

DEPARTMENT OF COMMERCE AND LABOR

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S. W. STRATTON, DIRECTOR

No. 30

LIME: ITS PROPERTIES AND USES

[1st Edition]

Issued April 15, 1911



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I. INTRODUCTION

Lime has been used as a building material for centuries, but until recently very little exact information about its properties has been obtainable. It has always been such a cheap commodity that the transportation cost was of more importance to the consumer than the quality of the lime. Recently the chemical industries have opened a new market for lime in which quality is of paramount importance, and contractors and builders have learned that low cost and cheapness are by no means synonymous. Therefore it has now become necessary to study the properties of lime with a view to drawing up standard specifications so that manufacturer and consumer will be enabled to reach an exact understanding. Such a study must include the distribution of economically available deposits of limestone, the methods of manufacture, the methods of testing lime, and the properties which the lime must have in order to satisfy the various consumers. The first two of these subjects will be treated more in detail in articles by Mr. Burchard and Mr. Emley shortly to be published by the United States Geological Survey and the United States Bureau of Standards respectively.

II. LIMESTONE

Limestone is one of our commonest rocks. It is of sedimentary origin, having been deposited originally from solution by living organisms, or by chemical or physical processes not related to changes in living matter. It consists essentially of calcium carbonate, but, as may be expected from its origin, is never found pure. The impurities generally present are magnesia, iron, alumina, and silica.

On the basis of chemical composition, limestones may be divided into several classes. Very pure crystallized limestone is known as "calcite." As the content of magnesia increases the stone is called "magnesian limestone" until the ratio of calcium carbonate to magnesium carbonate becomes 100 to 84, when the name is changed to "dolomite." If the magnesia content remains low, but the other impurities increase, the series becomes "argillaceous (clayey) limestone," "natural cement rock (with suitable clay content for cement manufacture)," and "calcareous shale."

Limestones may also be classified according to their physical properties as hard or soft, porous or dense, coarsely crystalline or fine grained. When metamorphosed—that is, when through the agency of heat limestone has been recrystallized after deposition—it is known as "marble."

III. LIME

1. METHOD OF MANUFACTURE

In the manufacture of lime, limestone is quarried, broken into convenient sizes, and burned in a kiln. There are three types of kilns in common use—the pot kiln, the patent kiln, and the rotary kiln. All consist essentially of shafts lined with fire brick. The stone is fed in at the top and the lime drawn out at the bottom. In the pot kiln fuel is fed in with the stone in alternate layers; the patent kiln is provided with external fire boxes, so that only the gases of combustion come into contact with the stone; the rotary kiln is of the ordinary type used in the cement industry. Of the three, the patent kiln is much the best for the production of lime, because where the fuel is in actual contact with the stone the ashes of the fuel will contaminate the lime produced. This objection does not, of course, apply to rotary kilns fired with gas.

Some limestones are composed of coarse crystals, loosely bound together, and others contain so much silica that di-calcium silicate is formed during the burning. This substance increases in volume on cooling,¹ thus causing disintegration of the lime. If either of these kinds of stone is used, the fine powder produced will choke the draft in a shaft kiln, and consequently a rotary kiln must be used.

Limestone consists essentially of calcium carbonate. During the burning process enough heat is supplied to break up this compound. The carbon dioxide is driven off as a gas, leaving the calcium oxide, or lime. Magnesium carbonate is broken up in the same manner. The amount of heat to be supplied depends on the character of the stone, and may vary within rather wide limits. Under ordinary conditions, calcium carbonate will break up at 910°C (1670°F).² At about 1200°C (2192°F) the impurities form chemical combinations with the calcium oxide. This results in incipient vitrification on the outside of the lump, so that when water is added it can not penetrate so readily, and therefore the lime slakes more slowly. Therefore, the temperature at which lime is burned may vary from 910°C to 1200°C , or a little higher if the stone is very pure. The amount of heat supplied varies as the temperature used, and also as the time. Consequently it is optional with the manufacturer whether he shall use a high temperature for a shorter time or a lower temperature for a longer time. His choice depends on the economic relation between interest on investment and cost of fuel. However, the activity of the impurities becomes noticeable much below 1200°C , and therefore the lower the temperature at which lime is burned the better will be its quality. This is the reason why "wood-burned" lime generally commands a higher price than that burned with coal. Moreover, the minimum temperature for the decomposition of calcium carbonate may be decreased from 910°C to 790°C (1454°F) by the introduction of steam into the kiln.³ Thus the presence

¹ Day and Shepherd: The lime-silica series of minerals, Jour. Amer. Chem. Soc. 1906, p. 1089.

² Zavriev: Chem. Abs., 3, p. 1112. J. chim. phys., 7, p. 31; 1909.

³ Orton and Peppel: Limestone and Lime Industry in Ohio, Geological Survey of Ohio, Bull. No. 4, p. 294; 1906.

of steam in the gases of combustion from wood tends to the production of a better quality of lime.

From the above discussion it is apparent that both manufacturer and consumer must see to it that the lime is burned at the proper temperature. In the present state of our knowledge, an accurate practical test for this important property has not been devised. The establishment of such a test is one of the objects of the present work of the bureau.

2. DEFINITION AND CLASSIFICATION

A consideration of the burning process as just described shows that lime is merely limestone from which the carbon dioxide has been removed by heat. This, then, must constitute a definition of lime. The wide variation in the chemical and physical properties of limestones necessitates a similarly great difference in the kinds of lime. Therefore, some system of classification becomes necessary. The National Lime Manufacturers Association has officially adopted a classification based on the content of magnesia as follows: ⁴

High-calcium lime contains	0 % to	5 %	magnesia.
Magnesian lime	"	5 % " 25 %	"
Dolomitic lime	"	25 % " 45 %	"
Super-dolomitic lime	"	over 45 %	"

The association has also agreed that the product of calcination of limestone shall be called lime only when the total amount of impurities (not including magnesia) is less than 5 per cent. The writer has found it convenient to use a system based on the purpose for which the lime is best fitted, as, *building, finishing, chemical, or agricultural* lime. Both systems of classification will be used in this circular.

