Ohio Agricultural Experiment Station

CIRCULAR No. 123

WOOSTER, OHIO, APRIL 15, 1912

CARRIERS OF LIME

By JOHN W. AMES

The uniformly beneficial results which have followed the intelligent use of lime on soils deficient in basic material, have caused an increasing interest in the practice of liming as a necessary method of soil improvement. Consequently the supplying of lime for agricultural purposes has developed into a profitable industry, and at the present time there are many different forms and grades on the market. The claims frequently made by dealers concerning the value of a particular brand or form of lime, and the further fact that, in many instances, lime products are sold without a guarantee of quality or composition, often cause the farmer to be somewhat in doubt as to the carrier of lime best adapted for use on his soil.

In view of the numerous inquiries received at this Station concerning the composition and relative values of different lime carrying materials, a general description of the several forms and of the by-product materials containing lime is presented in this circular.

LIME A SOIL AMENDMENT, NOT A FERTILIZER

While the majority of dealers are selling their product as some form of lime, in some cases the representation or rather misrepresentation has been made that lime is a fertilizer, and the terms, "Fertilizer lime" and "Lime fertilizer" are applied to the products offered for sale.

There should be no misunderstanding in regard to the fact that lime does not take the place of other fertilizing materials. With the exception of small amounts of phosphorus and insoluble potassium which are sometimes found in limestone and marl, it does not supply any of the available nutritive elements which are ordinarily contained in fertilizers. When the need of lime is indicated by the reaction of the soil or by the failure, partial or complete, of the leguminous plants which thrive best on calcareous soil, the fullest returns cannot be secured unless lime is added as a soil amendment in conjunction with materials carrying phosphorus, potassium and nitrogen. However, no form of lime should be mixed or used directly in combination with manure, or with fertilizers containing organic nitrogen or ammonium salts. These materials should be applied after the lime has been thoroughly incorporated with the soil.

The functions of lime in relation to plant life are somewhat complex, since it affects both the physical and bacteriological

conditions of the soil, and at the same time has a specific action on the chemical constituents present in the soil mass. It will be sufficient for practical purposes, however, to state that while lime is a necessary substance for plant growth and is one of the mineral compounds present in greater or less amounts in all plant life, it is used primarily for neutralizing the so-called acid condition of soils. Legumes in particular remove considerable amounts from the soil. Nevertheless, the supplying of lime as a plant food may be considered of minor importance for the reason that any deficiency in this respect will be furnished in excess of the needs of the plant when the soil conditions, of which soil acidity is a symptom, are corrected.

FORMS OF LIME

The term lime is applied indiscriminately to the basic calcium compounds, calcium-oxide, calcium hydroxide and calcium carbonate. Strictly speaking, the use of the term is restricted to the combination of calcium with oxygen, namely: calcium oxide.

Calcium carbonate, which is the natural source of all lime compounds applicable for increasing the basic lime content of soil, is abundantly distributed in limestone, marl and shells. It is also found in wood ashes and occurs as a by-product from various manufacturing processes.

Limestone belongs to that class of rocks known as carbonate rocks. In addition to calcium carbonate, it contains varying proportions of magnesium carbonate, together with alumina, iron oxide and silica from mechanically included clay and sand. The variable composition of limestone from several different localities is shown by the calcium and magnesium content of samples analyzed by this Station. These analyses are not to be understood as typical for the entire county. The results are given below:

County	Calcium carbonate percent	Magnesium carbonate percent	County	Calcium carbonate percent	Magnesium carbonate percent
Athens	87.27	1.96	Lucas	55 31	*
Athens	94.46	2.31	Lucas	63.09	*
Athens	72:77	1.50	Marion	72 25	22.41
Belmont	94.20	1.05	Mahoning	90.39	1.12
Belmont	84.86	1.77	Muskingum	92.30	1 52
Belmont	70.10	9.90	Meigs	77.59	*
Belmont	92.78	3.05	Meigs	93.09	*
Belmont	57.03	16.56	Meigs	84.54	*
Belmont	77.15	6.56	Ottawa	77.74	17.84
Clarke	78.99	*	Summit	77.39	13.34
Clinton	74.58	*	Tuscarawas	93.35	1.21
Franklin	83.62	6 13	Tuscarawas	91.35	1.59
Hamilton	92.01	4.16	Van Wert	54.15	44.30
Harrison	79 93	*	Van Wert	54.35	45.14
Harrison	89.21	*	Van Wert	54.05	44.55
Jefferson	75 75	2.25			

* Magnesium carbonate not determined.

