THE CALCINATION OF DOLOMITIC LIMESTONES.

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The temperature of burning is of especially great importance in the calcination of dolomitic limestone. Magnesium carbonate is more easily dissociated than calcium carbonate. There is danger, therefore, that dolomitic lime may be easily "overburned"; at least, there must be considered the factor of the magnesia which has been made more or less inert during the comparatively high temperature calcination of the calcium carbonate.

Orton and Peppel[1] found that chemically prepared magnesium carbonate dissociated at temperatures as low as 400° C. Dolomites did not show any dissociation at 700°, or if magnesia was produced at this temperature, it was only one-twenty-fifth as active as that produced from the prepared carbonate. The probable truth of this matter lies in the fact that chemically prepared magnesium carbonate is really the basic carbonate. The hydroxide dissociates at a lower temperature than the carbonate, and the oxide produced from it is very active, since it has not been subjected to any but very low temperatures. Orton and Peppel have shown that the oxide, whatever its source, is rendered inactive by heating at high temperatures. Magnesia, which had been produced at 900°, was only one-fifteenth as active as magnesia produced at 500°. Calcium oxide, which had been produced at 1,200°, showed no loss in activity until it had been heated for several hours.

Kallauner[2] concludes that dolomite is a double salt of calcium and magnesium carbonates. He states that dolomite begins to dissociate at 500° C. and reaches a first maximum at 710-730°. Up to 870°, he found a slow evolution of carbon dioxide increasing above that temperature and reaching a second maximum at 900-915°. Kallauner assumes that, at the lowest temperature of dissociation and up to 730°, the double salt decomposes into the separate carbonates with the simultaneous dissociation of the magnesium carbonate. The dissociation of the calcium carbonate reaches a maximum at the highest temperature mentioned. It seems unnecessary to the writer to explain the 710°-730° maximum as due to the dissociation of the double salt, since it may be due to the decomposition of free magnesium carbonate.

Bleininger and Emley[3] found that the minimum temperature for the complete dissociation of calcium carbonate in limestone was 898° C. with some evolution of carbon dioxide at 800°. In case of dolomitic stones dissociation at 750° was noticed.

The effect of overburning has been observed and reported by many investigators. Orton and Peppel have shown that lime burned at 1,200°

[1] Orton, Ed., Jr., and Peppel, S. V., Geol. Sur. Ohio, 4th Series, *4*, 287.

[2] Kallauner, O., Thermal Dissociation of Normal Dolomites, Chem. Zeit., *37*, 1317, also Chem. Abs., *8*, 1074.

[3] Bleininger, A. V., and Emley, W. E., Trans. Nat. Lime Assoc., *13*, 618.

"Proc. Ind. Acad. Sci., vol. 34, 1925 (1926)."

requires two and one-half times as long to completely hydrate as lime burned at 900°. Although it has been the general belief that calcium oxide is the only portion of dolomitic lime that hydrates, there is no real reason for believing that magnesia that has been produced at relatively low temperatures will not hydrate at least partially during the hydration of the calcium oxide. Kiepenheur[4] has shown that the magnesia may be hydrated to different extents. Campbell[5] has shown that magnesia, that has been produced from magnesite, is capable of a high degree of hydration if it has been burned at temperatures between 700° and 1,000°. If the temperature of burning is high, correspondingly less magnesia will be hydrated. Limes burned at different temperatures and hydrated in the ordinary ways should not contain the same amounts of magnesium hydroxide and would consequently not possess the same properties.

The amount of water with which a lime will react in any way is determined largely by the conditions under which it has been burned, the temperature and the length of the period of burning. The amount of the water combined in the form of hydroxides, the rate of slaking, and the ability of the lime, as it hydrates or after it has been hydrated, to adsorb water or react in other ways to produce a paste possessing colloidal properties are at least in part controlled by the temperature factor. The amorphous or crystalline condition of the oxides, the size of the grains, whether incipient fusion has occurred, and the densities of the lime will also be determined by the temperature and time of burning. Different crystalline forms and different chemical compounds of the hydrates may possibly be produced by differences in the rates of hydration which in turn is determined largely by the conditions under which the quicklime has been produced.

The purpose of the investigation, therefore, was to determine the properties of lime produced at various temperatures, especially at temperatures as far below those used in commercial practice as possible; to determine the effect of different characteristics of the stones upon the rate of their dissociation and thus to determine whether calcium and magnesium carbonates exist as double salts or as solid solutions in dolomites. The texture of the quicklime and their dry hydrates and the activity of the limes in the reaction with water were the properties investigated.

