydrated. A decrease of 1 cal in the heat of solution therefore represents the hydration of 83.2÷78.5, or 1.06 percent of magnesia.

After this lime had been soaked for 1 day its heat of solution, as determined experimentally, was 661.1, a decrease of 7.6 cal. This number, 7.6, is multiplied by the factor 1.06 giving 8.1 percent of magnesia hydrated during the soaking period. As 16.8 percent of the magnesia was originally hydrated, the percentage of the total magnesia hydrated after 1 day of soaking is 24.9.

VI. RATE OF HYDRATION OF MAGNESIA IN DOLOMITIC LIME PUTTIES AT ROOM TEMPERATURE

The heat-of-solution method of determining the degree of hydration of magnesia in dolomitic limes was used to study the rate of hydration of the magnesia when the limes were soaked at room temperature. The limes, whose analyses were given in table 2, were made into putties of such consistency as to be readily workable, yet sufficiently stiff that water would not separate appreciably on standing. The putties were kept in sealed glass jars which had been coated on the inside with paraffin, and the heat of solution was determined from time to time. When a determination was to be made, a sample of the putty was taken from the jar, thoroughly mixed and placed in a weighing tube. This tube was about 0.5 in. in diameter and 3.5 in. in length. It was fitted with a plunger held in position by a stopper, and to one end was attached a small glass tube about 1 in. in length. By means of the plunger the desired amount of putty could be forced

from the tube. The weighings were made by difference. The end of the small glass tube was closed by means of a rubber cap to prevent loss by evaporation during weighing. A sample for determination of heat of solution and one for ignition loss were taken from the same filling of the weighing tube.

The putties had an ignition loss of from 50 to 60 percent, and samples of from 3 to 4.5 g were taken for determinations of heat of solution. In making the calculations of heat of solution, approximate corrections were made for the water in the putties in excess of that required for complete hydration.

It should be noted that the accuracy of drying is not involved in this method because the calorimetric data were obtained with the undried putty. The ignition loss, which was used to calculate the heat of solution from the calorimetric results, was that of the wet putty and not of the dried material.

TABLE 5.—*Relation between the time of soaking and the percentage of hydration of magnesia in dolomitic lime putties maintained at room temperature*

Soaking period	Total magnesia hydrated in putties						
	1	2	3	4	5	6	7
Days	Percent	Percent	Percent	Percent	Percent	Percent	Percent
0	9.1	22.8	16.8	7.4	15.5	3.3	0.0
1	17.4	27.6	24.9	11.8	22.1	10.7	61.7
3	22.9	36.8	31.0				91.7
7	37.3	48.9	42.0	33.5	48.5	35.1	100.1
14	51.8	56.7	59.3		65.2		
21	69.9	68.5		67.0	79.8	71.9	
28	82.2	75.6	80.0				
35		77.1	84.5	82.4	88.7	88.1	
42	89.1	81.3					
56	94.0	89.8	92.3	91.9	97.4	90.8	
77	98.2	93.6	93.2				
98		95.1	99.4			92.4	
119						96.7	
140		98.5		96.8			

The results of the determinations are shown in table 5 and graphically in figure 1. Lime 7 was obtained from the manufacturer as ground limestone. It was burned in a muffle furnace for 7 hours at 950 to 980° C, and then immediately made into a putty. Since it was burned at a lower temperature than is customary in industry, its rapid hydration indicates that the temperature of burning has a marked effect on the rate of hydration. Campbell [3] obtained practically complete hydration of magnesia in 3 days when magnesite was burned at 800° C, but only about 70 percent of it had hydrated after 6 years when the temperature of burning was 1,450° C.