3. GENERAL PROPERTIES

Since lime has such an indefinite commercial meaning, any description of properties must be very general. There are, however, several properties which are common to all limes in a greater or less degree. Thus it may be said that lime is a white or nearly white substance which will slake when water is added to it. When lime slakes, it enters into chemical combination with the water. This reaction generates heat, and is accompanied by an increase in volume. Slaked lime when exposed to air will set. First the excess water evaporates, and then carbon dioxide from the air attacks the lime, converting it back to the original calcium carbonate. Setting is always accompanied by a decrease in volume, or shrinking.

The degree in which any lime possesses the above properties is more or less dependent on its chemical composition. For example, a dolomitic lime will slake more slowly, combine with less water, generate less heat,

⁴ Warner and Lazell: Glossary of terms in connection with the manufacture of lime, Proc. Nat. Lime Mfrs. Assn.; 1910.

undergo less increase in volume, set more slowly, and shrink less than a high-calcium lime. This statement must be taken as a generalization, for the properties are decidedly influenced by the impurities, the temperature of burning, and many other factors.

When lime is exposed to the air, it absorbs carbon dioxide and water. This air-slaking is accompanied by the generation of heat, so that if lime is to be stored it must be in an air-tight receptacle, or else precautions must be taken to prevent the outbreak of fire. Completely air-slaked lime is practically identical with finely ground limestone, and therefore has no value as lime.

Underburned lime is produced when the temperature of burning is too low or the time is too short. Some calcium carbonate is retained in the lime. Such lime can be used for certain purposes, the calcium carbonate acting merely as an inert filler. Since underburned lime does not contain so much of the active calcium oxide, its reactions will be much slower than if it were burned in the proper manner. It is possible, therefore, to produce a lime having many of the properties of a dolomitic lime from a high-calcium limestone merely by underburning it.

Overburned lime is produced when the temperature of burning is too high or the time too long. Since it is due to the activity of the impurities,⁵ it follows that a very pure lime can not be overburned within practical limits. Overburned lime will react similarly to lime burned in the proper manner, except that the reactions will take place much more slowly. There is no reason why it can not be used instead of good lime for any purpose, provided sufficient care is taken to insure its complete hydration before using. However, some of the compounds formed by the impurities in lime hydrate very slowly, so that it is hardly practicable to use an impure overburned lime for the final coat of plastering.

4. COMMERCIAL ARTICLES AND PREPARATION FOR USE

Lime is put on the market as either lump or ground lime. Lump lime is shipped in bulk, or in wooden barrels holding from 100 pounds to 300 pounds. Ground lime is lump lime which has been ground and screened generally through 60 mesh. It is shipped in air-tight iron casks holding about 400 pounds.

To prepare lime for use in building or plastering operations, it must first be slaked. This is accomplished merely by the addition of water, but there are several points to be noted in this connection.

The plasticity, or spreading quality of lime, depends on the presence of colloidal calcium hydroxide.⁶ Since the quantity of colloidal, in distinction from crystalline, calcium hydroxide produced depends on the rapidity of the reaction,⁷ it follows that the warmer the water used in slaking

⁵ Bleining: Burning Temperature of Limestone, Proc. Nat. Lime Mfrs. Assn.; 1911.

⁶ Ashley: The spreading and setting qualities of lime mortars, Trans. Nat. Lime Mfrs. Assn.; 1910.

⁷ Von Weimarn: Zs. für Chem. & Ind. der Kolloide, 2, p. 76.

lime the more plastic will be the product, and also that as little excess water as practicable should be used.

Calcium oxide generates so much heat during slaking that unless this heat is removed or some means provided to prevent too great a rise in temperature the lime will "burn." It is not known just what this reaction is, but the resultant product, burned lime, will not slake and acts very similarly to ground limestone. Therefore, it is necessary when slaking a high-calcium lime to watch it and stir it continually. If every particle of lime is in intimate contact with plenty of water, this water will absorb the heat generated and prevent burning.

With a dolomitic lime the reaction of slaking is so slow and the quantity of heat generated so small that the danger of burning is eliminated. On the contrary, the danger in this case is that the lime may not be completely slaked when used. Subsequent hydration would be accompanied by an increase in volume, which would be very detrimental to construction work. To insure complete slaking, it is customary to age dolomitic limes under water for from 24 hours to 1 month before using.

After lime has been slaked, sand is added to it. This decreases the cost by making the same amount of lime cover a larger surface. It improves the spreading quality. It decreases the shrinking when the lime sets, and produces a more porous mass into which the carbon dioxide can penetrate more readily, so that the setting takes place more rapidly. When neat lime is used, the tendency to shrink on setting will weaken the bond. The quantity of sand should be so proportioned that it will just prevent shrinking. Thus we find that one volume of sand added to one volume of lime paste gives a stronger mortar than the neat lime. When the sand is increased to the ratio 3:1, the mortar has about the strength of neat lime, and any further increase of sand will tend to weaken it still more.⁸ These ratios are for high calcium limes only. For dolomitic limes, theoretical deductions would give about the same ratios, but no tests seem to have been made.

The setting of lime is caused first by the evaporation of excess water, and finally by the action of carbon dioxide, causing the lime to revert into the original calcium carbonate.⁹ Therefore, setting will take place more rapidly if the amount of carbon dioxide in the air is increased.¹⁰ Dry carbon dioxide will not react with dry slaked lime,¹¹ so that it is necessary for the air to be moist. Indeed, it is advisable to soak the mortar thoroughly at frequent intervals during the setting process.