Limestone from the same quarry may also vary considerably in composition. The upper or more exposed ledges, which have been subjected to leaching, contain a less amount of calcium and magnesium carbonates and a greater proportion of the insoluble

materials, silica, iron and alumina. Considerable differences in the character of the lime would be made by burning limestones which vary to an appreciable extent in their composition.

When the content of magnesium carbonate in limestone amounts to 30 percent or more it is classed as magnesian limestone or dolomite. There is some difference of opinion as to the advisability of using magnesian limestone on soils. Experiments which have been conducted by different investigators show that too large an excess of magnesium over calcium in the soil may produce an injurious effect on plant life. Magnesium, however, is an essential element for plant growth, being found in all plants, the seeds being relatively richer in magnesium than the other parts of the plant.

The chemical analyses of a large number of soils from various sections of the state show that, when a deficiency of lime is indicated by the calcium and magnesium carbonate content, there is generally an excess of magnesium over the calcium present, and that when soil contains a sufficient supply of these bases, the content of calcium is greater than the magnesium. This being true, it would seem that attention should be given to both the composition of the soil and of the lime used. On soils deficient in calcium carbonate a limestone having a low content of magnesium is to be preferred. A good grade of limestone should contain at least 90 percent of calcium and magnesium carbonates.

Calcium oxide, commonly known as quicklime, burned lime and caustic lime, is the most concentrated form in which lime is supplied. It is produced by heating limestone or some other form of calcium carbonate to a red heat in kilns. This procedure decomposes the calcium carbonate into the two products, carbon dioxide "CO_2" and lime "CaO." The carbon dioxide, which comprises 44 percent of the weight of calcium carbonate, is driven off as a volatile gas, and the resultant product is calcium oxide or lime. From every 100 pounds of limestone burned, assuming that the stone is pure calcium carbonate, there will be produced 56 pounds of calcium oxide or lime. Or in other words, nearly two tons of limestone must be used to make one ton of burned lime. The composition of burned lime is variable and depends upon several conditions:

(1) The composition of the stone from which lime is burned.

(2) Care used in burning.

(3) Amount of contamination from the fuel.

(4) Length of time and conditions under which the burned lime is stored.

Hydrated lime or slaked lime is the product of the combination of burned lime or calcium oxide with water. Commercially it is prepared by treating freshly burned lime with slightly more water than will combine freely with the calcium oxide present. It is then

roasted to remove the excess of water and finally reduced to a powder by grinding. One of the claims made for properly prepared hydrated lime is that it can be safely stored in paper bags without materially changing in composition. By the process of hydration the weight of 56 pounds of freshly burned lime or calcium oxide is increased to 74 pounds, or expressed on the basis of pounds per 100, a ton of hydrated lime contains approximately 486 pounds of water, which is chemically combined with the calcium oxide. Some of the hydrated limes on the market contain a considerable proportion of calcium carbonate and, aside from their better mechanical condition, these products are worth little more than ground limestone. The greater number of samples of hydrated lime which have been submitted for examination contained too large an amount of calcium carbonate to be properly classed as hydrated lime.

The combination of calcium oxide with water is accompanied by a violent evolution of heat, therefore, when the fine dust from burned lime comes in contact with perspiring men or animals considerable discomfort and oftentimes serious burning results. Hydrated lime is also caustic, but is less disagreeable to handle than unslaked lime. Quicklime and hydrated lime both absorb carbon dioxide from the soil and air and eventually change back to carbonate of lime, from which they were formed by the process of burning. The beneficial results following the use of lime will therefore be due mostly to carbonate of lime, regardless of the form originally applied.

Air slaked lime, formed when quicklime and hydrated lime are exposed to the air, is mostly a mixture of hydrate and carbonate of lime. Its composition depends upon the length of time and conditions under which it has been exposed. Quicklime first absorbs water and then carbon dioxide; and if this change is complete, the resulting product will be calcium carbonate in a finely divided condition.

Agricultural lime is an indefinite term frequently applied to lime supplied for soil purposes. It is usually a mixture of hydrated lime and calcium carbonate. In some cases incompletely burned limestone is ground and mixed with partially slaked lime which is not salable for building purposes and the mixture sold as "agricultural lime." Several samples submitted to this Station for examination were composed chiefly of air slaked lime and kiln ashes. The term, "agricultural," used in connection with lime, may mean that it is intended for agricultural purposes, but does not necessarily signify anything in regard to composition or value. Intending purchasers should ascertain pretty carefully the value of any carrier of lime before paying burned lime prices for carbonate lime.

