

Temperature Studies on Lime Burning

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Examination of recent literature shows very little information on the optimum time and temperature needed for burning limestone to a good lime for Steffens use. Hartman and McGinnis (1)² have given theory, conditions, and procedures necessary for good lime burning. Clark (2-3) has covered the mechanics of good kiln operation. Daniels and Cotton (4) have described a process for re-burning lime cake. A considerable amount has been written about the fundamentals of lime burning for commercial use (5), and Azbe (6) has examined the effect of time, temperature, and the rate of burning of limestones for the production of commercial lime. Work has been carried on at Massachusetts Institute of Technology under the sponsorship of the National Lime Association, and Murray, et al. (7-8) have examined the effect of temperature and time on lime burned from a number of limerocks.

Limes of similar chemical composition very frequently act differently in a given chemical use, and this difference in behavior is quite pronounced in Steffens operation. The nature of the limestone, the conditions of temperature, and time under which it was burned to a lime seem to be the factors that cause these differences in behavior. Physical properties rather than chemical composition seem to be the governing factor and very little is known about the differences that do occur.

As part of a program on Steffens operation we undertook burning studies on limerocks that are used in all of our Steffens operations. A large number of different rocks were studied but the results of only two will be reported here. Rock A is a limestone giving excellent lime for Steffens operation. It is a gray limestone consisting of lightly-packed, well-cemented oörites with crystals of recrystallized calcite. In it can be observed a few fossil fragments. Rock B is a dark, gray, crystallized limestone showing a wide range of crystal sizes. The calcite crystals are larger than those in A and very few fossil fragments are present. It is a difficult rock to burn, giving poor to fair Steffens lime.

Both rocks are high in calcium carbonate: Rock A, 96.75 percent and Rock B, 98.53 percent. Rock A has 1.3 percent silica and insoluble, while Rock B is 0.5 percent. The amount of iron and aluminum oxide is about 0.3 percent in each rock, while Rock A contains 1.63 percent magnesium carbonate as to a 0.9 percent for Rock B.

Preliminary tests on burning with a small coke-fired kiln proved unsatisfactory due to difficulty in controlling the many variables and inability to reproduce results. Small laboratory furnaces have been found unsatisfactory except for burning very small amounts of lime, so it was necessary to construct our own furnace. With a basic design furnished us by The Carborundum Company, a large electric-type muffle furnace was built (Figure 1). Using large Globar heating elements, special refractories and

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² Numbers in parentheses refer to literature cited.

insulation, we are able to maintain very good control of temperature and obtain a very rapid recovery of furnace temperature due to temperature drops when samples are being placed in or taken out of the furnace. A

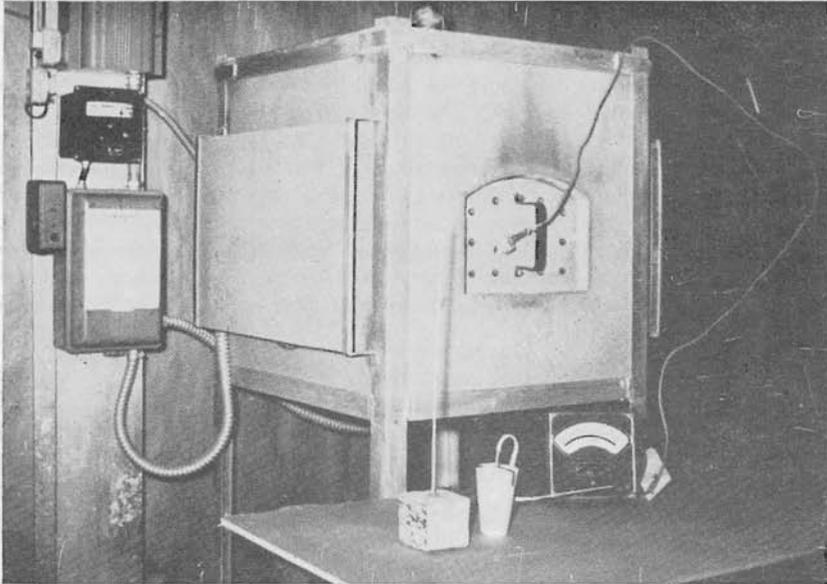


Figure 1.—Furnace for burning tests.