The final, or "skim" coat in plastering is often put on without sand in order to obtain a better color.

⁸ Burchartz-Luftkalke u. Luftkalkmörtel-Mitt. d. Kgl. Materialprüfungsamt, p. 53; 1908.

⁹ Burchartz: Same, p. 81.

¹⁰ Ashley: Trans. Nat. Lime Mfrs. Assn.; 1910.

¹¹ Wolters: Dinglers Polytech. Jour., 196, p. 344.

IV. HYDRATED LIME

1. MANUFACTURE

Lime that has been slaked has recently become an article of commerce under the name of "hydrated lime." This substance is prepared by adding to ordinary lime just sufficient water to assure complete slaking, and so that the heat generated will evaporate all the excess water, leaving the product dry. Since slaking is accompanied by an increase in volume, the lumps of lime fall into powder during the process. Any impurities in the lime will not slake, will not fall into powder, and consequently can be removed from the finished product by screening.

2. PROPERTIES

Hydrated lime is therefore a fine, dry powder, consisting essentially of calcium hydrate and magnesium oxide; for it is generally conceded that the magnesia does not slake during the ordinary process of manufacture. The quantity of water contained varies from 24.3 per cent for pure high calcium hydrate to 11.3 per cent for impure dolomitic hydrate. The proportion of impurities is generally less than that in the lime from which it was made.

In building operations hydrated lime may be used for any purpose in place of lump lime, with precisely similar results. The consumer must pay the freight on a large amount of water, but the time and labor required for slaking lime is eliminated, and there is no danger of spoiling it either by burning or by incomplete slaking.

Hydrated lime will keep better than lump lime, because the powder packs together into a dense mass, rendering the penetration of carbon dioxide very difficult. It can be stored with absolutely no danger of fire.

3. COMMERCIAL ARTICLE AND PREPARATION

Hydrated lime is put on the market in paper sacks of 40 pounds each and in burlap sacks of 100 pounds. The Urschel-Bates valve bag is used almost universally. There are many varieties of hydrated lime, depending on the fineness of grain. It can be obtained screened through any mesh from 10 to 200.

To prepare hydrated lime for use, the mere addition of water is all that is necessary. It is a rather difficult powder to wet, however, so that it is advisable to let the hydrated lime and water stand for 24 hours before using. Or it can be used immediately if the hydrated lime is added to the water, rather than water to the hydrated lime.

V. USES OF LIME

1. LIME AND HYDRATED LIME

(a) **Building Lime.**—By far the greatest use of lime is as a mortar for building purposes. Whether a dolomite or a high calcium lime is best suited for this purpose has long been an important question for both lime manufacturers and builders. In considering this question, the points of difference between the two limes should be noted.

A high calcium lime slakes quickly and generates a large amount of heat, hence it is apt to "burn" if it is not watched carefully. A magnesian lime slakes slowly, generates comparatively little heat, and is never in danger of burning. A high calcium lime increases in volume much more than a magnesian lime, and requires more water, both for the hydration and the formation of a paste. Magnesian mortars generally work smoothly and freely under the trowel, while high calcium mortars are apt to be sticky and work "short." When laid in the wall both limes set by absorbing carbon dioxide from the air. During this process a high calcium lime shrinks noticeably, while the change of volume of a magnesian lime is much less. It must be borne in mind that the above properties are subject to radical modifications, due to different porosities of the stones or to different conditions of burning.

The usefulness of lime as a bonding agent probably depends more on the method in which it is handled than on its content of magnesia. Aside from the larger cities where machine-mixed mortar can be had, the slaking of lime is generally left to unskilled labor. In such cases, the kind of lime to be used is the kind the laborer is accustomed to handle. Thus, a laborer used to high calcium lime will probably not be able to get good results with a dolomite lime, and vice versa. Moreover, a high calcium lime will give a much larger volume of putty than a magnesian lime, hence the laborer is deceived into adding an extra quantity of sand. However, this is not an unmixed evil, for the sand improves the spreading qualities of the mortar and lessens shrinkage. Masons generally prefer magnesian lime because it works more smoothly and sets more slowly. This latter property permits of a larger batch of mortar being made up, and gives the mason plenty of time to spread it. On the other hand, the contractor prefers a quick slaking lime, so that the job can be finished as soon as possible. The fact that a high calcium lime gives a larger volume of putty and carries more sand is also of advantage to him.

As to the actual strength of the two mortars, recent tests conducted by this Bureau indicate that dolomitic limes are stronger than high calcium limes.¹²

It has been shown¹³ that the strength of a lime-sand mortar may be changed 25 or 30 per cent by different methods of adding the water or by

¹² The complete results of these tests will be published in a subsequent article.

¹³ H. Burchartz, *Luftkalke und Luftkalk-mörtel*.

using different kinds of sand. Thus, the crushing strength of lime-sand mortar (one part lime to three of sand by weight) when 1 year old was found to vary with the method of slaking, as follows:

	Kg per sq. cm
Water added a little at a time, with constant stirring	28.1
Water added all at once, no stirring	26.0
Slaked with large excess of water	32.1

The influence of the size and uniformity of the sand grains is shown by comparison of the crushing strength of lime-sand mortars (one part lime to three of sand) when six months old, using different kinds of sand. The results are:

Normal sand	26.6
Building sand	30.6
Fine sand	24.2

The sizes of grains of these sands are shown in the following table:

	Per cent of sand remaining on sieve having — meshes per sq. cm								through
	1	4	9	20	60	120	324	900	
Normal	0.0	0.5	89.4	0.6
Building	0.0	0.8	5.2	19.5	19.0	31.0	17.0	7.5
Fine	0.0	0.1	0.1	0.9	1.9	28.5	61.0	7.5

These results, therefore, agree with the conclusions reached by Feret,¹⁴ that a mixture of two grades of sand of different sizes gives a stronger mortar than when any particular size is used alone, and also that if the sand used is of one size only the larger that size the stronger will be the mortar.