Oyster shells contain approximately 95 percent of calcium carbonate. If ground sufficiently fine they are as valuable as calcium carbonate in limestone for use on soil.

Wood ashes are valued chiefly for their content of potassium and phosphorus. Average analysis of unleached wood ashes show that they contain about 50 percent of calcium carbonate*, which is equal in value to the same amount of calcium carbonate in ground limestone.

Marl is a loose, earthy deposit, consisting of calcium carbonate or dolomite often intermingled with clay. The amounts of calcium and magnesium carbonates in marl may vary from 10 to 90 percent. The value of marls depends entirely upon their composition; they should be purchased only on the basis of actual amounts of carbonates present. Equal amounts of calcium carbonate, whether supplied by marl or limestone, are of the same value for soil application.

BY-PRODUCT LIME

Under this heading are included the lime-containing materials which accumulate as waste or by-products from various industrial processes. Samples of practically all the materials mentioned in this connection have been submitted at various times to the Chemical Department for examination. These waste limes are mostly carbonate of lime or a mixture of hydrated and carbonate lime. A number of these materials are produced in such small quantities that their use will be necessarily restricted to the immediate vicinity in which they are made. Some of the by-products from other sources, however, accumulate in such large amounts that an effort has been made by those interested to utilize them for soil purposes. When the values of these materials, as indicated by their composition, are consistent with the prices asked, their use will be as satisfactory as that of the natural lime products.

Waste lime from the manufacture of soda ash contains lime as hydrate, carbonate, and chloride, together with sodium chloride or salt. As it accumulates in large quantities, exposed to the weather, it contains an excess of water which must be removed by drying before it can be handled economically. A sample of this material dried and prepared for the market, contained the following amounts of the several constituents determined:

Insoluble material	2.00	percent
Ferric oxide and alumina	4.72	"
Calcium carbonate	67.75	"
Calcium hydrate	8.34	"
Magnesium hydrate	6.47	"
Sodium chloride	8.53	"

Refuse carbonate of lime from the manufacture of acetone is a granular form of calcium carbonate which has recently been placed on the market. Calcium acetate is a chemical compound obtained in the manufacture of chemicals from the destructive distillation of wood. When this substance is subjected to heat in iron retorts it is

* Together with about 5 percent of "potash" and .1 to 1.5 percent of "phosphoric acid," as expressed in the termology of the fertilizer trade.

decomposed into two products, acetone which distills over, and carbonate of lime of approximately 98 percent purity which remains as a waste product. This form of calcium carbonate has the same value as an equivalent amount of calcium carbonate in the form of limestone.

Refuse lime from water softening plants is composed chiefly of calcium carbonate in a finely divided condition, which has been precipitated from the water by the addition of hydrated lime. Any excess of lime remaining in solution is in turn removed by the action of sodium carbonate. The lime is removed from the settling tanks as a sludge and contains a large amount of water. In this condition it will not be worth more than the cost of hauling.

Carbonate of lime from soap factories. Large quantities of this material accumulate as a residue from the manufacture of caustic soda. If properly dried, it may prove to be an excellent form of calcium carbonate.

Lime from acetylene gas generators. Calcium carbide, the material used for generating acetylene gas, is changed by the action of water into acetylene and hydrated or slaked lime. After removal from the gas machine the slaked lime should be exposed to the air for some time before applying to the soil. During this period it will be partially changed into carbonate of lime.

Waste lime from sugar beet factories. Quicklime is used in the manufacture of sugar beets for the purpose of purifying the juices previous to their conversion into granulated sugar. The lime as it comes from the filter presses is partially hydrated and partially carbonated lime; the hydrated lime will eventually change into carbonate during storage. It frequently contains other refuse from the factory which has been dumped on the same pile. Analysis of a sample of lime waste from a sugar beet factory showed the following composition:

Water	46.08	percent
Insoluble matter	1.53	"
Calcium carbonate	42.60	"
Magnesium carbonate	3.31	"
Ferric oxide and alumina	1.77	"

When the material contains the amount of water shown to be present in the sample analyzed it is evident that it cannot be economically utilized until the water is partially or completely removed. In addition to the lime present, the material contains small amounts of the fertilizing elements, nitrogen, potassium and phosphorus, as well as organic matter, which have been absorbed from the beet juices.

Lime from gas purifyers. In the manufacture of coal gas various sulphur compounds are expelled by distillation from the coal. These are absorbed by passing the gas through suitable chambers containing hydrated lime and other material. The spent lime is

mostly in the form of carbonate, and contains, in addition, combinations of lime with sulphur and other volatile compounds, which are exceedingly injurious to plant life. It should never be used until after exposure to the weather for several months. Owing to changes in the methods of manufacturing gas only small quantities of this waste material are at present produced.