The National Lime Association has assigned numbers to the limestones of their various members. These numbers have been used by the writer. Two stones have been used which have been assigned no numbers. These, W 1 and Vienna, are from Knowles and Manitowoc, Wisconsin, respectively.

Various dolomites were burned at 1,000° C. for different periods of time. The extent of the burning as well as the activity of the lime was approximated by the gains in weight, when samples of the product were placed over water in a closed vessel. The temperature was that of the

[4] Kiepenheur, L., Hydration of Slaked Dolomitic Lime, Tonind. Ztg., *30*, 696 and also Chem. Abs., *10*, 1087.

[5] Campbell, E. D., Influence of the Temperature of Burning upon the Rate of Hydration of Magnesia, Ind. Eng. Chem., *1*, 665.

TABLE 1—Gain in weight during hydration in atmosphere of water vapor after burning at 1000°

Time of Hydration in Hours	3	20	48	72	96	170	260
Limestone							
103	7.8	28.0	39.6	45 6	50.8	57.4	60.4
Vienna	4.0	24.4	30.2	35.4	39.8	47.6	52.0
23	7.6	27.6	38.4	44.2	49.0	56.4	60.0
47	4.0	24.0	30.8	36.8	40.8	48.6	54.4

laboratory. Results are given in table 1. It will be noted that in each of the four cases reported that the amount of water taken up by the lime is much greater than the 17 per cent which commercial limes are supposed to gain. In the latter case the entire gain is supposedly due to the hydration of the calcium oxide. From the chemical analyses of the stones, we learn that, in general, it seems that the higher the percentage of magnesia, the lower the total amount of water removed from the atmosphere of water vapor. Vienna and Number 47, for instance, contain larger amounts of magnesium carbonate than the other stones represented. Dolomites 103 and 23, which produce non-plastic hydrates, show a greater gain. A relation seems to exist between the rate of hydration and the porosity and hardness of the stone, which would be expected to make a difference because of the ease with which the more porous stones are overburned. Dolomites 103 and 23, which are generally very closely related in physical properties, show practically the same rate of hydration and the same final gain. These stones are hard, dense, and uniformly crystalline in character. The other stones are very much alike in physical characteristics. They contain numerous solution cavities and abundant fossils.

Vienna stone was burned at 1,000° for different periods, and the limes were hydrated as before. The results for different periods of burning and hydration are given in table 2. A few results on other

TABLE 2—Relation of length of period of burning to extent of hydration

Time of Burning in Hours	Time of hydration in hours and gain in weight in per cent						
	24	48	72	96	170	240	400
Vienna, 5	24.4	....	....	....	47.6	54.4	53.0
Vienna, 24	27.0	....	....	36.6	45.0	....	50.1
Vienna, 48	24.2	....	....	....	38.5	....	46.0
Vienna, 72	25.4	....	....	....	39.0	....	47.6
Vienna, 96	....	29.4	....	....	....	....	46.2
Vienna, 156	....	....	....	31.2	....	....	45.8
47, 5	24.0	....	36.8	....	....	54.0	55.1
47, 1	....	....	46.4	....	....	68.4	....
47, ½	....	....	48.0	....	....	67.0	....
47, ⅓	....	....	46.8	....	....	64.2	....
47, 4 (730°)	....	34.4	....	....	....	....	67.8
47, 8 (730°)	....	37.6	....	....	....	....	68.0
47, 4 (750°)	36.4	....	....	....	....	....	64.6

stones are included to show the effects of low temperature burning. In general these results indicate that the maximum activity of the lime is to be obtained by burning it for the shortest period of time that will

permit the complete expulsion of the carbon dioxide. Attention is also called to the greater final gains in weight obtained by burning the stones at the lowest possible temperatures. The activity of the lime is affected and the total amount of water with which it will combine is decreased by moderately short periods of burning after the dissociation of the limestone is complete.

When dolomite 47 is burned for one hour the final gain in weight is more than 60 per cent and is comparable to the gain in weight of limes from stones 103 and 23 after the latter have been burned for five hours. When stone 47 was again heated for five hours the total gain in weight of the lime upon complete hydration over water dropped to a lower level. This brings out the fact that some of these dolomites are more easily overburned than others. It would seem that the more readily overburned stones produce the more plastic dry hydrates.

Samples of the dolomitic limes, which had been hydrated in an atmosphere of water vapor, were dried in carbon dioxide free air at 100° C. The dried samples showed gains of 47 to 50 per cent over the weights of the original samples of quicklimes. Some of the water which is taken up by the lime in a water vapor atmosphere is probably adsorbed and some is chemically combined. It is not likely that all the water left in the dried samples is of constitutional character. It seems probable that under these conditions of hydration the magnesia is partially or even completely slaked. Hydrated forms of the oxides, other than the commonly accepted hydroxides, may account for a part of this extraordinary increase in weight. Limes hydrated in this manner are not plastic after soaking, although the dry powders are very finely divided, soft, and smooth in texture.