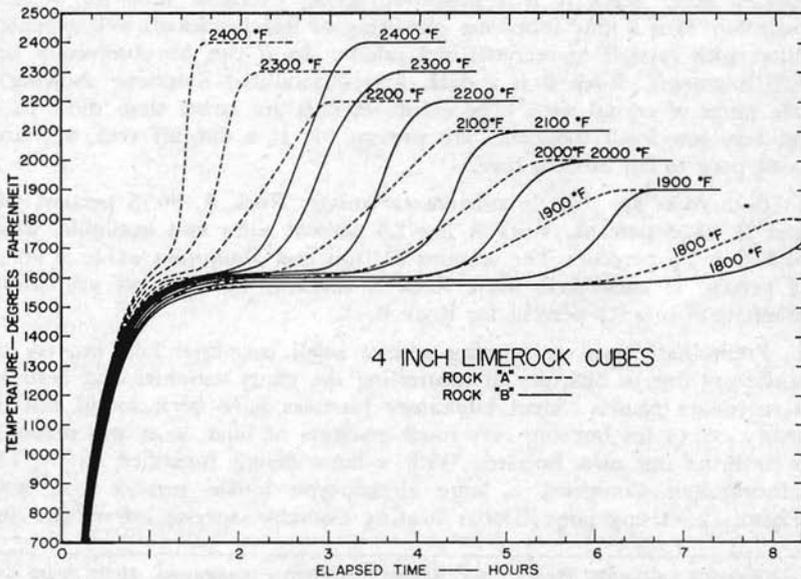


Figure 2.—Difference in burning rate 4" cubes Rocks A and B.

Wheelco temperature controller is used with a platinum, platinum-rhodium thermocouple which gives good control within 20° of any pre-set temperature.

The first studies were made on rate of burning. Large pieces of limestone were cut into cubes of 2 inches, 3 inches, and 4 inches. A small hole was drilled into each cube to the center and a thermocouple was sealed into the center of the cube. Figure 1 shows a cube with a thermocouple inserted. Before the cubes were put into the muffle furnace it was pre-heated to about 100° F. above the temperature being studied. By the time the samples were set in place and the thermocouples connected we found that the furnace would drop to just about the desired temperature. From there on the temperature controller held the furnace at any pre-set temperature. Temperature readings were made on the rock at ten minute intervals and the resulting temperature then plotted against time.

From Figure 2 you can see that the temperature rises very rapidly to about 1600° F., which is the approximate dissociation temperature of calcium carbonate at about one atmosphere pressure (5). The temperature remains constant until almost all of the CO_2 is calcined off, at which point the temperature again rises very rapidly to the surrounding furnace temperature. From CO_2 analysis of the lime burned on a number of cubes we found that almost all of the CO_2 was driven off at about half way up on the second steep part of the curve.

Rock B requires considerably longer time to burn out than Rock A, the difference in time varying with the temperature.

Figure 3 shows the difference in rate of burning of 2-inch, 3-inch, and 4-inch cubes and of a large slab 12 inches by 6 inches by 4 inches at 2200° F. temperature. The data on this curve shows very clearly the importance

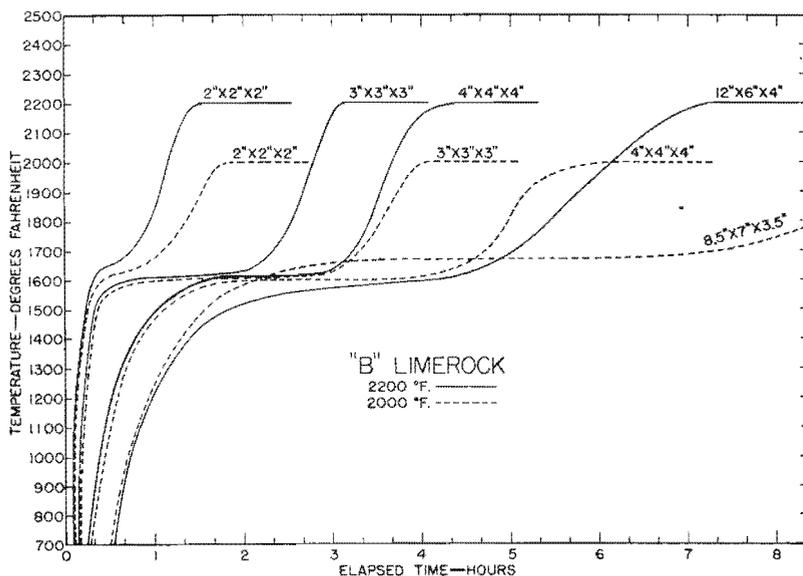


Figure 3.—Difference in burning rate for various size rock.

of even sizing of limestone to a kiln and that the thickness in dimension is not the determining factor of the rate of burning as the 12-inch by 6-inch by 4-inch slab required a much longer time to burn out than the 4-inch cube. The 8½-inch by 7-inch by 3½-inch slab required over 9 hours at 2000° F. to burn out as compared to a time of 5 hours for a 4-inch cube at the same temperature.