Figure 1 shows that the rate of hydration is not a linear function of the time, but that it becomes decidedly slower when about 80 percent of the magnesia has been hydrated. Roughly speaking, 80 percent of the magnesia in these limes is hydrated in from 20 to 46 days and 95 percent in from 2 to 4 months. It is also seen that the customary 1-day soaking leaves the bulk of the magnesia still unhydrated.
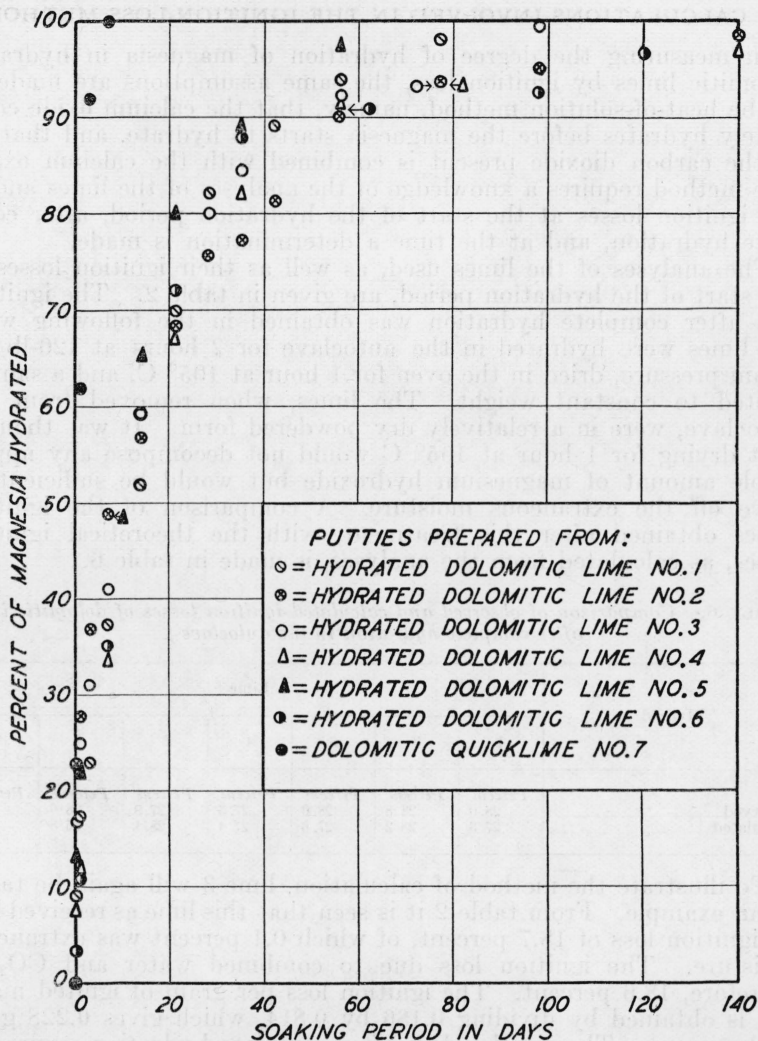
PUTTIES PREPARED FROM:
⊘ = HYDRATED DOLOMITIC LIME NO. 1
⊗ = HYDRATED DOLOMITIC LIME NO. 2
○ = HYDRATED DOLOMITIC LIME NO. 3
△ = HYDRATED DOLOMITIC LIME NO. 4
▲ = HYDRATED DOLOMITIC LIME NO. 5
◐ = HYDRATED DOLOMITIC LIME NO. 6
● = DOLOMITIC QUICKLIME NO. 7

FIGURE 1.—Rate of hydration of magnesia in dolomitic lime putties maintained at room temperature.

VII. CORRELATION OF IGNITION-LOSS AND HEAT-OF-SOLUTION METHODS FOR DETERMINING THE DEGREE OF HYDRATION OF MAGNESIA IN DOLOMITIC LIMES

The determination of the degree of hydration by the heat-of-solution method appears to be theoretically sound and to give satisfactory results. However, for practical purposes a shorter and simpler procedure is desirable. It, therefore, seemed worth-while to make some measurements by loss on ignition and to compare the results with those obtained from determinations of heat of solution.

1. CALCULATIONS INVOLVED IN THE IGNITION-LOSS METHOD

In measuring the degree of hydration of magnesia in hydrated dolomitic limes by ignition loss, the same assumptions are made as in the heat-of-solution method, namely, that the calcium oxide completely hydrates before the magnesia starts to hydrate, and that all of the carbon dioxide present is combined with the calcium oxide. The method requires a knowledge of the analyses of the limes and of the ignition losses at the start of the hydration period, after complete hydration, and at the time a determination is made.