The literature is full of conflicting statements regarding the temperature at which limestones can be completely dissociated. The theoretical considerations indicate that much lower temperatures could be employed than those used in practice. Different temperatures were, therefore, used to calcine the same and different stones, and the properties of the quicklimes produced were studied. The calcinations were carried out in a tube furnace made by wrapping an alundum tube with resistance wire and coating the whole with alundum cement and sheets of asbestos. The temperature was carefully measured and regulated by means of a thermocouple. The results are given in table 3. At a temperature of 750° and after burning for six hours, limestones 103 and 23 still contained large amounts of carbon dioxide. Under similar conditions, stones 47, Vienna, and 65 were completely burned. Stones 103 and 23 produce commercially non-plastic limes, while the others mentioned along with 111 and W 1, which were completely burned at this temperature with a slightly longer period, produce plastic hydrates under proper conditions. The two classes contain individual members which closely resemble one another in physical characteristics.

It was found in all cases that limes produced at temperatures below 950° were comparatively hard and crystalline in character. They were much more active in the reaction with water sometimes combining with almost explosive violence. The hydrates of such limes were also harsh, gritty or sandy in texture and non-plastic when soaked. The increased

TABLE 3—Temperature and the Extent of Dissociation

LIMESTONE	Temperature in Degrees C	Time of Burning in Hours	Per cent CO_2 in Product	Properties of Lime
Vienna	650—700	10	9	Hard, sandy, active
Vienna	675—710	10	2	Hard, sandy, active
Vienna	700—740	10	9	Hard, sandy, active
Vienna	750	2	28	Unburned
Vienna	750	4	24	Unburned
Vienna	750	8	4	Hard, sandy, active
Vienna	750	18	1	Hard, sandy, active
Vienna	750	46	0	Hard, sandy, active
Vienna (Burned in steam)	750	7	0	Hard, sandy, active
Vienna	800	3	7	Hard, sandy, active
Vienna	800	9	0	Hard, sandy, active
Vienna (Burned in steam)	875	11	0	Hard, sandy, active
Vienna	935	7	0	Hard, sandy, active
Vienna	960	9	0	Softer and fairly fine
Vienna	1000	1	0	Hard, but smooth and yields smooth and voluminous hydrate.
Vienna	1000	5	0	As above
Vienna	1000	17	0	As above
Vienna	1050—1150	½	0	As above
Vienna	1200	½	0	As above
47	700	3	26	....
47	700	5	2	Hard, coarse, active
47	730	9	0	Hard, coarse, active
47	750	4	1.2	Hard, coarse, active
47	800— 860	9	0	Hard, coarse, active
47	1000	5	0	Hard, but of fine texture and gives soft hydrate
103	680— 700	8	large	....
103	680— 700	13	14	Hard, coarse, active
103	740— 760	6	17	Hard, coarse, active
23	750	1.5	large	....
23	750	4	32	....
23	750	6	28	....
65	730— 800	18	0	Hard, coarse, active
65	800— 860	9	0	Hard, coarse, active
111	900	3	0	Hard, but of finer texture
111	950	6	0	....
W1	800	23	0	Hard, coarse, active
W1	750	33	0	Hard, coarse, active
W1	850	12	0	Hard, coarse, active

activity of the limes burned at low temperatures is due to the active magnesia which they contain and also to the fact that the grains have not had the opportunity to grow or partially fuse. The amount of surface is therefore greater than it would be if overburning were possible. In many cases it seems that the original crystalline character of the limestone has not been completely destroyed during the decomposition of the carbonates at low temperatures. These limes were found to gain about 67 to 69 per cent in weight when hydrated over water. This is considerably more than the gain of the same limes when burned at 1,000° or higher. When some of the stones were burned at the lowest temperatures, the limes possessed a very pronounced blue or steel color. When the temperature of burning was above 850°, the color of the lime is white or slightly pink. When burned at high temperatures for fairly long periods, the lime becomes brown or buff in color. Whatever the compounds may be that cause these color changes, it seems that they are finely and uniformly distributed throughout the stones. It is probable that they consist of ferrites and ferrates, aluminates and silicates but their composition has not been determined.