The strength of a lime mortar, therefore, depends on a variety of conditions, chief of which is the method of preparing it. Magnesian limes give a stronger mortar for several reasons: (1) The greater shrinking of a high calcium mortar is apt to cause a weakening of the bond; (2) magnesian mortars contain less water and, therefore, there is more actual binding material contained in them; (3) the common practice of overloading the high calcium mortars with sand tends to give a weaker material. However, the previous experience of the men who handle the lime is probably of greater importance than the content of magnesia.

For all building purposes hydrated lime is to be preferred to lump lime. By its use the time and labor involved in slaking the lime may be saved, and the experience of the laborer is eliminated as a factor in the problem. In this event the mortars will stand on their own merits, and dolomitic hydrate is therefore to be preferred.

¹⁴ Feret, *Les Matériaux de Constructions*, vol. 1, p. 139.

(b) **Plastering.**—Lime to be used for plastering must work smoothly under the trowel, must not “pop” or “pit,” and must not undergo too great a change of volume during setting, and, if it is to be used for the finish coat, it must have a good color.

It was noted above, when discussing the properties of the two kinds of lime, that magnesian limes work more smoothly under the trowel and shrink less on setting than high calcium limes.

Cracking of plaster is obviously due to the shrinking of the lime. It may be overcome by the use of sand, hair, or some such inert material, and by preventing the lime from drying out too rapidly.

The cause of popping or pitting is not very well understood. In some cases it has been traced presumably to the impurities in the lime, such as clay, iron oxide, silicate, and pyrites. These seem to form various chemical compounds during the burning, which hydrate very slowly and expand during the process. For this reason it is generally conceded that lime to be used for plastering must be more nearly pure than that for any other purpose. Another probable cause of popping is the slow hydration of particles of calcium oxide which have been burned during the slaking. This is one more reason for the preference of magnesian lime for plastering, although extraordinary care must be taken to slake the lime properly, whichever kind is used.

Magnesian limes are also to be preferred because they are generally more nearly white than high calcium limes.

On the other hand, a given weight of high calcium lime yields a larger volume of putty than the same weight of magnesian lime, and hence will cover a larger surface.

The time of setting is an important item, since it regulates the time required between coats. High calcium limes set more quickly than magnesian limes, but both rather are slower than the contractor would like. It is suggested that some accelerator might be added to the lime to hasten its setting, or an atmosphere of carbon dioxide might be created for the same purpose.¹⁵

For plastering also, hydrated lime will generally be found more economical and convenient to use than lump lime. Moreover, it has the important advantage of containing less impurities than the lime from which it was made.

(c) **Hydrated Lime and Portland Cement.**—For both building and plastering purposes, hydrated lime may be used interchangeably with quicklime and is often preferred, especially for the final coat in plastering. Hydrated lime is added to Portland cement mortars to make them impervious in water. Quicklime will produce a similar effect, but from the nature of the substance it is obvious that hydrated lime is much more suitable.

¹⁵ H. E. Ashley: *The Spreading Quality of Mortars*, Trans. Natl. Lime Mfrs. Assn.; 1910.

In a series of experiments in which the Portland cement in a mortar was replaced by varying amounts of hydrated lime it was found: (1) That hydrated lime up to 15 per cent does not materially affect the strength of the mortar, even when stored under water; (2) this amount of hydrated lime will materially increase the imperviousness to water of even a one to five cement-sand mortar; (3) the addition of hydrated lime increases the plasticity of the mortar and makes it easier to work.¹⁶

3. LIMESTONE, LIME, AND HYDRATED LIME IN THE CHEMICAL INDUSTRIES

Under this head are grouped all the uses of these substances which depend principally on their chemical properties. The three materials are discussed together because in some industries they may be used interchangeably.

Wherever in the following discussion it is stated that "the impurities are not harmful," it is meant simply that their presence is of no importance chemically. It must be remembered that they reduce the amount of the useful constituents of the lime, and may cause mechanical difficulties by forming a sludge which must be removed.

As stated in the section on hydrated lime, this product should contain fewer impurities (especially calcium carbonate) than the lime from which it was made. Moreover, it will keep better and is easier to handle than lump lime. In some industries the lime is used in a hydrated condition, and in all such cases, unless the heat generated by the slaking can be utilized, hydrated lime will prove more economical. It will cost more for freight per unit of available oxide because of its water content, but this will generally be counterbalanced by the saving in time, labor, and apparatus necessary when quicklime is used.

(a) **Natural Cement.**—Lime also plays an important part in the natural cement industry. These cements, whether made from rock or from blast-furnace slag, are much more acid in character than Portland cement. It is to be supposed, therefore, that an addition of lime, by increasing the basicity, will increase the strength. Experiments have shown that the addition of 5 per cent of lime to some natural cements increases the tensile strength from 100 to 200 per cent.¹⁷

A hydrated lime high in calcium must be used. Magnesia is objectionable because it is apt to carbonate after the cement has set, which weakens it. Other impurities are of little importance. The lime may be added either during the grinding of the cement, or when mixing the mortar. The former time is to be preferred, since it permits more thorough mixing.

Lime improves the spreading qualities of the mortar, as well as increases the strength.

¹⁶ E. W. Lazell: Hydrated Lime and Cement Mortars, *Am. Soc. for Test. Materials*, 8, p. 418; 1908. Also, Wig, *Proc. Natl. Lime Mfrs. Assn.*; 1911.