The analyses of the limes used, as well as their ignition losses at the start of the hydration period, are given in table 2. The ignition loss after complete hydration was obtained in the following way: the limes were hydrated in the autoclave for 2 hours at 120-lb/in.² steam pressure, dried in the oven for 1 hour at 105° C, and a sample ignited to constant weight. The limes, when removed from the autoclave, were in a relatively dry powdered form. It was thought that drying for 1 hour at 105° C would not decompose any appreciable amount of magnesium hydroxide but would be sufficient to drive off the extraneous moisture. A comparison of the ignition losses obtained after this treatment, with the theoretical ignition losses, as calculated from the analyses, is made in table 6.

TABLE 6.—*Comparison of observed and calculated ignition losses of dolomitic limes after complete hydration in the autoclave*

Method	Lime						
	1	2	3	4	5	6	7
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
Observed	28.0	28.8	28.0	27.3	27.9	26.9	26.2
Calculated	27.3	28.2	27.6	27.4	28.1	26.8	25.8

To illustrate the method of calculation, lime 3 will again be taken as an example. From table 2 it is seen that this lime as received had an ignition loss of 18.7 percent, of which 0.1 percent was extraneous moisture. The ignition loss due to combined water and CO_2 is, therefore, 18.6 percent. The ignition loss per gram of ignited material is obtained by dividing 0.186 by 0.814, which gives 0.228 g, or 22.8 percent. The ignition loss after complete hydration, expressed on an ignited basis, is 0.28÷0.72, or 38.9 percent.

It is seen in table 4 that 16.8 percent of the total magnesia in this lime is hydrated at the start. Therefore, the hydration of 83.2 percent of the magnesia is accompanied by a change in ignition loss of 16.1 percent. Since the ignition loss has been expressed on an ignited basis, its increase is directly proportional to the percentage of magnesia hydrated. That is, for each percent increase in ignition loss there is 83.2÷16.1, or 5.17 percent of magnesia hydrated. After lime 3 had been hydrated in the autoclave for 11 minutes at 120-lb/in.² pressure, it had an ignition loss, on an ignited basis, of 34.4 percent, an increase of 11.6 percent. This increase is multiplied by the factor 5.17, giving 60.0 percent. As 16.8 percent of the magnesia was originally hydrated, the percentage of the total magnesia now hydrated is 76.8.

2. CORRELATION OF HEAT-OF-SOLUTION AND IGNITION-LOSS METHODS IN THE CASE OF AGED PUTTIES

A comparison was made of the results obtained when the hydrated magnesia in aged dolomitic lime putties was determined both by ignition loss and heat of solution. The three following procedures of drying the putties prior to the ignition loss determination were tried:

A. Samples of about 1.5 g were placed in platinum crucibles and oven-dried overnight at 105° C.

B. Samples of about 1.5 g were placed in platinum crucibles and dried in a desiccator over concentrated sulphuric acid for 20 hours. The samples were then oven-dried for 1 hour at 105° C.

C. Samples of about 5 to 10 g were thoroughly stirred in approximately 25 ml of alcohol, filtered by suction, and washed with several small portions of alcohol and ether. The material was then pulverized and oven-dried for 1 hour at 105° C.

Table 7 shows the results obtained by the ignition-loss method when the putties were dried by the three procedures just described, and also the results from determinations of the heat of solution on the same putties, undried.

TABLE 7.—*Comparison of ignition-loss and heat-of-solution methods for determining the degree of hydration of magnesia in dolomitic lime putties*

Method of drying	Determination numbers	Magnesia hydrated as determined by—	
		Ignition loss	Heat of solution

PROCEDURE A

Method of drying	Determination numbers	Ignition loss	Heat of solution
		%	%
	1	38.3	22.9
	2	41.5	27.6
Oven-dried overnight at 105° C	3	49.3	31.0
	4	54.8	36.8
	5	46.6	36.8
	6	64.4	56.1

PROCEDURE B

Method of drying	Determination numbers	Ignition loss	Heat of solution
	1	42.3	38.6
	2	39.5	42.0
	3	78.8	80.0
Dried in desiccator for 20 hours at 25° C, then oven-dried 1 hour at 105° C	4	75.8	81.3
	5	85.5	92.3
	6	95.5	93.2
	7	89.5	94.0
	8	94.0	98.2

PROCEDURE C

Method of drying	Determination numbers	Ignition loss	Heat of solution
	1	14.0	11.8
	2	22.7	22.1
	3	45.5	48.5
	4	62.2	65.2
Washed with alcohol and ether, then oven-dried 1 hour at 105° C	5	74.6	67.0
	6	79.4	79.8
	7	88.4	82.4
	8	87.9	89.8
	9	85.4	92.3
	10	94.8	93.2
	11	96.0	98.2

The uniformly high results obtained by the ignition-loss method when the putties were entirely oven-dried were no doubt due to additional hydration during the drying period. An increase of 75 or 80 degrees in temperature greatly accelerates the rate of hydration, as will be shown later.

