CHAPTER IV

USES OF MARLS, LIMESTONES, AND DOLOMITES BASED ON THEIR CHEMICAL COMPOSITION

The uses of marls, limestones, and dolomites discussed in this report are based on their composition and are therefore distinct from structural uses which depend only on strength, color, hardness, and other physical properties. The composition of both limestones and dolomites makes it possible to use them in the making of lime, and as agricultural limestone on acid soils. Both are used by paper makers and for fluxing certain ores. As a flux, limestone is commonly preferred. Most so-called natural cements were made from impure dolomites. Natural cements are now used very little in the United States. Only high-grade limestones or marls very low in magnesia are desired for making Portland cement and lime for sand lime brick. Sugar factories also use only very pure limestones. These various uses are taken up in detail farther on. Marl, because of its water content, is used very little excepting for agricultural limestone and for Portland cement.

LIME AND LIME HYDRATE

The Manufacture of Lime and Lime Hydrate

Lime and lime hydrate are made by driving off all or nearly all the carbon dioxide, water, and other volatile constituents from limestone or dolomite by means of heat. The heat applied should be sufficient to do this work, but not high enough to cause a chemical union of the lime and magnesia of the limestone with the impurities such as silica, iron, and kaolin. When this takes place, the lime is said to be overburned, has a yellow color, and does not slake well. The amount of heat which should be applied in order to get the best results varies with the composition, grain, and pore space of the stone. It should be the minimum amount. From experimental evidence it has been assumed to be 722 B. t. u. per pound of calcium carbonate and 464.3 B. t. u. per pound of magnesium carbonate. One B. t. u. represents the amount of heat required to raise the temperature of one pound of water at a temperature of 39° F. one degree Fahrenheit.

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The lime produced by burning limestone or dolomite consists chiefly of the oxides—lime and magnesia. The lime from an impure limestone or dolomite may contain free silica and alumina. The latter in most cases is probably present as a silicate. Iron oxides may also be present. As already stated, overburning may cause the lime and magnesia to combine with the impurities and thus to form a slag. The active constituents of the lime which make it commercially useful are the oxides of lime and magnesia.

Lime is usually burned in vertical kilns built of stone or of steel and stone. Four principal types of lime kilns are in use. The one most commonly used is the flame or patent kiln, which consists of a vertical shaft usually about 30 feet high, and about 5 to 8 feet in diameter, either rectangular, circular, or elliptical in cross-section. It is charged from the top and is continuous in operation. The distinctive feature of this kiln is that only the flame and not the fuel come in direct contact with the lime and rock.

A pot kiln is a vertical shaft which is continuous in operation. Its peculiar feature is that fuel and stone are dropped in it in alternate layers. The field kiln is the only kiln which is intermittent in operation. It is fired until a charge is completely burned, when it is emptied and recharged. In all these kilns wood is the fuel commonly used in Wisconsin. In 1918, 56.4 per cent of the kilns of the United States used coal, 12.4 per cent wood, 9.6 per cent coke, and 4.8 per cent producer gas.

The rotary kiln is a gently inclined hollow cylinder built of steel plates and lined with a refractory material. In all essentials it is like the Portland cement kiln. The stone is finely ground, and the charge fired with ground coal. The temperature used is about 800° C, whereas it is about 1425° C. in the cement kiln. The product is a lime flour and not lump lime. In 1918¹ there was an increase of 42 per cent in the number of rotary kilns in the United States despite the decrease of 20 per cent in the total number of kilns. This increase seems to indicate that the rotary kilns are beginning to be recognized as a very efficient type. They burn the small sizes of stone which choke the draft in upright kilns, and produce a good quality of lime, especially for hydrated lime.

Lime is put on the market either as lump lime or ground lime. Since lump lime falls to a powder when air slaked, the market has been prejudiced against fine lime. When lime is exposed to the air it first absorbs water and forms a lime hydrate and then the water is replaced by the carbon dioxide of the air. In this last step the lime goes back to the composition of limestone or dolomite. When this condition has been attained, the lime is said to be air slaked. A considerable expansion of

volume takes place in this process; hence the lumps fall to pieces. It has been found, however, that finely ground lime keeps better than lump lime, since it does not permit such ready access of air. A thin film of air-slaked lime forms on the surface of a pile of fine lime and protects the interior from the action of the atmosphere.

Hydrated lime is lime which has been mechanically slaked. It is prepared by adding to ordinary lime just sufficient water to assure complete slaking, which leaves the product a fine dry powder. Any lumps which do not slake are removed by screening. In composition it is essentially a hydrate of calcium and magnesium oxides. The water content varies from 24.3 per cent for pure calcium hydrate to 11.3 per cent for impure dolomitic hydrate. If properly screened, it usually contains less impurities than the lime from which it was made.

Qualities of Limestone and Dolomite for Lime Burning

The chief property of limestone and dolomite which determines fitness for lime burning is chemical composition, although size of grains and porosity affect the cost of burning considerably. Experience has shown that a fine-grained, dense stone can be burned at a lower temperature and with less heat than one which is coarse grained and porous. Coarsely crystalline stones, especially if very pure, are apt to fall to pieces in the kiln, thus reducing the production of lump lime. The same is sometimes true of porous stones, but in this case, the falling to powder is thought to be due to the rapid expulsion of water which may fill the voids. Laboratory tests made by the U. S. Bureau of Standards seem to contradict the results of practice. Bleininger and Emley found that "all naturally porous stones lost their carbon dioxide at a lower temperature (about 900° C. or 1652° F.) than the denser materials."

It is suggested by the Bureau that the discord between laboratory and practical results may arise from differences in the size of stone used, the quantity of material, and similar factors.