In order to determine the relation of the chemical structure of the stones to the temperature and rate of dissociation, one gram samples of different stones were burned for one, two and three hour periods at 600°, and at 650°. These results are given in table 4. From these

TABLE 4—Rate of Dissociation

LIMESTONE	Temperature Degrees C	Loss in Weight after burning one hour (per cent)	After two hours	After three hours
103......................	600	4.3	6.7	10.0
W1......................	600	3.0	4.5	5.5
111......................	600	4.0	5.5	6.9
47.......................	600	5.7	8.3	10.7
103......................	650	14.4	16.0	21.5
W1......................	650	3.6	5.4	8.7
111......................	650	4.6	7.5	9.2
47.......................	650	11.0	11.7	13.9

results, it may be seen that the rate of burning is slow but progressive at these low temperatures. Different stones exhibit markedly different rates of dissociation at the same temperatures.

For a more systematic study of the rate of burning at various temperatures uniform samples of stone were prepared by crushing and screening. The material used for the tests passed through a 20 but stopped on a 40 mesh screen. The loss of carbon dioxide during one hour of burning was calculated as per cent of the original weight of the stone samples. Curves showing these results are shown in figure 1. It will be noted that breaks occur in the curve for stone 103 at temperatures betwees 700° and 735°. In all other cases the curves are smooth and regular and indicate the gradual, progressive decomposition of the carbonates. The breaks in the curves represent the decomposition of double salts. The regular curves represent the dissociation of mixed crystals or solid solutions. The rapid rate of dissociation of stone 65 at the lowest temperatures is noteworthy. In general, those stones which contain double salts show smaller losses of carbon dioxide at the lower temperatures. This is due to the fact that there is no free magnesium carbonate until after the dissociation of the double salt at about 725°. The limestones, which seem to be made up of double salts are dense, finely crystalline and rather free of cavities and fossils. All other stones are quite porous and contain mixtures of variously colored materials. The stones, which are used commercially to produce plastic hydrates, belong to the class represented by 111 and 47, stones composed of mixed crystals or solid solutions.
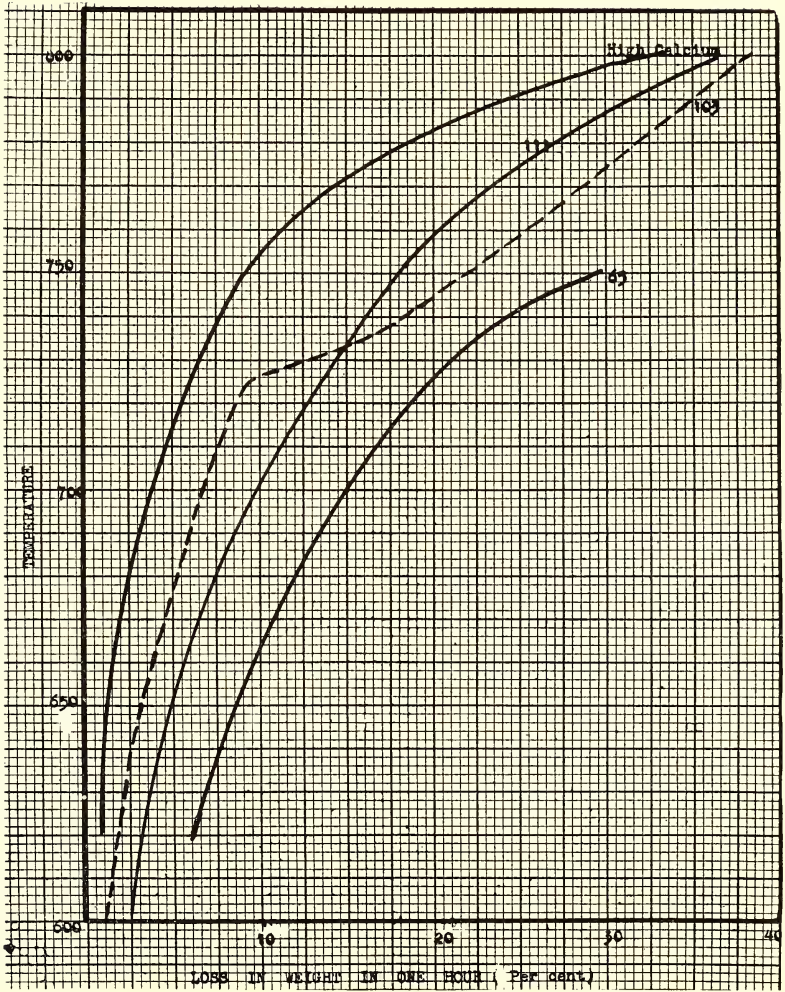
Fig. 1—Representative Curves Showing Rates of Dissociation of Stones Belonging to the Two Groups, Double Salts and Solid Solutions.