Although the results, when the putties were dried by procedures *B* and *C*, correlated only approximately with those of the heat-of-solution method, it is believed that such determinations are accurate enough to be of practical use in industry. By means of these methods, the manufacturer of aged lime putties can easily determine the approximate amount of unhydrated magnesia in the putty being aged. For such uses, the alcohol-ether-oven procedure of drying is probably preferable, for in this way a complete determination can be made in 4 or 5 hours.

3. CORRELATION OF HEAT-OF-SOLUTION AND IGNITION-LOSS METHODS IN THE CASE OF STEAM HYDRATION

Several samples of a dolomitic lime were hydrated with steam under pressure for various periods and were oven-dried for 1 hour at 105° C upon their removal from the autoclave. The percentages of hydrated magnesia in these samples were then determined by the ignition-loss and heat-of-solution methods. The results are shown in table 8.

TABLE 8.—*Comparison of ignition-loss and heat-of-solution methods for determining the degree of hydration of magnesia in dolomitic limes hydrated with steam*

Determination	Percentages of total magnesia hydrated	
	Ignition loss	Heat of solution
1	32. 8	37. 5
2	48. 3	43. 0
3	77. 8	78. 9
4	81. 4	83. 4
5	85. 5	87. 5
6	96. 0	93. 0
7	94. 8	96. 1

The samples were in a comparatively dry powdered form when removed from the autoclave, and it does not seem probable that appreciable hydration was caused by oven-drying, as was apparently the case when the putties were dried in this way. The fact that the results by the two methods correlate reasonably well indicates, on the other hand, that the drying was nearly complete, since underdrying would not affect the heat of solution perceptibly.

VIII. EFFECT OF TEMPERATURE ON THE RATE OF HYDRATION OF MAGNESIA IN DOLOMITIC LIMES

Section VI of this discussion reports that several months were required to completely hydrate the magnesia in the dolomitic lime putties which were soaked at room temperature.

The aging period may, however, be greatly shortened by soaking the putties at higher temperatures. Also a dry, completely hydrated dolomitic lime may readily be produced by steam hydration. The time

required for this process will vary markedly with the temperature (or pressure) of the steam. The following experiments were carried out, with the object of determining the approximate effect of temperature on the rate of hydration in such cases as those just mentioned.
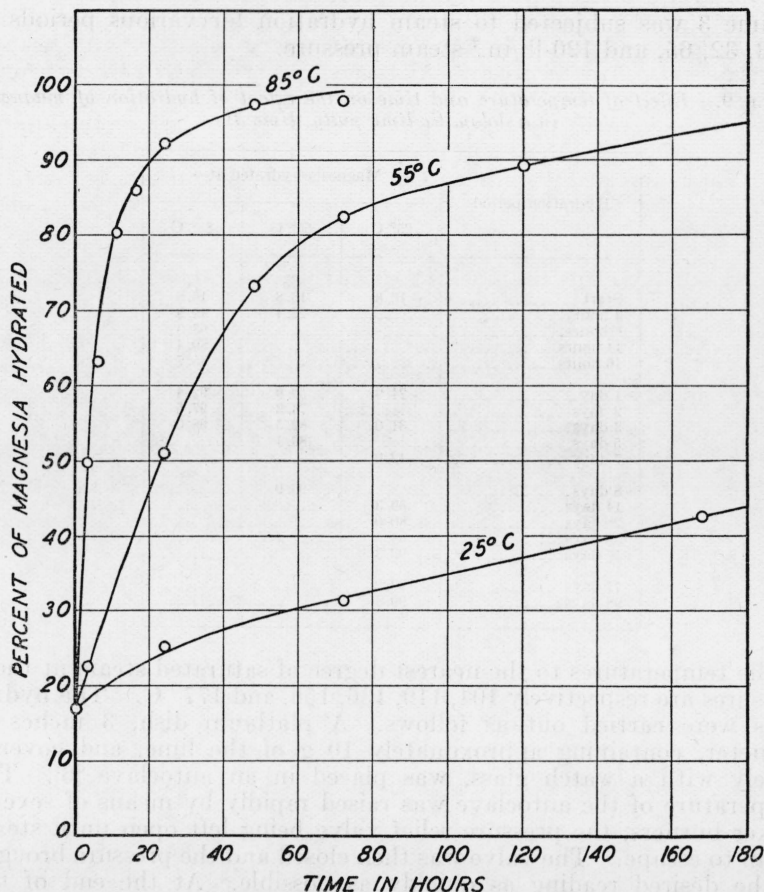