Every gradation from limestone containing nearly 100 per cent calcium carbonate to dolomite containing 54.35 per cent calcium carbonate and 45.65 per cent magnesium carbonate is believed to exist. In most cases, however, rocks of this type are composed of calcium carbonate with less than 15 per cent of magnesium carbonate or of nearly pure dolomite with less than 10 per cent of calcium carbonate in excess of the calcium carbonate required to satisfy the dolomite ratio. Most of the commercially important limestones used for burning lime have at least 97 per cent of carbonates. The other constituents are chiefly

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silica, alumina, and iron oxides. These may be regarded as impurities. The silica is usually present as quartz and in combination with the alumina, probably as kaolin. The iron is usually present as the ferrous carbonate and the ferric oxide. All of these accessory constituents may occur in other combinations than those given.

The chemical composition of limestone and dolomite affects the cost of burning and the texture, composition, plasticity, sand-carrying capacity, hardness, strength, spreading quality, time of set, and constancy of volume of lime. Lime has the same constituents as the limestone from which it is made minus the carbon dioxide; hence the chemical composition of the lime depends upon the composition of the limestone from which it is made.

Water, magnesia, and the impurities affect the cost of burning. If for instance the limestone or dolomite contains much water, this water must be evaporated in the kiln. Consequently, some heat which should be active in driving off the carbon dioxide will be spent in evaporating the water. In this way the amount of lime produced per unit of heat is less than it should be. In other words, the efficiency of the kiln is reduced. The greater the proportion of impurities, the more easily is the lime overburned, and therefore too large a proportion of impurities will cause a diminution of kiln capacity. Experience has shown that it generally takes less heat and a lower temperature to burn a magnesian than a high calcium stone.

The texture of the lime is determined chiefly by the water content and impurities of the limestone. The driving out of a large content of water by the heat of the kiln tends to break the lumps of lime into pieces. When the proportion of silica is high enough, lime orthosilicate (2CaO·SiO₂) may form in the kiln. On cooling slowly to 675° C. (1247° F.) this substance increases considerably in volume. This causes the lime to fall to pieces, a phenomenon known as "fire slacking."  

The effects of the various constituents of limestone on the physical properties of lime will be considered in order. On the basis of calcium and magnesium content, limes have been classified as:

High calcium limes—containing 0 per cent—5 per cent magnesia
Magnesian lime—containing 5 per cent—25 per cent magnesia
Dolomitic lime—containing 25 per cent—45 per cent magnesia
Super-dolomitic lime—containing more than 45 per cent magnesia

A dolomitic lime will slake more slowly, generate less heat, combine with less water, undergo less increase in volume, set more slowly, and shrink less on setting than a high calcium lime. These are gen-

eralizations, however. The properties are decidedly influenced by the
impurities, the temperature of burning, and many other factors. The
high calcium lime will take up more sand and spread more easily
than dolomitic lime. In slaking, however, the high calcium limes
need more vigorous stirring and closer attention than the cooler dolomitic limes. If not properly handled, the high calcium lime is easily
overheated in slaking and then becomes lumpy and hard to work.
Very few experiments have been made to give all these properties,
such as time of set and spreading quality, a definite meaning. No
standard tests have been adopted. Though it can be said that one kind
of lime has a certain quality to a greater degree than another, there
are almost no quantitative measurements on record which give a
precise idea as to the relative qualities of various limes.

One of the fundamental steps to such measurements would be to
have the limes burned under standard conditions. If their qualities
are to be correlated with their chemical composition, all other factors
which affect the physical properties, such as overburning in the kiln
and time of burning, must be eliminated. The U. S. Bureau of
Standards is now engaged in making such investigations and their
results may be expected to furnish buyers and sellers of lime with
standard tests which in the future may figure in determining the
value of limes.

The impurities of limestones, the sandy, clayey, and iron com-
ounds, are of very little value in lime, and most of them are decidedly
injurious. They may interact with the lime during burning and form
silicates, thus reducing the output of lime and increasing the per-
centage of inert materials. Emley\(^1\) states that a limestone should
have no more than 2\(\frac{1}{2}\) per cent of silica and oxides of alumina and
iron, and concludes that the presence of a small amount of silica
tends to decrease the plasticity, sand carrying capacity, and yield
of a lime, but has no apparent effect on hardness or strength. The
same is said of iron, except that large amounts of it, 25 per cent,
show a marked increase in both strength and hardness. It may be
said, however, that it is difficult to find a natural limestone or dolo-
mite with so high an iron content and which at the same time is free
from silica and other impurities. Of course iron affects the color,
therefore an iron bearing lime can be used only where a white color
is not needed. Alumina is said by Emley to increase the strength,
hardness, plasticity, and sand-carrying capacity of a lime and to im-
prove the color. This laboratory result probably has little value in
practice, since a limestone containing a high percentage of alumina

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\(^1\) Emley, W. E., Manufacture of Lime: U. S. Bur. of Standards Tech. Paper 16,
p. 9, 1913.
almost always has a considerable content of silica as well, and the deleterious effect of the silica would probably offset any benefit that might come from the alumina. The alumina is usually present in the form of kaolin which has about the same effect as the oxides of silica and iron. Gypsum is reported to have a bad effect even when only 1 per cent is present.

The Uses of Lime and Hydrated Lime

*Mortar and plaster.—* The uses of lime and hydrated lime especially in the building trades are nearly identical. As shown on page 109, for certain uses dolomitic and high calcium limes may be used interchangeably. For some other uses one is more desirable than the other. High calcium lime produces more mortar per unit of weight than a magnesian lime.

Actual tests made by the U. S. Bureau of Standards show that dolomitic mortar is stronger than a high calcium mortar. It was found, however, that the most important element in the strength of a mortar was not its composition but its manner of preparation. For instance, the strength of a lime sand mortar was changed 25 to 30 per cent by different methods of adding water or by using different kinds of sand. For most ordinary buildings, however, the relative strength of the mortars need not be considered. Whether a dolomitic or high calcium is to be preferred for mortar depends entirely on the relative cost of the two at the particular place where they are to be used, and the experience of the workmen in handling them.