Basic slag phosphate, commonly known as Thomas slag or Thomas phosphate powder, is a by-product from the manufacture of steel from pig iron by the open hearth process. It is valued chiefly for its content of available phosphoric acid, of which it contains about 16 percent, and is especially efficient as a carrier of phosphorus on acid soils. It contains some free lime and has therefore a decidedly alkaline reaction. It would not be advisable to use basic slag for the purpose of correcting soil acidity, because lime is a much more economical material for this purpose. In a few cases basic slag phosphate has been confused with blast furnace slag, which contains lime combined with silica as calcium silicate. Blast furnace slag is of no value either for correcting soil acidity or as a carrier of phosphorus.

RELATION BETWEEN COST AND VALUE OF DIFFERENT LIME MATERIALS

The advisability of using calcium carbonate, fresh burned lime, hydrated lime, or any of the by-product materials carrying lime, depends upon several factors. The chief thing to be taken into consideration, of course, will be the cost of a given amount of calcium oxide or its equivalent in hydrated or carbonate lime. In general, the best course to pursue will be the purchase of that form of lime which supplies the greatest amount of basic material for the least money, provided its mechanical condition is satisfactory. In addition to price of the lime material F. O. B. quarry or works, the items freight, hauling and handling, must also be taken into account in estimating the cost of lime applied to the soil.

If burned lime containing 90 percent calcium and magnesium oxides is quoted at $5.00 per ton F. O. B. kiln, the total cost of the material applied will be $7.60, estimating the freight rate to shipping point at $1.00 per ton; hauling 60c per ton, and cost of applying $1.00 per ton.

In estimating the cost of an equivalent amount of lime furnished by hydrated lime quoted at $5.00 per ton, it must be remembered that approximately 2,640 pounds of hydrated lime will be required. The first cost will therefore be $6.60; freight rate, $1.32; hauling, $0.80; applying, $1.05, which makes a total of $9.77. The difference between $7.60 and $9.77 is due to the extra freight and expense of hauling 640 pounds of water combined with calcium oxide. The convenience of handling and storing hydrated lime may partially offset its increased cost over unslaked lime, calcium oxide.

Prices of ground limestone vary from $1.00 to $1.50 per ton in carload lots, F. O. B. quarry. About two tons of calcium carbonate are required to make one ton of burned lime, this at the lowest price quoted, means $2.00 for material, to which must be added double freight and hauling charges, and a little more labor for spreading, which makes a total of $6.40 for lime equivalent to the amount contained in one ton of burned lime.

The above computations relating to cost are approximate only, being based on average conditions for freight and distance of hauling.

Ground limestone can be handled with much less discomfort than the other forms, and when the cost of lime treatment per acre by using limestone is not greater than that for caustic lime it is the best form for most soils.

Limestone can be reduced to a much finer powder by the process of burning and subsequent grinding than is possible by grinding alone. The fineness of the material has always been regarded as important, if there is any advantage in this respect, it will be in favor of the burned and hydrated lime. The more finely divided the material applied to the soil, the more rapidly will it be taken into solution and disseminated throughout the soil; and if immediate effects only are sought, the finer material will be of greater benefit.

No experiments have been conducted which give an indication as to the relative efficiency of limestone of different grades of fineness. Good results, however, have been secured from stone ground so that all of it passed a 10-mesh sieve and about 50 percent of it through a 50-mesh sieve. It is possible to purchase limestone dust, 90 percent or more of which will pass a 100-mesh sieve.

It must be remembered that the organic acids and carbon dioxide which act upon calcium carbonate are constantly being formed from the decomposing organic matter, so that when lime is applied provision for future needs as well as any present deficiency must be considered. The amount of calcium carbonate dissolved from the soil by the action of the agencies just referred to is vastly greater than the quantities removed by crops. In some instances the character of the soil will also be a determining factor in the selection of the most suitable material. The caustic forms of lime, oxide and hydrate, decompose the organic matter in the soil and liberate nitrogen. For soils markedly deficient in organic material, especially light sand or gravel soils, the use of limestone is advised. When it is necessary to improve the physical condition, and at the same time correct acidity, as in the case of heavy clay soils, caustic lime should be used. On muck or peat soils, which are composed almost entirely of organic matter containing an abundance of unavailable nitrogen, caustic lime can be used with profit.