FIGURE 2.—*Effect of temperature on the rate of hydration of magnesia in lime 3 dolomitic lime putty.*

1. HYDRATION OF PUTTIES AT DIFFERENT TEMPERATURES

The results of the hydration of dolomitic lime putties at room temperature are shown in table 5 and figure 1. Lime 3 was also hydrated in the putty form at 55° C and 85° C. The putties were put into glass bottles of about 50-ml capacity, the bottles stoppered and placed in an electric oven maintained at the desired temperature. Samples were taken at various intervals and the percentage of the total magnesia which was hydrated was determined by the ignition-loss method. Prior to the ignition-loss determinations, the samples were washed with alcohol and ether and oven-dried for 1 hour at 105° C.

The results for the hydration of this putty at 25° C (room temperature), 55° C, and 85° C are shown in table 9 and figure 2. It is seen

that while it takes about 75 days to hydrate 95 percent of the magnesia at room temperature, the same results can be accomplished in 35 hours at 85° C.

2. HYDRATION WITH STEAM AT DIFFERENT TEMPERATURES

Lime 3 was subjected to steam hydration for various periods at 2, 13, 32, 65, and 120-lb/in.² steam pressure.

TABLE 9.—*Effect of temperature and time on the extent of hydration of magnesia in a dolomitic lime putty (lime 3)*

Hydration period	Magnesia hydrated at—		
	25° C	55° C	85° C
Start	% 16.8	% 16.8	% 16.8
3 hours		22.4	49.9
6 hours			63.3
11 hours			80.4
16 hours			85.7
1 day	24.9	50.9	92.4
2 days		73.3	97.5
3 days	31.0	82.5	98.0
5 days		89.1	
7 days	42.0		
8 days		95.9	
14 days	59.3		
28 days	80.0		
35 days	84.5		
56 days	92.3		
77 days	93.2		
98 days	99.4		

The temperatures to the nearest degree of saturated steam at these pressures are respectively 104, 119, 136, 156, and 177° C. The hydrations were carried out as follows. A platinum dish, 3 inches in diameter, containing approximately 10 g of the lime, and covered loosely with a watch glass, was placed in an autoclave [6]. The temperature of the autoclave was raised rapidly by means of several Meker burners, the pressure relief valve being left open until steam began to escape. The valve was then closed and the pressure brought to the desired reading as quickly as possible. At the end of the hydration period, the steam pressure was rapidly lowered to atmospheric pressure by cooling the autoclave with water. The sample was then immediately removed, oven-dried for 1 hour at 105° C and the percentage of the total magnesia which was hydrated was determined by ignition loss.

Several minutes were required to raise the steam pressure of the autoclave to the desired reading and to cool to atmospheric pressure at the end of the experiment. This required a correction of the hydration period which was arbitrarily made as illustrated in the following example. In a hydration at 65 lb/in.² steam pressure, 13 minutes elapsed from the time the pressure relief valve was closed until the pressure-gage reading was 65. At the end of the experiment 3 minutes were required to cool to atmospheric pressure. The pressure was actually at 65 lb/in.² for 27 minutes. A correction of one-half the sum of the preheating and cooling periods, or 8 minutes, was added, making the total hydration period 35 minutes. The