A good plastering lime ought to spread easily, not crack on shrinking, pot or "pit" and if used for the finishing coat must have a good color. Pitting is believed to be due to impurities in the lime and to particles of unslaked lime which were "burned" in slaking. It is therefore important to get a pure lime and the dolomitic white limes are conceded to be better suited for plastering than the high calcium limes. Hydrated lime is probably more convenient and economical to use than quick lime. It is also purer than the lime from which it was made.

Hydrated lime has the advantage of being already slaked and is ready for use. Lime, especially high calcium lime, may be spoiled in slaking if not properly stirred. Since lime hydrate is stirred mechanically, all elements of carelessness or misjudgment are eliminated in its manufacture and a perfectly correct product is obtained. It does not heat on storing. It will, however, spoil or air slake as easily as quick lime of the same fineness. Being like flour in consistency, a thin outer film of air slaked material will form an impervious covering which prevents air from entering the interior of the pile.
The only disadvantage which hydrated lime has for the consumer is that 15 to 25 per cent of it is water, on which he must pay the freight. To the manufacturer it has the advantage of being an article which can be stored when the market is dull. It also enables him to use some grades of stone which fail to make good lump lime because of their dark color or because they fall to pieces. In 1919 there was in the United States an increase of 25 per cent in the production of hydrated lime, and but 4 per cent increase in total lime produced.

**Portland cement.—** Hydrated lime is added to Portland cement mortars in order to make them impervious to water. Lazell has shown that (1) hydrated lime up to 15 per cent does not affect the strength of the mortar even when the test specimens are stored under water, (2) this amount of hydrated lime will materially increase the impermeability 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. Quicklime will give the same results but hydrated lime is more convenient to use.

**Sand-lime brick.—** Sand lime bricks are made by compressing mixtures of sand and hydrated high calcium 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 magnesium limes make a weaker brick. Impurities in the lime are generally not harmful unless they check the slaking of the lime. Kaolin up to 2½ per cent seems to be beneficial.1

**Distillation of wood.—** The products of the destructive distillation of wood are gas, pyroligneous acid, tar, and charcoal. From the pyroligneous acid are prepared wood alcohol, acetic acid, and acetone. In all of these processes, lime is essential. The crude acid is first distilled with lime. Wood alcohol is distilled off in this process, whereas acetic acid and acetone are held in the still in chemical combination with the lime. Acetone is produced either by dry distillation of the residue in the still, or it may be treated with sulphuric acid and the acetic acid distilled off. The wood alcohol is purified by again treating it with lime and then redistilling it. In this last process, only a high calcium quicklime can be used. For the others either a high calcium quicklime or the hydrated lime may be used. Magnesia and impurities are not harmful but are useless.

**Paints.—** Finely ground lime, air slaked lime, levigated chalk, and chemically precipitated calcium carbonate are used in the paint industries. In addition to fineness of grain, color and purity are important

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1For a thorough presentation of the properties of sand lime brick and their method of manufacture, see S. V. Peppel, The manufacture of artificial sand stone or sand-lime brick: Geo. Survey of Ohio, Bull. 5.
properties. Air slaked and hydrated lime are preferred because of their white color and fine grain.

Cold water paints consist chiefly of hydrated lime, pigments, and casein ground together. The hydrated dolomitic lime is probably to be preferred to the high calcium lime because of the better spreading quality of the magnesia.

Glycerine, lubricants, and candles.—Most of the common fats consist of glycerine with some organic acid. The glycerine is liberated by treating fats with a pure, high calcium quicklime. Quicklime is preferred to hydrated lime because the heat produced by slaking helps the process of breaking up the fats. The calcium takes the place of the glycerine, the glycerine is liberated, and the calcium and the acids form an insoluble soap. This soap is mixed with heavy mineral oils and is sold as a lubricant for heavy machinery, or for use at high temperatures. The calcium soap may be broken up with sulphuric acid. The products are solid calcium sulphate and the liquid organic acids. The organic acids are used in the manufacture of soap and allied products.

Tanning.—Lime water is used for loosening the hair from hides. For this purpose only a very pure calcium quicklime or hydrated lime is used. Iron oxide is objectionable because it may become mechanically fixed in the grain of the hide and cause stains. Magnesia is of no use in this process.¹

The paper industry.—Grease and some colors are removed from rags used for paper pulp by boiling them with lime. The lime forms an insoluble soap with the grease.

Wood pulp consists of macerated cellulose or wood fiber from which all intercellular, resinous, starchy, or siliceous materials have been removed. These undesirable materials are removed either by boiling the wood with caustic soda or by boiling it with a liquor containing sulphur dioxide gas and calcium bisulphite or calcium and magnesium bisulphite. When the wood is boiled with caustic soda, the latter is converted in part into sodium carbonate. The sodium carbonate is recovered or reconverted into caustic soda by treating the liquor with lime. The reaction is Na₂CO₃ + Ca(OH)₂ → CaCO₃ + 2NaOH.

The bisulphites of calcium and magnesium are made by conducting sulphur dioxide gas up through a tower containing limestone or dolomite fragments. A porous stone is preferred. A standard amount of water permitted to trickle downward through the tower takes up the calcium and magnesium bisulphites formed by the interaction of limestone and sulphur dioxide or of dolomite and sulphur dioxide and a certain excess of sulphur dioxide gas.

The reactions between the limestone and the SO₂ may be represented as follows:

(a) CaCO₃ + SO₂ = CaSO₃ + CO₂. The CO₂ escapes from the top of the tower.

(b) MgCO₃ + SO₂ = MgSO₃ + CO₂.

When the sulphites of calcium and magnesium are dissolved in water containing an excess of SO₂, they are called bisulphites, and are represented as CaH₂(SO₃)₂ and MgH₂(SO₃)₂.

Another process of making the bisulphites of lime or of calcium and magnesium is to conduct SO₂ into a tank containing water and either a high calcium lime or a dolomite lime.