The data shown in Figure 2 give the time and rate of burning of the two limerocks but does not give any indication of the quality of the resulting lime for Steffens use. Previous work we had done on fineness of grind and surface area, and work done by Shafor (9), had shown that fineness of grind of the lime was a very critical factor in Steffens operation. We found it impossible to grind the lime obtained from the rate of burning tests to any comparable fineness or surface area. The lime obtained from the cubes burned at 1800° F. was soft and tended to mush up on grinding surfaces, while that burned at 2400° F. was very hard. After many attempts at trying to obtain the same fineness of grind with different equipment we gave up trying to grind the burned lime and, instead, ground a large sample of the limestone being investigated to as fine a grind as possible. From this one sample we burned portions of it in large refractory-melting crucibles at the various temperatures in order to evaluate the lime for sugar recovery. Extreme care was taken in getting samples of Rocks A and B and resulting lime to the same degree of fineness.

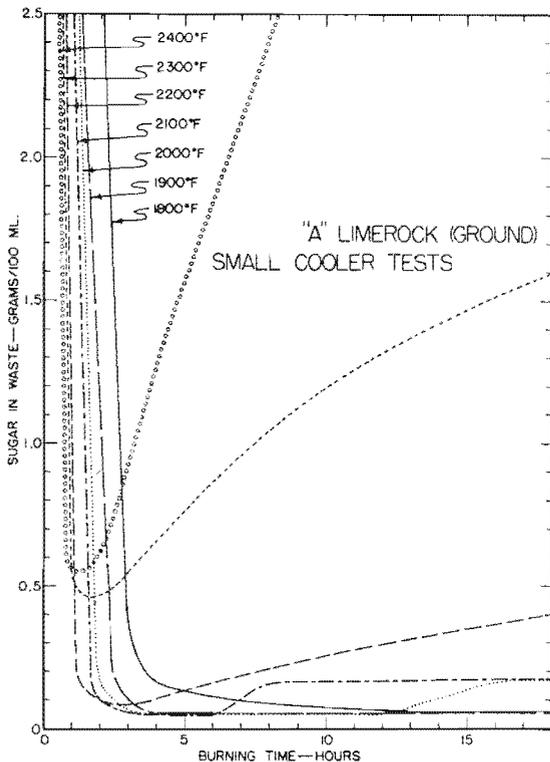


Figure 4.— Sugar recovery for lime from Rock A at different temperatures.

A standard cooler test was worked out which gave very reproducible results and in comparison with factory operation, using the same lime used in factory coolers, we obtained parallel results, getting slightly better sugar recovery with lower lime additions than that obtained in factory coolers. Lime addition was standardized at 90 lime addition per 100 sugar in molasses. Standard molasses was used at 6.1 percent sugar. The length of lime addition, temperature, and time were all held constant, with the only variable being the lime under test.

Figure 4 shows the results obtained on Rock A and Figure 5 shows the results obtained on Rock B.

Burning time in hours is plotted against grams sugar per 100 ml. in cold waste at various temperatures.

Rock A curves in Figure 4 show that at 1800°, 1900°, and 2000° F. sugar recovery is optimum and no overburning takes place up to 24 hours at these temperatures. At 2100° F. a very slight overburning is observed with increasing time which becomes more pronounced at 2200° F. However, fair Steffens lime is still obtained at 18 hours at this temperature. At 2300° and 2400° F. overburning is very rapid and the resulting lime gives very poor sugar recovery.