corrections added varied from 1 minute at 2 lb/in.^{2} pressure to 9 or 10 minutes at 120 lb/in.^{2} pressure. The hydration periods are therefore approximations, since the exact time could not be determined with the autoclave available for this work. The results of the steam hydrations are shown in table 10 and figure 3.
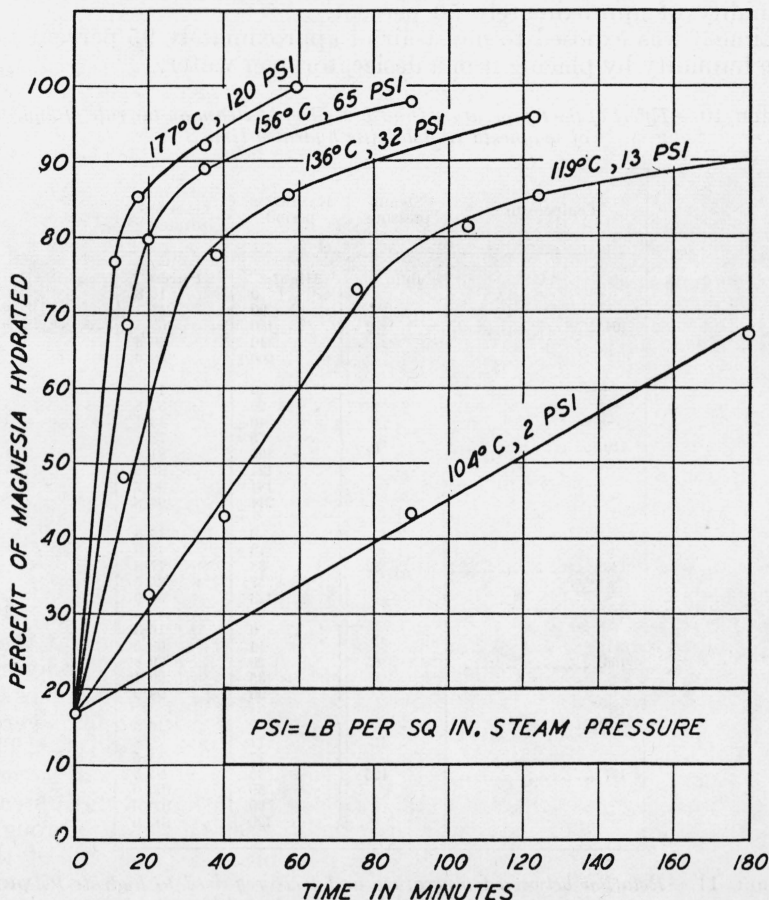

FIGURE 3.—*Effect of the temperature and pressure of steam on the rate of hydration of magnesia in hydrated dolomitic lime 3.*

Although the steam and putty hydrations are not strictly comparable, a rough idea of the effect of temperature on the rate of hydration of magnesia in this lime may be seen from table 11, which gives the approximate time required to hydrate 95 percent of the magnesia in lime 3 at the various temperatures.

IX. EFFECT OF MOISTURE CONDITIONS ON THE RATE OF HYDRATION OF MAGNESIA IN DOLOMITIC HYDRATED LIMES

It has been noted that when dolomitic limes are stored in paper bags, sufficient expansion occasionally takes place, in the course of a few months, to burst the containers. This indicates that appreciable

hydration is occurring. It further suggests that if hydration takes place under these conditions, it can also occur in plastered walls under certain atmospheric conditions. Some preliminary experiments were therefore made to determine the rate of hydration of magnesia when the dolomitic lime was exposed to moist air of approximately 95 percent relative humidity and to air kept at a relative humidity of approximately 50 percent.

Lime 3 was exposed to moist air of approximately 95 percent relative humidity by placing it in a desiccator over water.

TABLE 10.—*Effect of the temperature (and pressure) of steam on the rate of hydration of magnesia in dolomitic hydrated lime 3*

Temperature	Steam pressure	Hydration period	Total magnesia hydrated
° C	lb/in.²	*Minutes*	*Percent*
104	2	0	16.8
		90	43.3
		180	67.1
		340	90.3
		600	98.0
119	13	0	16.8
		20	32.8
		40	43.1
		75	73.1
		105	81.4
		124	85.5
		184	90.2
		244	94.8
136	32	0	16.8
		13	48.3
		38	77.8
		57	85.5
		123	96.0
156	65	0	16.8
		14	68.5
		20	79.8
		35	89.1
		90	98.0
177	125	0	16.8
		11	76.8
		17	85.5
		35	92.3
		59	100.0
		90	100.0
		120	100.0