The magnesium sulphite is not objectionable. In fact it is said to be desirable. It is a more soluble sulphite than calcium sulphite, and hence a more effective liquor can be made with magnesium sulphite than with calcium sulphite. Magnesium sulphite gives pulp a better color, makes it softer to the touch, and causes it to felt together better when made into paper.

Another use of lime in the paper industry is as a carrier of chlorine. In this form it is used for bleaching paper.

Glass making.—Calcium oxide is an important constituent of plate, sheet, and bottle glass. It acts as a flux. Magnesia raises the melting point of the glass, and is not used very much unless special optical properties are desired. The calcium oxide may be introduced in the form of quicklime or hydrated lime, but ground limestone is more commonly used. For white glass the content of oxide of iron must be less than 0.3 of 1 per cent.

Ceramics.—Dolomitic limes are used as fluxes in the manufacture of pottery and porcelain. The natural carbonate is used more than the oxide since it is cheaper. The carbonate is preferred when a porous ware is desired. For wares burned at moderate temperatures, calcium oxide tends to bring the points of vitrification and fusion close together, whereas magnesia tends to separate them, to lower the temperature of vitrification, and to decrease the change of shape due to burning. If the ware is to be burned at a higher temperature, magnesia has little effect on the points of vitrification and fusion, and increases the shrinkage. For glazes, magnesia is generally undesirable. By absorbing SO₂ from the kiln gases, it causes the production of a scum. Only small quantities of carbonate are used; hence a small percentage of impurities is not harmful.

Water softening.—High calcium lime is used in softening water which has “temporary hardness.” Temporary hardness is due to the presence of calcium carbonate held in solution by carbon dioxide gas. Hot quicklime reacts with this excess of carbon dioxide and forms
the insoluble calcium carbonate. The removal of the carbon dioxide causes the lime and magnesia carbonates in the water to be thrown down. The magnesia in the quicklime has no effect; hence it is desirable to use a high calcium lime.

*Soda ash and caustic soda.*—Soda ash is the trade name for carbonate of soda. It is made by saturating a solution of common salt with ammonia and the mixture is treated with CO₂. When the solution is evaporated, the soda ash is obtained by crystallization. The ammonia is recovered by treating the mother liquor with lime and then distilling it. The lime replaces the ammonia, and its compounds, and thus the gas is set free to distill off. In this process both the lime and the carbon dioxide of the limestone are used. Dolomitic limestone is believed to be unsuitable for this industry.

Caustic soda is made by dissolving soda ash in water and adding lime. The lime replaces the soda and forms insoluble calcium carbonate; the soda goes into solution as the caustic soda. In this industry, a very pure, high calcium lime is used. Magnesia takes no part in the process, and impurities are apt to interact with the caustic soda to form gelatinous substances which do not settle clear. Quicklime is preferable to hydrated lime because it hastens the reaction.

*Bleaching powder.*—Bleaching powder is an oxychloride of lime formed by the action of chlorine gas on a hydrated high calcium lime of great purity. Magnesium is very objectionable since it combines with chlorine and forms magnesium chloride, a compound which absorbs water. Bleaching powder containing magnesium chloride is weak, sticky, and hard to handle.

*Calcium carbide.*—Calcium carbide, the source of acetylene gas, is formed by heating a mixture of coke and very pure, high calcium lime in the electric furnace. The cost of the process makes a very pure lime desirable since only the calcium oxide enters into combination with the coke to form the desired product.

*Illuminating gas and ammonia.*—Illuminating gas is purified of useless and harmful ingredients, such as carbon dioxide, hydrogen sulphide, and hydrocyanic acid by passing through layers of moist, slaked lime. Only the calcium oxide is effective in this process; hence a pure high calcium lime is preferred.

Before reaching the lime purifiers, the crude gas is forced through water, which takes out ammonia, and some ammonia compounds. The ammonia is driven off or distilled off by heat and is recovered by cooling. The ammonia compounds in the water are broken up with pure, high calcium quicklime and the ammonia set free is distilled off and recovered.
Calcium cyanamide and calcium nitrate.—Calcium cyanamide and calcium nitrate are used as artificial means of converting the nitrogen of the air into plant food. The calcium cyanamide is a compound of calcium, carbon, and nitrogen formed by treating a fused mixture of pure, high calcium lime with nitrogen. The nitrogen is obtained from the fractional distillation of liquid air.

When air is permitted to pass through the heat of an electric arc, the nitrogen and oxygen combine to form the oxide of nitrogen, which, when passed into water, forms nitric acid. In this form, the nitrogen would be a deadly poison to plant life. When the nitric acid is permitted to act on lime, which is the cheapest base obtainable, lime nitrate is obtained. The lime is in itself a fertilizer for certain plants. For this purpose lime, hydrated lime, or limestone could be used. The impurities remain inert but are not harmful. It does not seem to be certain whether or not magnesium nitrate, which would form with dolomitic limes, is injurious to plants.

Agricultural lime.—Lime and hydrated lime can be applied as a plant food to some soils which are very deficient in lime; as a neutralizer of acids which have a very harmful effect on the growth of certain valuable plants such as red clover and alfalfa; as liberators of certain fertilizers in the soil which by their action become available to plants; and as improvers of soil tilth on clayey, sticky soils which are not easily penetrated by air.

The action of lime and hydrated lime is drastic. If their addition to the soil is not followed up by liberal applications of fertilizers, they tend to convert the fertilizers present into ammonia and other easily dissolved products which are removed from the soil by rain water or may escape into the air as gases. Ground limestone or dolomite is used most commonly on soils. Lime is quicker acting and 100 pounds is about equivalent to 200 pounds of limestone. The cheapness and milder action of the limestone make it more desirable. This is discussed at length later.

Spraying.—Finely powdered, hydrated lime is used as an insecticide for spraying vegetation. The impurities and magnesia are not objectionable, but calcium oxide is the only useful constituent.