Rock B (Figure 5), burned under identical conditions as Rock A,

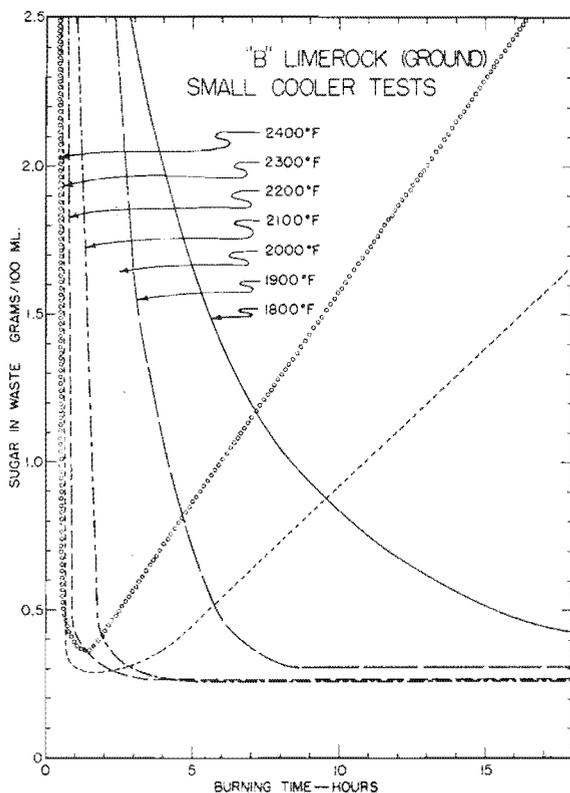


Figure 5.— Sugar recovery for lime from Rock B at different temperatures.

shows that this rock requires burning for 24 hours to reach maximum sugar recovery at 1800° F. obtained in 6 to 8 hours with Rock A. At 1900° and 2000° F., again, a longer time is required for Rock B than Rock A. No overburning was found after 24 hours with Rock B at 2100° or 2200° F., but again, at 2300° and 2400° F. overburning takes place but not as rapidly as with Rock A. A second sample of Rock B, obtained from a different part of the quarry, gave almost identical results as shown in Figure 5. Rock from one of our other plants had a rate of burning as slow as Rock B and yet showed very good Steffens results at 1800° F. in a shorter time than Rock A.

By inserting a thermocouple in the center of the fine ground limestone in the melting crucibles at a furnace temperature of 1800° F., 1 hour 10 minutes was required for both Rocks A and B to reach approximately 1600° F. At 4 hours 10 minutes the temperature in Rock A rose rapidly to the furnace temperature but it required 5 hours 10 minutes to reach the furnace temperature with Rock B.

From Figure 4 Rock A reached maximum sugar recovery in about the same time, 4 hours 10 minutes, that it reached the furnace temperature; but with Rock B (Figure 5) 24 hours at 1800° F. was required to reach maximum sugar recovery. Yet, it required only 5 hours 10 minutes to reach furnace temperature.

Figures 6 and 7 on Rocks A and B were obtained by combining the data of the rate of burning tests on various sizes of cubes, and the data obtained on the powdered limestone for sugar recovery correcting for the time required for the powdered lime to rise to furnace temperature. Within

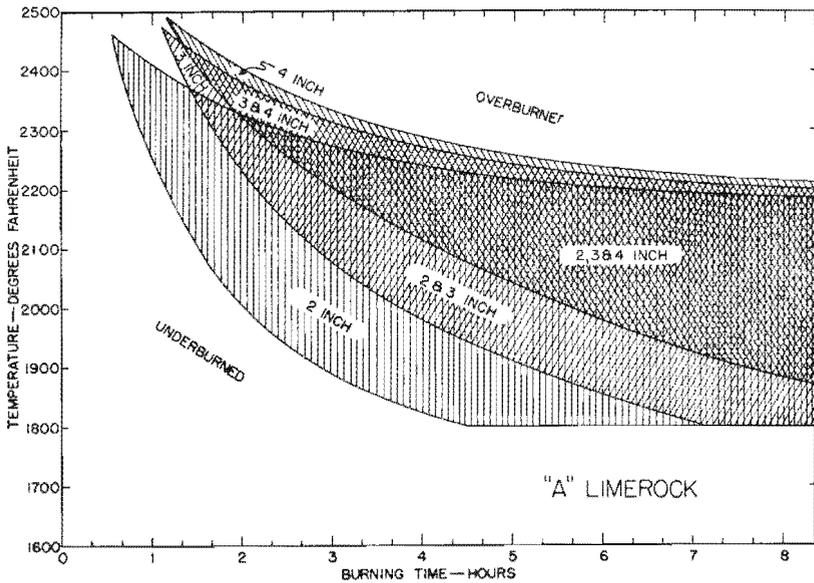


Figure 6.—Curves showing optimum time and temperature for good Steffens lime for Rock A.