TABLE 11.—*Relation between temperature and time required to hydrate 95 percent of the magnesia in dolomitic hydrated lime 3*

Temperature	Time
°C	*Hours*
25	1,800
55	180
85	35
104	7.7
119	4.1
136	1.9
156	1.1
177	0.7

The lime, which was in a layer about ³⁄₁₆ in. in depth, was covered loosely with a watch glass to protect it from any drops of condensed water which might be formed.   Also, samples of this lime, in layers of approximately the same depth, were placed in a desiccator over a 43.4-percent sulphuric acid solution to maintain a relative humidity approximating 50 percent [7].   The rate of hydration of magnesia under these conditions, as well as when the lime was soaked as a putty at room temperature, is shown in table 12 and in figure 4.   It is seen from figure 4 that aging the lime from 3 to 4 months in air at a relative
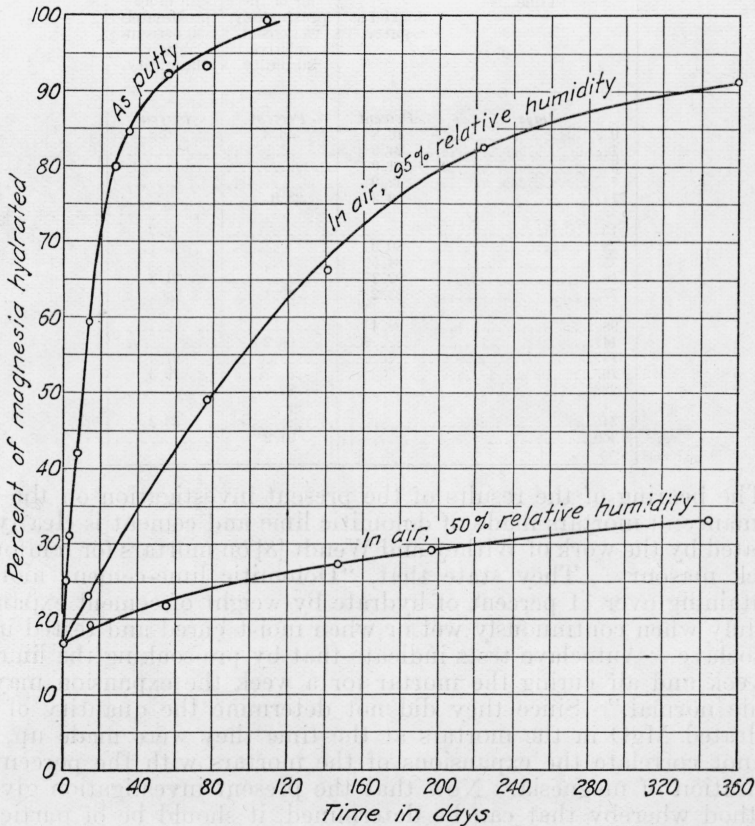

FIGURE 4.—*Effect of moisture on the rate of hydration of magnesia in hydrated dolomitic lime 3.*

humidity of approximately 50 percent is equivalent to aging it for 1 day as a putty.   From a comparison of the rates of hydration, as indicated by the curves in figure 4, it is evident that at relative humidities lower than 50 percent the rates of hydration would be very slow.   It is believed that these very slow rates may explain in part why there is not more damaging expansion of set plasters containing dolomitic limes, especially since the relative humidity of the air in buildings is usually considerably lower than 50 percent during those months that the buildings are heated.   However, before definite conclusions can be drawn, it will be necessary to conduct a more com-

prehensive study of this phase of the subject, and, in particular, of the relation between the amount of free magnesia in such plasters and the expansions taking place under various conditions of moisture.