Sugar making.—In the manufacture of sugar both carbon dioxide and calcium oxide are used; hence sugar manufacturers buy limestone and burn their own lime. A very pure limestone low in magnesia and impurities is used.

The juice extracted from beets and cane contains impurities which if allowed to remain would discolor the sugar. It also contains organic acid which changes sugar into uncrystallizable glucose. Lime is added to the juice. It neutralizes the acids and impurities by forming in-
soluble compounds with them. It also forms an insoluble compound with the sugar. At this juncture carbon dioxide is forced into the juice. This precipitates the calcium in solution and the calcium combined with the sugar as calcium carbonate and leaves a clear sugar solution which can be filtered off. Magnesium is objectionable since it is more soluble than calcium carbonate in sugar solutions. Some of it remains with the sugar solution until it is precipitated on the tubes of the evaporating pans, thus making it necessary to clean these pans more frequently. When silica is present in the lime, it is thrown out as a gelatinous precipitate, which clogs the filter presses.

*Summary of uses of lime.*—The following is a tabulation\(^1\) of the uses of lime. The letter c indicates high calcium lime; m indicates magnesian lime. Brief notes on the most important uses are given in the preceding pages.

**Chemical Uses of Lime**

**Agricultural industry**—
- as a soil amendment, c.m.
- as an insecticide, c.m.
- as a fungicide, c.m.

**Bleaching industry**—
  - Manufacture of bleaching powder
    - Chloride of lime, c.
  - Bleaching and renovating rags, jute ramie, and various paper stocks, c.m.

**Caustic alkali industry**—
- Manufacture of soda, potash, and ammonia, c.

**Chemical industries**—
- Manufacture of ammonia, c.
- Manufacture of calcium carbide, calcium cyanamide, and calcium nitrate, c.
- Manufacture of potassium dichromate and sodium dichromate, c.
- Manufacture of fertilizers, c.m.
- Manufacture of magnesia, m.
- Manufacture of acetate of lime, c.
- Manufacture of wood alcohol, c.
- Manufacture of bone ash, c.m.
- Manufacture of calcium light pencils, c.
- In refining quicksilver, c.
- In dehydrating alcohol, c.
- In distillation of wood, c.

**Gas manufacture**—
- Purification of coal and water gas, c.m.

**Glass manufacture**—
- In most varieties of glass and glazes, c.

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Milling industry—
   Clarifying grain, c.m.

Miscellaneous manufactures—
   Rubber, c.m.
   Glue, c.m.
   Pottery and porcelain, c.m.
   Dyeing fabrics, c.m.
   Polishing material, c.m.

Oil, fat, and soap manufacture—
   Manufacture of soap, c.
   Manufacture of candles, c.
   Manufacture of glycerine, c.
   Renovating fats, greases, tallow, butter, c.m.
   Removing acidity of oils and petroleum, c.m.
   Lubricating greases, c.m.

Paint and varnish manufacture—
   Cold water paint, c.m.
   Refining linseed oil, c.m.
   Manufacture of linoleum, c.m.
   Manufacture of varnish, c.m.

Paper industry—
   Soda method, c.
   Sulphite method, m.
   For strawboard, c.m.
   As a filler, c.m.

Preserving industry—
   Preserving eggs, c.

Sanitation—
   Disinfectant, deodorizer, c.
   Purification of water for cities, c.
   Purification of sewage, c.

Smelting industry—
   Reduction of iron ores, c.m.

Sugar manufacture—
   Beet root, c.
   Molasses, e.

Tanning industry—
   Tanning cowhides, c.
   Tanning goat and kid hides, c.m.
   Water softening and purifying, e.

The Present State of the Lime Industry in Wisconsin

The rise of the Portland cement industry has led to a decline in lime production in Wisconsin. The outlook at present for hydrated lime is more hopeful than for lump lime. This is because hydrated lime is rapidly coming into use in connection with cement because of its advan-
tage for water proofing and increasing plasticity. In 1919 Wisconsin produced 100,120 tons of quicklime and 23,470 tons of hydrated lime, an increase in total production over 1918 of 13 per cent. More than 95 per cent of the production came from one formation in the eastern part of the state, the Niagara dolomite.

Wisconsin probably has over 150 lime kilns, of which perhaps more than half did not produce during the past 5 years. In 1918, the kilns reported as active included 35 flame kilns, 6 pot kilns, and 1 field kiln. The total number reported was 117, which did not include some of the kilns which produce occasionally for local purposes.

Most of the flame kilns in use are about 30 feet high measured from the grates. At the fires they are between 5 to 8 feet square. Nearly all burn wood. The lime output varies from 1.5 to 2.5 tons per cord of wood. A few kilns have been fired with coal gas. The continuous kilns are usually drawn about every 4 hours and yield 16 to 20 barrels per draw. The yield per kiln per day varies from 10 to 20 tons. No technical means of measuring temperatures are in use. Firing is controlled by the judgment of skilled operators.

Agricultural Use of Marl, Limestone, and Dolomite

The chief purposes for which limestones and dolomites are applied to soils are (1) to supply plant food, and (2) to neutralize the injurious acids of many soils.

Uses as Plant Food

The chief plant foods which they supply are calcium and magnesium. Some have a small percentage of phosphorus. Both calcium and magnesium are essential to crops, but the amounts required are in most cases small. Clovers use an exceptionally large amount of calcium. Most soils have enough of these elements to supply the demands of growing crops.