¹⁷ A. V. Bleining: *Manufacture of Hydraulic Cements*, *Geol. Sur. of Ohio, Bull.*, 3, p. 191.

(b) **Sand-Lime Brick.**—Sand-lime brick, although a rather new material, is of some importance in the building industry. The process of manufacture consists in forming bricks of a mixture of sand and hydrated lime by means of hydraulic pressure. The bricks are then treated with high-pressure steam, which causes chemical combination between the sand and lime. The lime may be hydrated before or after adding the sand, but hydration must be complete before the bricks are pressed, in order to prevent any further change of volume.

High calcium lime is preferable to magnesian lime, because there is less danger of incomplete hydration, and it produces a stronger brick. The impurities generally present are not harmful, except in so far as they may cause the lime to slack more slowly. In fact, kaolin, up to $2\frac{1}{2}$ per cent, may be considered beneficial.¹⁸ Hydrated lime is to be preferred to quicklime because it is more easily mixed with the sand.

(c) **Glass.**—Calcium oxide is a necessary constituent of plate, sheet, and bottle glass, and of a large portion of pressed and blown glass. It acts as a flux. Magnesia makes the glass more difficult to melt,¹⁹ but is sometimes a valuable constituent when particular optical properties are to be obtained.

The calcium oxide is generally introduced as ground limestone, but in this industry, also, the use of lime or hydrated lime is sometimes necessary in order to avoid the evolution of gas at high temperatures.

The ordinary impurities of limestone are, in general, of no importance to the glass manufacturer. For white glass, however, the content of oxide of iron must be less than three-tenths of 1 per cent of the stone.²⁰

(d) **Ceramics.**—Lime and magnesia, generally, however, as carbonates, are used to some extent as fluxes in the manufacture of pottery and porcelain. It has been found that for wares burned at moderate temperatures, calcium oxide tends to bring the points of vitrification and fusion close together, while magnesia tends to separate them, to lower the temperature of vitrification, and to decrease the change of shape due to burning.²¹ On the other hand, if the ware is to be burned at higher temperatures, magnesia has little effect on the points of vitrification and fusion, and increases the shrinkage.²² In a series of experiments to determine the values of different bases when used as fluxes for a mixture of feldspar, flint, and clay, it was found that magnesia gave the best results of the five bases tried (oxides of calcium, magnesia, barium, strontium, and zinc). It gave an excellent color, high tensile strength, and only moderate shrinkage.²³

¹⁸ S. V. Peppel: Sand-Lime Brick, Geol. Sur. of Ohio, Bull. No. 5.

¹⁹ Gelstharp: Fallacies and Facts Pertaining to Glass Manufacture, Trans. Amer. Ceramic Soc., **12**, p. 327; 1910.

²⁰ Walter Rosenhain: Glass Manufacture, p. 45.

²¹ A. E. Hottinger: The Influence of Magnesia on Clays, Trans. Am. Ceramic Soc., **5**, p. 130; 1903.

²² L. E. Barringer: Influence of Magnesia on Clays, Trans. Am. Ceramic Soc., **6**, p. 86; 1904.

²³ Herford Hope: Comparative Effects of CaO, MgO, BaO, SrO, and ZnO on some China Bodies, Trans. Am. Cer. Soc., **11**, p. 494; 1909.

The above results all indicate that magnesia is better than calcium oxide as a flux for ceramic bodies.

The carbonates are generally used, since they are the cheapest forms. Levigated natural whiting is preferred on account of high colloidal content.²⁴ In some cases, however, vitrification sets in before the carbonates are all decomposed, and further evolution of gas may cause pin-holing or internal strain. Under these circumstances it is necessary to use either the oxide or hydrate. It is sometimes desirable to use the carbonates in wares burned at low temperatures in order to obtain a porous body.²⁵

Since the quality of carbonate used is generally small, and the chemical composition of the mixture may vary slightly, it follows that the impurities generally found in limestones are entirely negligible.

In glazes, magnesium oxide tends to absorb SO_3 from the kiln gases with production of a scum appearance. Although this can be overcome by skillful firing, it makes a low magnesia content desirable in most glazes.

(e) **Water Purification.**—"Temporary hardness" of water is caused by the presence of calcium carbonate. This substance is practically insoluble in pure water, but is held in solution by the presence of carbon dioxide, which is found in practically all natural water. If this carbon dioxide is removed, the calcium carbonate will be thrown out of solution. The carbonic acid may be removed by boiling, but it is cheaper to neutralize it with lime. The lime reacts with the carbon dioxide to form calcium carbonate, and, since the carbon dioxide is thus removed, this calcium carbonate, together with that originally present, will be thrown down as an insoluble precipitate. While any magnesium carbonate present in the water will be removed by the same process, the magnesium oxide in the lime will take no part in the reaction and must be considered as an impurity.

The lime to be used should contain as much calcium oxide as possible. The generation of heat on slaking is of advantage in this process, for the reaction takes place more efficiently at elevated temperatures. Therefore the quantity of impurities should be low, and the use of hydrated lime is not advisable.

(f) **Soda Ash and Caustic Soda.**—Most of the soda ash sold in this country is made by the "ammonia-soda" process. A solution of common salt is saturated with ammonia, and the mixture is treated with carbon dioxide. When the resultant solution is evaporated, the soda ash is obtained by crystallization. Ammonia is expensive, and consequently the gas must be recovered and used over again. For this purpose the mother liquor is treated with lime and distilled. The lime replaces the ammonia in its compounds, and thus the gas is set free to distill off.