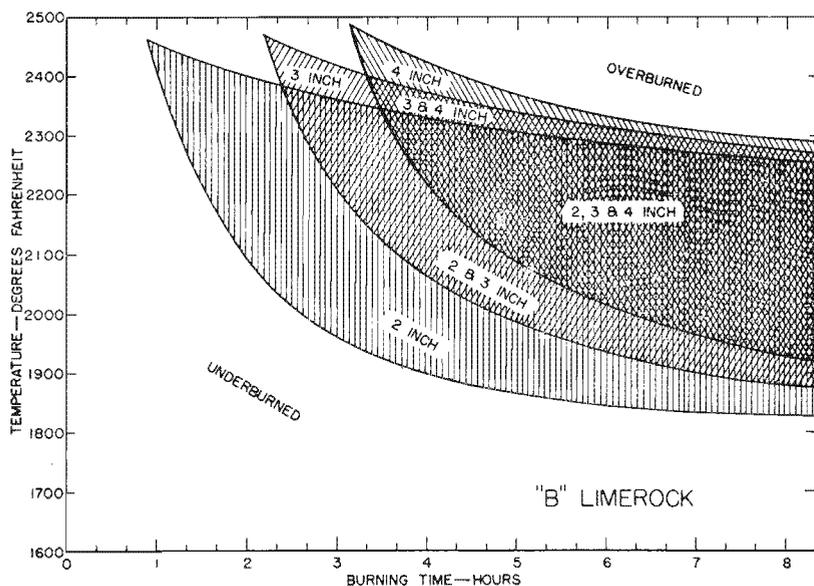


Figure 7.—Curves showing optimum time and temperature for good Steffens lime for Rock B.

the shaded area for each size rock represents the time and temperature at which the rock can be burned to an optimum Steffens lime, and outside of these areas is either overburning or underburning.

One of the quarries which is a source of limestone for one of our plants has two definite types of limestone, one very soft and the other extremely hard. Samples of these two types were ground to the same degree of fineness and burned at several temperatures. Very little difference in the small cooler test curves was obtained; or was there any difference in the rate of burning of cubes cut from the two different type rocks.

We have found considerable variation between the temperature of overburning existing between different limestones. One limestone considered good for Steffens lime showed almost the same degree of overburning at 2000° F. as shown in Rock B at 2300° F., and at 2200° F. for this rock the resulting lime was worthless for Steffens recovery in a very short time.

The conditions of temperature and time under which we conducted our studies do not approach those that exist in a vertical lime kiln using coke as a fuel. However, the results we obtained have shown the importance of burning temperature and time on lime for Steffens use and the large variation that exists between limestones. Even with the difficult to burn limestone, such as B, good Steffens lime can be obtained if the optimum conditions of temperature and time are met.

Control of temperature in a vertical coke-fired kiln is very difficult and extreme variations of temperature exist that vary from day to day

or even from hour to hour. Accurate measurement of the temperature through a vertical kiln is very difficult to obtain, and probably once obtained, is not too accurate.

Figure 8 shows the data from a series of 12 different determinations made over a period of several days on one of our lime kilns in regular operation. To obtain the difference between the outside porthole-temperature measurements and the actual temperature at the center of the kiln a number of comparison measurements were made by driving a 1¼ inch tubing into the center of the kiln and then sighting through the tube with an optical pyrometer and measuring the temperature at the end of the tube. Over a number of measurements taken with considerable difficulty the average difference was 140° F. from the center to the outside wall of the kiln. Shown in Figure 8 is the kiln divided into zones and the approximate time the rock is in each zone based on a 24-hour cycle obtained by the average time a number of firebricks took to pass through the kiln when charged with the linerock while in regular operation. The temperatures

% OF TOTAL VOLUME	ELAPSED TIME IN KILN	TIME IN EACH ZONE	ZONE TEMPERATURES DEGREES FAHRENHEIT		
			HIGH	LOW	AVERAGE
8.3	2 HRS. 0 MIN.	2 HRS. 0 MIN.			
9.3	4 HRS. 14 MIN.	2 HRS. 14 MIN.			
5.4	5 HRS. 32 MIN.	1 HR. 18 MIN.			
5.9	6 HRS. 57 MIN.	1 HR. 25 MIN.	2190	1670	1879
6.4	8 HRS. 29 MIN.	1 HR. 32 MIN.	2370	1660	1985
7.0	10 HRS. 10 MIN.	1 HR. 41 MIN.	2560	1700	2102
7.5	11 HRS. 58 MIN.	1 HR. 48 MIN.	2400	1700	2011
8.0	13 HRS. 53 MIN.	1 HR. 55 MIN.	2500	1670	2044
7.9	15 HRS. 47 MIN.	1 HR. 54 MIN.			
8.4	17 HRS. 47 MIN.	2 HRS. 0 MIN.			
21.2	22 HRS. 52 MIN.	5 HRS. 5 MIN.			
4.7	24 HRS. 0 MIN.	1 HR. 8 MIN.			