There are no published investigations of a comprehensive nature regarding the lime content of Wisconsin soils. That some of our soils need limestone as a plant food is certain. It is true of many sandy soils of the Driftless Area. Phosphorus is a highly important plant food. Unfortunately our Wisconsin limestones and dolomites have a very low content of this desirable element. In over 200 analyses, the content of phosphoric acid (P₂O₅) varied from about 0.01 to 0.2 per cent. None of them can be regarded as having any value as sources of phosphorus. In the decay of limestone to soils, there is a tendency for a large part of the phosphorus to remain in the soil, whereas the carbonates of lime and magnesia are largely removed by solution. Hence soils derived from limestone not infrequently show about the same, or even a higher percentage of phosphorus than the parent material. For information
on the amounts of calcium, magnesium, and phosphorus used by various crops see "Soil fertility and permanent agriculture," C. G. Hopkins, Ginn & Co., New York.

The chief dolomite formations of Wisconsin are not alike in their phosphorus content. The Niagara dolomite has the lowest content, the Galena and Black River has the highest, and the Lower Magnesian dolomite holds an intermediate position.

Uses as Neutralizers of Acids in Soils

The application of lime carbonates and dolomite to soils for overcoming a condition known as soil acidity is of great value in growing certain crops. The use of marl, limestone, and dolomite for this purpose in Wisconsin is increasing under the leadership of the College of Agriculture.¹

Soil acidity is due to acid whose exact nature is not fully known. It is common in new soils rich in decaying vegetation, in peat bogs, in sandy soils, and in soils that have been cropped for a long time. It is usually accompanied by a low content of lime, magnesia, and phosphorus in forms usable by plants. It hinders or even prevents the growth of certain crops, and favors that of others.

The most baneful effect of soil acidity is that it stunts or even inhibits the growth of alfalfa and red clover, the most efficient of the nitrifying plants. Plants which do better in acid soils are radish, flax, blackberry, black raspberry, and cranberry. For carrying out the most profitable methods of crop rotation and for getting the nitrogen content of soils renewed by growing alfalfa and red clover, it is vitally important to overcome soil acidity.

Soil acidity can be detected by means of blue litmus paper which can be purchased from any reliable druggist. Soil which is naturally wet from rain or thaw can be slit open by a knife. The litmus paper is inserted in the slit and the soil is pressed against the paper. The contact of the soil and litmus paper should be maintained for five minutes. If the blue paper turns red in spots or over the whole end, the soil is acid.

The test can also be made by fashioning a ball of wet earth and then breaking it in half. The blue litmus paper is laid on one of the freshly broken surfaces. The other half of the ball is covered over it, and the two halves are pressed together.

¹ For valuable information on soil acidity and its remedy the reader is referred to Whitson and Weir's "Soil acidity and liming", Bull. 230, and "Testing soils for acidity", Bull. 312, by E. Truog. These bulletins can be obtained on application to the Agricultural Experiment Station, Madison, Wisconsin. Most of the facts in this report dealing with the properties of limestones and dolomites as soil neutralizers are taken from them.
In case dry soil is tested, the soil sample is put in a clean dish and moistened with soft water to a stiff mud. With a clean stick separate the wet soil into two portions. On one portion a piece of blue litmus is placed, which is then covered by the other portion. In all these tests the soil must not be contaminated with materials that might change its reaction with litmus paper, the soil must be damp preferably from rain or thaw, and the paper must be in direct contact with the soil for at least five minutes.

If a soil effervescences when treated with muriatic acid, carbonate of lime may be the cause of the reaction, in which case the soil cannot be acid. The bubbling may be caused, however, by the escape of air. If a soil is first soaked in water until the air is expelled and then treated with muriatic acid, effervescence shows that the soil is not acid. The lack of effervescence does not prove the soil to be acid, since in many of our Wisconsin soils the calcium is not in a form acted upon by muriatic acid.

The growth of certain weeds on soils is a good indicator of soil acidity. Weeds of this character are the sheep sorrel or sour sorrel, horsetail rush, corn spurry, and wood horse tail. These weeds may be found in all kinds of soils, because their seeds are widely scattered. When they take possession of fields, it usually means that the soil is acid and that for this reason other weeds do not thrive. Soils on which red clover and alfalfa no longer thrive should be tested for acidity.

The preceding tests and indications give no clue as to how acid the soil is. Truog has devised an ingenious method by which the amount of acidity can be measured. It is based on the principle that a moist acid soil of known weight when in contact with zinc sulphide gas in proportion to the acidity. This gas when brought in contact with lead acetate paper blackens the paper. The darkened paper is compared with the color of standardized paper and the amount of acidity can be read directly. See Truog’s Bulletin 312 of the Agricultural Experiment Station of the University of Wisconsin for details of method and results.

Truog states that three-fourths of the soils of Wisconsin are acid. The residual soils of southwestern Wisconsin, despite their origin from the decay of limestones, are frequently acid. Percolating waters have removed most of the lime which would neutralize acids. Nearly all the sandy soils of Wisconsin are likewise acid, because their original content of lime is low. The glacial soils of eastern and southern Wisconsin, although generally quite well supplied with lime when first cultivated, have in many cases, after years of cropping, become acid. Marshes which are underlain by limestones like those of the southeastern part of the state are as a rule not acid. The red clay soils along the coast of Lake Superior and in the Fox River valley as a rule are not acid. These
soils are marly clays which were deposited in lakes. Newly broken marsh soils are frequently acid from the decaying vegetation which they contain. This is particularly true of those which are underlain by sandstones or granites, rocks which have a low content of lime in a form which would overcome acidity.

The remedy for soil acidity is to add a neutralizer to the soil. A neutralizer is a substance which will react with the acid, the reaction producing new substances which are not acid. Fresh unleached wood ashes have this property. The cheapest material which can be used is limestone or some of the substances derived from limestone like quicklime, hydrated lime, air-slaked lime, the lime refuse from tanneries, beet sugar and glue factories. Ground shells and marl are also good for this purpose whereas gypsum or land plaster is not.