It is evident that this industry demands limestone, for both the lime and the carbon dioxide are used. The impurities in the stone are not harmful. It would seem that magnesium oxide should be as effective as calcium

²⁴ Ashley: *The Requirements of Pottery Materials*, *Trans. Amer. Cer. Soc.*, **12**, p. 445; 1910.

²⁵ Bourry: *Treatise on Ceramic Industries*, p. 79; 1901.

oxide in breaking up the compounds of ammonia, yet Lunge makes the statement that "magnesian limestone is not suitable for this industry."²⁶

Caustic soda is made by dissolving soda ash in water and adding lime. Insoluble calcium carbonate is precipitated, and caustic soda is left in solution. In this reaction, the magnesia is entirely inert.²⁷ The impurities are undesirable because they form a gelatinous precipitate which does not settle clear, and therefore leads to a contamination of the finished product. In this industry, quicklime is preferable to hydrated lime because it hastens the reaction.

(g) **Bleaching Powder.**—Bleaching powder is an oxychloride of calcium which is formed by the action of chlorine gas on moist slaked lime. The resultant product is sold on the basis of available chlorine. Any impurities in the lime will lower the amount of chlorine absorbed, and consequently the value of the product. Magnesia is especially objectionable because it forms magnesium chloride.²⁸ This substance absorbs water from the air and makes the powder sticky and hard to handle.

Hydrated lime is better suited for this industry than quicklime, because it contains fewer impurities, is easier to handle, and requires no preparation before using.

(h) **Calcium Carbide.**—This substance, the source of acetylene, is made by heating a mixture of lime and coke in an electric furnace. For this purpose, the only useful ingredient of the lime is calcium oxide.²⁹ Magnesia and other impurities are objectionable because the whole charge must be fused, and electric power is too expensive to waste it by heating useless material. For the same reason, quicklime is preferable to either hydrated lime or limestone.

(i) **Illuminating Gas and Ammonia.**—When illuminating gas is made by the distillation of coal, the crude product contains, among other compounds, carbon dioxide, hydrogen sulphide, and hydrocyanic acid. All of these would be objectionable to the consumer. Their removal may be effected by passing the gas through layers of moist slaked lime. For this purpose calcium oxide only is useful, although the magnesia and impurities are not harmful.³⁰ Hydrated lime is to be preferred to quicklime, because it is easier to handle and requires no preparation.

Crude coal gas is the chief source of ammonia. This is removed by washing the gas with water before it has reached the lime purifiers. The solution thus obtained carries both free ammonia gas and some compounds of ammonia. The free gas is driven off by heat and collected. Lime is then added to break up the compounds, and the ammonia thus liberated is also distilled and collected.

Calcium and magnesium oxides should act with equal facility in liberating the ammonia, but, according to Lunge, magnesium limestone is not

²⁶ Lunge: Sulphuric Acid and Alkali, **3**, p. 37.

²⁷ Lunge: Sulphuric Acid and Alkali, **2**, p. 799.

²⁸ Lunge: Sulphuric Acid and Alkali, **3**, p. 440.

²⁹ G. F. Thompson: Acetylene Gas and Calcium Carbide, p. 47.

³⁰ Chas. Hunt: Gas Lighting, p. 136.

applicable to this industry. The impurities are not harmful. Either quick or hydrated lime may be used, with little advantage in favor of either.

(j) **Calcium Cyanamide and Calcium Nitrate.**—These substances, known technically as “lime-nitrogen” and “nitrate-lime,” have recently been put on the market as commercial fertilizers. They represent means of converting the nitrogen of the air into plant food.

Calcium cyanamide is prepared by heating a mixture of lime and coke in an electric arc furnace, and treating the fused mass with nitrogen. The nitrogen is obtained from the fractional distillation of liquid air. Pure, high-calcium quicklime is required for this industry.³¹ Any impurities are undesirable on account of the expense required to heat them.

If air is passed through an electric arc, the nitrogen and oxygen contained in it will combine. The oxide of nitrogen thus formed, when dissolved in water, produces nitric acid. This will combine with any base to form the corresponding nitrate. Since lime is the cheapest of all bases, and has a fertilizing value of its own, it is obviously the base to use. Hence calcium nitrate is formed. Magnesia acts in a similar manner, and its use is dependent on whether or not it would be harmful as a fertilizer. The presence of impurities in the lime is a matter of indifference, and quicklime, hydrated lime, or limestone will produce identical results. Hydrated lime is probably the most economical.

(k) **Fertilizer.**—Lime is used extensively as a fertilizer. The Department of Agriculture and the various State agricultural experimental stations have carefully investigated the use of lime for this purpose and have published their conclusions in several bulletins.³²

A correlation of these results will lead to the following general statements: 1. A plot of ground is in need of lime when it fails to produce a good crop of common red clover, or when the clover crop contains patches of sorrel. 2. Lime should never be used alone, but always in connection with some organic fertilizer. 3. Care must be taken not to use too much lime, as this will tend to waste the plant food stored in the soil. If the lime is coarsely ground, more must be used, but its effect will be more lasting. 4. The ratio of calcium oxide to magnesium oxide varies for each plant, but for general farm purposes may be taken as seven to four. Therefore the lime to be used should contain sufficient magnesia to establish this ratio in the soil. 5. Whether the lime should be applied as ground quicklime, hydrated lime, air-slaked lime, or ground limestone, depends chiefly on the cost per unit of calcium oxide (it being assumed that the four substances are of the same fineness). Thus 500 pounds of ground

³¹ J. B. C. Kershaw: Calcium Cyanamide, *The Electrician*, 60, p. 548.

³² Gardner: Fertility of Soils as Affected by Manures. U. S. Dept. Agri., Bu. of Soils, Bull. No. 48.

Loew and May: Relation of Lime and Magnesia to Plant Growth. U. S. Dept. Agri., Bu. of Plant Industry, Bull. No. 1.