TABLE 12.—*Effect of moisture conditions at room temperature on the extent of hydration of magnesia in dolomitic hydrated lime 3*

Time	Magnesia hydrated when—		
	Soaked as putty	Exposed to air of approximately 95 percent relative humidity	Exposed to air of approximately 50 percent relative humidity
Days	*Percent*	*Percent*	*Percent*
0	16.8	16.8	16.8
1	24.9		
3	31.0		
7	42.0		
14	59.3	23.0	
15			19.2
28	80.0		
35	84.5		
56	92.3		21.8
77	93.2	49.1	
98	99.4		
141		66.2	
147			27.4
197			29.3
223		82.5	
345			33.2
360		91.2	

The bearing of the results of the present investigation on the performance of mortars made of dolomitic lime and cement is clearly indicated by the work of Withey and Wendt [8] on mortars for reinforced brick masonry. They state that, "Dolomitic lime-cement mortars containing over 11 percent of hydrate by weight of cement expanded unduly when continuously wet or when moist cured and tested in an autoclave. Autoclave tests indicate that by pre-soaking the lime for a week and air curing the mortar for a week the expansion may be made normal." Since they did not determine the quantity of unhydrated MgO in the mortars at the time they were made up, one cannot correlate the expansions of the mortars with the percentage hydration of magnesia. Now that the present investigation gives a method whereby that can be determined, it should be of particular interest to carry out further investigations along the lines indicated by Withey and Wendt. That they were cognizant of the importance of the lineal changes in mortars is brought out in the following concluding sentence of their report. "The magnitude of the lineal changes of the lime-cement and clay-cement mortars in certain curing conditions necessitates determinations of the durability of the bond of these mortars to brick."

The question of the expansion of mortars containing magnesia is further complicated by the fact that the rate of hydration of magnesia, under any fixed condition of moisture, is markedly affected by the temperature at which the magnesia was burned. Although there appears to be considerable uniformity in the rates of hydration of the limes studied in the present investigation (which indicates that the

limes may have been burned under somewhat comparable conditions),
yet there is no reason to believe that others may not be burned at
considerably higher or lower temperatures. In some instances at
least, it appears that prolonged exposure periods are necessary before
an initial damaging expansion begins. This is more apt to be true if
the magnesia is burned at a high temperature. White [9] made ex-
pansion measurements of bars of neat portland cement soaked in
water, and containing known amounts of free magnesia. Marked
abnormal expansions occurred in the bars containing 3 percent or more
of free magnesia. The bulk of this expansion took place between the
third and tenth years, but some bars were still expanding after 26
years of continuous immersion in water.

X. SUMMARY

There has been obtained further evidence which indicates that in
hydrated dolomitic limes the calcium oxide is generally completely
hydrated, while the magnesia is only slightly hydrated. The heats of
solution of six hydrated dolomitic limes, calculated on the assumption
that the calcium oxide was completely hydrated, agreed reasonably
well with those determined experimentally.

A heat-of-solution method has been developed for measuring the
degree of hydration of magnesia in dolomitic limes and dolomitic
lime putties. By this method, the rate of hydration of magnesia in
six commercial hydrated dolomitic lime putties, and in one dolomitic
quicklime was studied. The quicklime, which was burned in the
laboratory at 950 to 980° C and made directly into a putty, hydrated
completely in 7 days. The other putties, which were made from the
commercial hydrates, required from 2 to 4 months for the hydration
of 95 percent of the magnesia. The rate of hydration is not a linear
function of the time, but becomes decidedly slower when about 80
percent of the magnesia has been hydrated.

Simple and quick ignition-loss methods have been developed for
determining the amount of magnesia hydrated when dolomitic limes
are aged as putties or hydrated with steam. Results obtained by
these methods agreed approximately with those of the heat-of-solution
method. The ignition-loss methods should be helpful in determining
the proper aging time in the production of aged lime putties.

The effect of temperature on the rate of hydration of magnesia in
dolomitic limes has been studied. A typical commercial product
was hydrated at five different temperatures (176, 156, 136, 119,
104° C) with steam, and at three different temperatures (85, 55,
25° C) in the putty form. By use of steam at 177° C (120-lb/in.²
pressure), 95 percent of the magnesia was hydrated in about 40 min-
utes; at 85° C, in the putty form, 95 percent was hydrated in 35
hours, while at approximately 25° C, a period of about 75 days was
required for the same amount of hydration.

A preliminary study indicates that the magnesia in dolomitic limes
may hydrate slowly but steadily in moist air. In air at a relative
humidity of 50 percent, a lime having originally 16.8 percent of the
total magnesia hydrated, had, after about 11.5 months, a total of 33.2
percent hydrated. At lower relative humidities the indications are
that the rate would be very slow.

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WASHINGTON, May 19, 1937.

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