In 1917 a state law controlling the sale of agricultural limes was adopted. The law reads as follows:

The term agricultural lime as used herein shall include all quicklime, both lump and ground, ground limestone, ground or pulverized oyster shells, sulphate of lime or land plaster, hydrated lime, gas lime, marl and all similar products, provided that nothing herein shall be construed as prohibiting persons engaged in quarrying and grinding limestone, within the state of Wisconsin, from selling their own products at the place where ground and quarried without complying with sections 1494c, 1494d and 1494e. Every manufacturer, person or firm who shall sell, offer or expose for sale or for distribution in the state of Wisconsin, any agricultural lime to be used as a fertilizer or soil improver, shall furnish with each shipment or lot or shall affix to each package or bulk of agricultural lime a statement clearly and truly certifying the kind of lime, the number of net pounds in each shipment or lot or package, the name of the manufacturer, place of business, and for all quicklime, hydrated lime, gas lime, marl, limestone, clam and oyster shells, the following statement of analysis: 

1. The maximum approximate percentage of water. 
2. The minimum neutralizing value expressed as the percentage of calcium carbonate. 
3. In the case of marl and ground limestone and clam and oyster shells, the additional analyses concerning fineness as follows: 
   a. Percentage not passing ten-mesh sieve. 
   b. Percentage passing ten-mesh sieve, but held on sixty-mesh sieve. 
   c. Percentage passing sixty-mesh sieve.

In the case of sulphate of lime or land plaster the maximum percentage of water and the minimum percentage of sulphur trioxide. 

Approximate water content as used in this section is to be taken to mean within five per cent. Neutralizing value is to be determined as follows: A determination of the carbon dioxide content is to be made directly on ground limestone, clam and oyster shells and marl. 

In the case of quicklime, hydrated lime, gas lime, and other partly slaked and carbonated material, the oxide and hydrate are to be changed to the carbonate and then a determination of the carbon
USES OF MARLS, LIMESTONES; AND DOLOMITES

Dioxide content is to be made in the same way as with ground limestone. The carbon dioxide value is then to be calculated over to its chemical equivalent as calcium carbonate and from this value the neutralizing value of the dry material compared to pure dry calcium limestone is to be calculated and expressed in terms of per cent.

Rock sold as limestone may contain as much as 45 per cent magnesium carbonate; that is, it may be a pure dolomite. According to Whitson and Weir dolomite is just as beneficial as limestone. In fact, a pound of pure dolomite has the power of neutralizing a little more acid than a pound of pure limestone. In addition to the carbonates of lime and magnesia, limestones usually contain sand, clay, moisture, and other impurities. In buying limestone, the aim should be to select one with a high content of carbonates. If possible, the carbonates ought to constitute 90 per cent or more of the rock. The earthy or sandy materials which make up the remainder of the rock have no effect on soil acidity. Rock from any of the Niagara limestone quarries of the eastern part of the state is the most uniform in quality of any limestone or dolomite in the state, and averages the best, although locally good limestone or dolomite can be obtained from other formations. The carbonates in the Niagara formation usually exceed 95 per cent. The Lower Magnesian dolomite is exceedingly variable in composition. Usually it has a high percentage of sandy and earthy constituents. The Galena and Black River dolomites are more uniform in composition, but on the average are inferior in quality to the Niagara limestone. Their content of earthy constituents averages about 10 per cent. The glass rock beds of the Black River formation in the lead and zinc region of the southwestern part of the state have a high content of lime carbonate, and are of good quality. Mine tailings from this district have been successfully used (p. 54). Locally the Mendota dolomite and dolomitic phases of the Cambrian sandstone may be used if they are the most available. They are likely to have about 30 per cent of insoluble matter.

As to what kind of limestone to use, no fixed rule can be laid down. The cost per unit of carbonates, not the cost per ton, should be considered. A fairly close estimate of the cost per unit of carbonate can be gotten by dividing the cost per ton by the percentage of carbonates. Thus if the cost per ton is $5.00 and the percentage of carbonates is 93, the cost per carbonate unit is approximately $5.00 ÷ 95 or $0.052+. If the cost per ton is $2.00 and the percentage of carbonates is 50, the cost per carbonate unit is about $0.04. In making such calculations, cost per ton should include not only the cost of the raw material, but expense of transportation and application as well.
Marl and ground shells have the same effect as limestone. They usually have a high content of moisture unless artificially dried. In buying these substances, the same rules should be followed as in buying limestone. They should be bought on the basis of carbonate content.

The amount of limestone or similar material to use per acre, Truog says, depends on the acidity of the soil, the kind of soil, the lime requirements of the crops to be grown, and the kind and quality of the lime. He has devised a chart from which the amount of limestone, etc., needed under various conditions can be obtained. The maximum amount recommended by him is 5 tons to the acre. This is on very strong acid soils of good quality and for crops having a high lime requirement. Such crops include alfalfa, sugar beets, tobacco, canning peas, cabbage, and most garden crops. Half the amount of quicklime is used in place of limestone.

According to Whitson and Weir, two tons of damp ground limestone, 20 to 30 per cent of which will pass a 60 mesh sieve, can be applied per acre. Most crops are not injured by an overdose of limestone or dolomite. The U. S. Department of Agriculture claims that the only crops positively injured by liming are radishes, flax, blackberry, black raspberry, and cranberry.

The more caustic forms of lime, such as quicklime, hydrated lime, and some forms of lime refuse should be used cautiously. This is especially true of quicklime. Their action is more drastic than that of the natural carbonates. Quicklime causes rapid decomposition of organic matter and fertilizers in the soil. This at first causes a spurt in the productiveness of the soil, but if it is not followed up by liberal applications of manures or other fertilizers, excess of fertility will be followed by exhaustion. Quicklime and hydrated lime improve the tilth of sticky, clay soils.