Wheeler: Liming of Soils. U. S. Dept. Agri., Farmers' Bull. No. 77.

Thorne: Maintenance of Fertility. Ohio Agri. Exp. Sta., Bull. No. 159.

Hopkins: Ground Limestone for Acid Soils. Univ. of Ill. Agri. Exp. Sta., Cir. No. 110.

Fippin: Relation of Lime to Soil Improvements. Trans. Nat. Lime Mfrs. Assn.; 1910.

quicklime, which is the quantity recommended for one acre, is equivalent to 950 pounds of hydrated lime or 1250 pounds of either ground limestone or air-slaked lime. 6. Lime is sometimes used to improve the drainage conditions in the soil, and for this purpose ground quicklime alone is suitable.

(l) **Spraying.**—Lime enters into the preparation of a number of insecticides used in spraying vegetation. For such purpose calcium oxide is the only useful constituent of the lime. Magnesia and impurities are not harmful. The physical quality of the lime is of paramount importance. The material is sprayed on the vegetation through some form of atomizer, and therefore must contain no coarse particles or grit. For this reason hydrated lime screened to pass 150 or 200 mesh (a commercial article) would certainly give better satisfaction than lump lime.

(m) **Sugar.**—In the manufacture of sugar, both carbon dioxide and lime are used. Therefore, sugar manufacturers prefer to buy limestone and burn their own lime.

The juice extracted from either beet or sugar cane contains various impurities. Some of these would discolor the sugar, and others (organic acids) would invert it. That is, they would change the sugar into uncrystallizable glucose, and thus reduce the yield. In order to remove these impurities the juice is heated almost to boiling in the presence of an excess of lime. This combines with the acids and breaks up the other organic compounds forming insoluble salts. But it also forms an insoluble compound with the sugar itself. For this reason after the lime has completed its action carbon dioxide is forced into the liquid. This breaks up the combination between the lime and sugar, and throws down all the lime as calcium carbonate. This precipitate carries with it all suspended matter, leaving a clear solution of sugar.

For the above purposes calcium oxide only is useful.³³ Impurities are apt to cause trouble. Thus, magnesium carbonate is more soluble in sugar solutions than calcium carbonate, and the salt so dissolved is later deposited on the tubes in the evaporating pans, thus making it necessary to clean them more frequently. Any silica present is thrown down as a gelatinous precipitate. This becomes a general nuisance by coating the cloth in the filter presses.³⁴

(n) **Distillation of Wood.**—The destructive distillation of wood gives rise to four products: Gas, pyroligneous acid, tar, and charcoal. Of these, pyroligneous acid is of most interest to the lime manufacturer. From this solution are prepared wood alcohol, acetic acid, and acetone, and lime is an essential ingredient in the manufacture of all of these. First, the crude acid is treated with an excess of lime and distilled. Wood alcohol passes over, but both acetic acid and acetone are held in the still in chemical combination with the lime. This mixture is known as "gray acetate of lime." Acetone may be produced from it simply by dry distillation; or it may be treated with sulphuric acid and the acetic acid distilled off. The wood alcohol is again treated with lime and redistilled in order to purify it.

³³ H. Classen: Beet Sugar Manufacture, p. 64.

³⁴ Manufacture of Sugar: Int. Lib. of Technology, sec. 50, p. 36.

For any of the above purposes calcium oxide is the only useful constituent of the lime.³⁵ Magnesia and impurities are not harmful. Hydrated lime may be used instead of quicklime for any of the above purposes except the final distillation of the wood alcohol. For the other purposes probably neither substance has any advantage over the other.

(o) **Paper.**—Wood pulp for the manufacture of paper is prepared by one of three processes: mechanical, soda, or sulphite, of which only the second and third interest the lime manufacturer.

In the soda process lime is used to causticize sodium carbonate, thus recovering the caustic soda used in cooking the wood.

Calcium oxide is the only constituent of the lime useful in the soda-pulp industry. The magnesia and impurities are not harmful. Hydrated lime may be used instead of lump lime, but the latter is to be preferred, since the heat generated by its slaking hastens the reaction with the soda.

Another solution which may be used in place of caustic soda for dissolving the cementing constituents of wood is "bisulphite liquor." This is a mixture of calcium and magnesium bisulphites held in solution by an excess of sulphur dioxide. The liquor is prepared by one of two methods. Limestone may be subjected to the solvent action of sulphur dioxide and water, or milk of lime may be treated with sulphur dioxide. The resultant solution is the same in either case.

For the maker of sulphite pulp, magnesia is a desirable constituent of the lime or limestone. Magnesium sulphite is more soluble than calcium sulphite, and consequently permits of making a stronger liquor. Moreover, the presence of magnesia in the liquor gives the pulp a better color and makes it softer to the touch, so that it will felt together better when made into paper. Therefore, dolomite, or magnesian lime, is much preferable to the high calcium compound. The impurities are not harmful.

If limestone is used, it should be as porous as possible to permit of rapid solution.

Hydrated lime is preferable to lump lime, because it is easier to handle and contains fewer impurities.

(p) **Paints.**—Ground lime, air slaked lime, levigated chalk (natural whiting), and chemically precipitated calcium carbonate are used to a large extent in the paint and allied industries. For these purposes, fineness of grain is essential, while sometimes the color or chemical composition is of equal importance. It is generally impossible to obtain a limestone of sufficient whiteness, or to grind it sufficiently fine to meet the requirements. It is, therefore, an advantage to use air-slaked lime, or hydrated lime.

Cold-water paints consist essentially of hydrated lime, pigments, and casein ground together. From the nature of the substances, it is obviously impossible to use quicklime, and magnesian hydrates are probably to be preferred over high calcium hydrates on account of their better spreading qualities.