Figure 8.—Retention time and temperatures measured in vertical kiln.

TOTAL KILN VOLUME—4170 CU. FT. WORKING VOLUME—3475 CU. FT.

in each zone are average temperatures obtained from a number of temperature determinations and corrected for the center to outside cross-sectional measurements. The high and low temperatures obtained are shown which were measured in each zone from day to day and from porthole to port-

hole in the same zone. The temperature differences in this kiln may not be typical of all vertical kilns but do show that large variations of temperature do exist in a kiln.

Zones 3 and 9 at times would show temperatures above 1600° F., but for the most part both were below this temperature and can be considered pre-heating and cooling zones. Considering that the calcining zone exists between 3 and 9 and calculating the time the rock is in this zone on a percentage volume basis, the time the rock is in this zone is approximately 7 hours 20 minutes with an average temperature of 2000° F.

From Figures 2 and 3 a 4-inch cube would burn completely out, but larger pieces, such as 8½ inches by 7 inches by 3½ inches would only be partially burned. Small pieces, such as 2-inch cubes, would burn out by the time 5 and 6 zones are reached and be badly overburned when subjected to the high temperatures in the hot spots of 2500° F. that sometimes exist in the zones below. We can see that the lime obtained from vertical kilns such as this is a mixture of overburned and underburned lime and probably very little of the lime has been subjected to the optimum conditions for good Steffens lime.

In general, longer cycles with lower burning temperatures using very even sized rock should give better lime for Steffens use, using vertical coke-fired kilns.

The temperatures that exist in the hearths Nos. 6 to 10 of a Skinner roaster should be ideal for burning limestone to good Steffens lime, and it has been shown that lime from such a roaster is excellent for Steffens use (4). The fluidized solids calciner developed in recent years with close temperature control should also give excellent lime for Steffens use, and it is not inconceivable that with proper mechanical technique a method of rapid flash calcination using finely pulverized material could be developed that would be the ultimate for producing lime for Steffens use.

Calcination at higher temperatures of lime for long periods of time is believed to result in the inter-atomic spacing in the crystal lattice becoming so small that water molecules can penetrate only slightly (6). We have shown in the limerocks which we have examined under the conditions reported here, that up to 2000° F. for 24 hours had little effect on the quality of lime for Steffens use. At 2000° F. some rocks undergo a slight modification after prolonged heating at this temperature (Figure 4), while others may overburn more rapidly. Rock B (Figure 5) did not show any change at 2100° F. up to 24 hours. Some rocks give good Steffens lime at 1800° F. in a short time, such as Rock A, while others, such as Rock B, require prolonged time even after the CO₂ is driven off to show maximum sugar recovery.

From our work we believe that thermal analysis of limestone is valuable in determining the suitability of limestone for Steffens use and, also, in determining the burning range for individual limestones. Of the many limestones we have examined, each has shown an individual characteristic curve which seems to be typical of the quarry from which it is obtained, regardless of place in the quarry or type of rock.

Chemical constituents, except very high levels of accepted fluxing agents, do not seem to have any effect on the resulting lime for Steffens

use. A number of reagent grade chemicals were added to pure reagent grade calcium carbonate. Both the calcium carbonate and chemicals were finely powdered and mixed well. Each sample prepared contained 1 percent of the added chemical and 99 percent calcium carbonate. All samples were burned at 2200° F. for eight hours under identical conditions and a check sample of the pure calcium carbonate was included for comparison. Small cooler tests on the resulting lime, using 80 lime addition, were made and the sugar recovery was identical for all samples with the check.

The following chemicals were used: aluminum silicate and acetate, sulfur, sodium carbonate, ferrous carbonate, sodium silicate, magnesium carbonate, and silica. Wide differences were observed in the physical appearance of the resulting limes. Both sodium samples were very dense, while others, such as magnesium carbonate, gave resulting powders that were very light and fluffy.

X-ray diffraction studies made so far have proven disappointing and inconclusive on both the original limestones and resulting lime burned from them. Burning tests and small cooler evaluation of the lime obtained from two different reagent-grade, high-purity calcium carbonates have shown wide differences to exist between the two in the temperature required to bring them to a good Steffens lime. This work is not completed and an X-ray diffraction study is indicated on these reagent-grade calcium carbonates and the lime obtained from them. Perhaps from such study, using these pure materials, a better interpretation of the results of X-ray diffraction on limestone and lime can be made.

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