LIMESTONE AND DOLOMITE AS FLUXES

Fluxes serve two purposes in smelting operations. When mixed with an ore they lower the melting temperature of the ore, and combine with its impurities to form a slag. The slag being lighter than the metals rises to the surface as a liquid and leaves the metals in a nearly pure state. Limestones are used as fluxes in iron blast furnaces, in the basic Bessemer process of steel-making, and in lead and copper smelting. In all of these operations a pure high calcium limestone is preferred. When this cannot be obtained, magnesian limestones are used in the iron blast furnaces. In copper smelting, the magnesia content of the slag should not exceed 12 per cent and even 4 per cent of magnesia usually has bad effects.
The objection to magnesia is that it makes a very sticky or viscous slag, which requires a great expenditure of heat to maintain in a condition of fluidity sufficient to permit it to flow readily from the furnace. Alumina has a similar effect and the presence of both alumina and magnesia is highly undesirable. Clayey iron ores, therefore, cannot very well be smelted with a magnesian limestone. A small content of silica is not objectionable, but it lowers the effectiveness of the limestone. The chief impurity in iron ore usually is silica and the limestone is generally added to the ore in such proportions as to form the lime meta-silicate, as this has the lowest formation temperature of any compound of lime and silica. If silica is the only impurity in the ore, 1.6 pounds of limestone are necessary to combine with 1 pound of silica to form the lime meta-silicate slag. If the limestone has 2 percent of silica, a ton of it would contain 40 pounds of silica. To slag this off, 64 pounds of the lime carbonate is necessary—therefore out of every ton of rock 104 pounds are not only useless but consume heat, and as they occupy space in the furnace, they reduce thereby the furnace capacity.

**Limestone and Dolomite as Natural Cement Material**

Natural cements include all those cements which are obtained by burning impure, clayey limestones at a low temperature, about 900 to 1000° C. Their composition and physical properties are extremely variable. As a rule they set more quickly than Portland cement. Much more sand can be used with Portland cement than with natural cement. They have the property of setting under water but have a lower tensile strength than Portland cement.

The raw material may be either soft or hard, porous or compact, dry or moist. A hard, dry, compact material is preferred. It can be burned with less expenditure of heat and does not tend to check the draft of the kiln. The carbonates in these cements may range from the pure or nearly pure calcium carbonate to one in which the weight of magnesium carbonate is about four-fifths of the weight of the calcium carbonate. The kind which has a high magnesium content is generally less desirable.

Their tensile strength being less than that of Portland cement, they have declined in importance as construction materials since Portland cement has come into vogue. In 1919 natural cements were but 0.6 per cent of the total cement production. They usually are cheaper than Portland cement. Natural cement averages two thirds the price of Portland cement. As to whether Portland or natural cement is to be used depends on the tensile strength required, the cost of each and of sand. Where great ultimate strength is necessary, or where variable strains must be provided for, Portland cement is preferred.
LIMESTONES AND MARLS OF WISCONSIN

LIMESTONE AND MARL IN PORTLAND CEMENT

The uses of limestone and marl in Portland cement are discussed in detail in Chapter V.

DOLOMITE AS A SOURCE OF MAGNESIA

Nearly all magnesia is obtained from the carbonate of magnesia, magnesite. It is a product of great value. Its chief uses are for making magnesia brick for furnace linings; Sorel cements, very desirable for floorings; stucco; and magnesium hydrate. It is also used for making metallic magnesium, magnesium alba, and the sulphates and chlorides of magnesium. Most of the magnesite used in the United States has been imported from Greece. Chewelah, Washington, is now an important producer of magnesite. Some is also produced in California.

Before the war magnesite was laid down on the Atlantic seaboard at $15.00 to $18.00 per ton. During the war the price rose to $100.00 a ton. Dead burned magnesite is now $33.00 a ton at Chewelah, Washington, and $58.00 to $64.00 a ton at Chester, Pennsylvania. Chicago prices are $57.00 a ton. On the Atlantic seaboard it is now $61.00 to $63.00 a ton. In Pennsylvania the value of one ton of dead burned magnesite is 37 to 39 times that of a ton of raw dolomite. In Pennsylvania the manufacture of magnesium alba is an established industry. Magnesia alba is a basic carbonate of magnesia and is used as a fire retarding paint and as a non-conductor of heat in coverings of steam pipes and in other heat insulators. It is also used in face powder and as an absorbent for making dynamite. It is made by the Johns-Manville Company of Milwaukuee. In view of the great usefulness of magnesia products, the industry of making them from dolomite seems to have very attractive commercial possibilities.

Schurecht has recently reviewed and studied the processes of making magnesia products from dolomite.1 For references see his paper. Some of these processes seem to be based on the apparently erroneous conception that the magnesium carbonate of dolomite is dissociated at a lower temperature than the calcium carbonate. Some of the methods outlined by Schurecht are essentially as follows:

1. Add 8750 parts MgCl₂ to 1250 parts of caustic dolomite. This forms soluble CaCl₂ and a precipitate of Mg (OH)₂. Remove soluble CaCl₂ by filter press and obtain 1000 parts of Mg (OH)₂ in press.

2. Calcine dolomite between 500° and 600° C. This dissociates MgO which can be removed either by air or water currents. The idea back of this is probably wrong.

3. Add a 10 to 15 per cent sugar or molasses solution to milk of
dolomite. The Ca(OH)$_2$ goes into solution and the Mg(OH)$_2$ remains
solid. The sugar and lime are recovered by passing CO$_2$ through the
solution.

4. Crush calcined dolomite to 8 to 40 mesh size and leach with cold
water. This dissolves CaO but leaves MgO as a residue. Leach until
residue contains 3 to 10 per cent Ca(OH)$_2$.

5. Treat dolomite with H$_2$SO$_4$. MgSO$_4$ is filtered from the less sol-
uble CaSO$_4$ precipitate.

6. Hydrated calcined dolomite is treated with H$_2$SO$_4$. Forms fine-
grained CaSO$_4$ and leaves bulkier Mg(OH)$_2$ which can be separated
by screening.

7. Dolomite is calcined and hydrated and the hydrate leached until
low in Ca(OH)$_2$. 