³⁵ P. Dumesny and J. Moyer: *Wood Products, Distillates, and Extracts*, p. 8.

(q) **Glycerin, Lubricants, and Candles.**—Most of our common fats are compounds of glycerin with various organic acids. These compounds can be broken up by heating the fat with lime and water under pressure. The glycerin is liberated, while the lime takes its place in the compounds. Practically all of the glycerin used in this country (mostly in the manufacture of explosives) is made in this way. The lime "soaps" formed by this process are sometimes mixed with heavy mineral oils and sold as lubricants or greases. They are of especial value for the lubrication of heavy machinery, or for use at high temperatures. Or, the soaps may be treated with sulphuric acid. The separated fatty acids are recovered and used in the manufacture of soap and allied products.

Calcium oxide is the only useful constituent of the lime, although the magnesia and impurities are not harmful.³⁶ Quicklime is probably preferable to hydrated lime, because the heat of slaking can be used.

(r) **Tanning.**—In the leather industry lime is used in the "depilation" process. The hair is so loosened from the hide by soaking it in lime water that it can be removed by subsequent scraping. In regard to the quality of lime to be used, the following statement is made: "The presence of magnesia and clay is injurious, not only by diminishing the amount of lime present, but by making the lime much more difficult to slake; and iron oxide, though quite insoluble, may become mechanically fixed in the grain of the hide, and may be the cause of subsequent stains."³⁷

The use of hydrated lime would remove the above objections to magnesia, but not those to iron. Hydrated lime is probably preferable to quicklime for this reason, as well as for the fact that it is easier to handle.

The uses of limestone and its products are so numerous that it would be practically impossible to discuss them all. However, those mentioned above include most which are of very great importance.

VI. TESTING LIMES

1. TESTS REQUIRED

General methods for testing lime should be devised to serve as a basis for mutual agreement between manufacturer and consumer. Such tests must ultimately depend on the physical and chemical properties of the lime, but so little is known about the subject at present that such terms as "plasticity" and "time of set," which so far have not been measured by a standard test, so as to have a definite meaning, must be used in a relative sense. Researches are in progress to correlate these terms with definite measurable properties and thus to eliminate them from the standard specification which the bureau hopes to offer.

From a consideration of the general purposes for which lime is to be used, it is believed that the following points should be covered.

Carbon dioxide.—To measure general conditions as affected by burning and air slaking. Quicklime of good quality should not contain over one per cent of carbon dioxide.

³⁶ S. P. Sadtler: *Industrial Organic Chem.*, p. 58.

³⁷ H. R. Proctor: *Principles of Leather Manufacture*, p. 121.

Rate of hydration.—Lime which has been burned properly will slake more rapidly than that which is underburned or overburned. Consequently, a knowledge of the rate of hydration furnishes a good indication of the burning conditions.

Chemical composition.—Different limes have different rates of hydration. Therefore, it is necessary to take the chemical analysis of the lime into consideration, or else to compare the sample with another of the same lime which is known to have been burned properly. It is sometimes desirable to know the quantity of water in hydrated lime, but this is not very important and is of no value unless a complete chemical analysis is made, which last is the only test required for limes that are to be used for chemical or fertilizing purposes.

For building limes the factors of importance are:

Sand-carrying capacity.

Crushing strength.

Tensile strength.

For plastering limes the factors are:

Spreading quality.

Time of set.

Color.

Hardness.

Constancy of volume.

2. METHODS OF TESTING

The methods for testing lime that are available will be described in detail in a bulletin to be published later. They are mentioned in the following paragraphs in very brief terms.

The carbon dioxide can be determined by means of an alkalimeter, and the rate of hydration by means of a calorimeter. The color may be measured by direct comparison with a series of standards. By the use of a modified viscosimeter the tenacity of lime pastes made with different amounts of water can be determined and a correlation of these should give a comparative indication of the spreading quality. For all other tests lime pastes brought to a standard consistency must be used. This arbitrary standard of tenacity will be determined by measuring the tenacity of a lime paste which is considered to have the proper consistency for practical work. By means of the viscosimeter the amount of water required to produce the standard tenacity can be determined, and all tests should be made under this uniform condition, so that the results will be comparable.

For determining crushing and tensile strength a mortar consisting of standard lime paste and standard sand should be used, the sand being in the ratio of 3 to 1 by weight of the dry lime. The crushing tests should be made on 2-inch cubes and the tensile tests on the standard cement briquette of 1 square inch area at minimum section. All specimens should be stored in air and broken when 3 months old.

To test sand-carrying capacity, specimens should be made up as for crushing strength, except that the proportion of sand varies from 0 to 5 times the weight of the lime. Specimens should be stored and broken as

for crushing tests. Some of these specimens containing no sand are to be measured when 3 months old, in order to determine the constancy of volume.

To determine the time of set, the standard lime paste is tested under a Vicat needle according to the official specifications adopted by the American Society for Testing Materials for testing cement.³⁸

Hardness is to be determined by exposing the standard paste, set one week or longer, to the action of a sand blast, and noting the rate at which it is worn off.

It should be noted that the above suggestions are merely tentative. The methods of carrying them out will be perfected as rapidly as possible, after which it will be necessary to apply them to a large number of commercial limes. From the data so obtained it will be possible to deduce what results these tests should give with good limes, and from this information specifications can be prepared. These specifications will then be subjected to constant research and revision, in order to eliminate such indefinite terms as spreading quality, plasticity, and time of set, and to substitute definite terms in their stead. The ultimate aim of the work is to devise specifications depending only on the exact physical and chemical properties of the lime.

³⁸ Proc. Am. Soc. Test. Mat., Report of Committee C; 1905.

