

# The Influence of Form and Fineness of Lime Compounds Upon the Correction of Acidity and Upon the Nutrient Status of Soils

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THE functions which lime compounds perform in the amelioration of acid soil conditions depend upon the rates with which they dissolve. These rates depend upon the form, whether oxide, hydrate, or carbonate; the fineness of subdivision, especially in the case of raw limestones; and finally, upon the density of the product. The relative content of calcium and magnesium likewise determines the relative speed of reaction. It has been customary for control laboratories to analyze for total CaO and MgO and to run a screen test. The combination of the percentage of total oxides and the screen test is supposed to determine the relative effectiveness of agricultural value.

Considerable evidence has been obtained by numerous workers indicating that very fine grinding of raw limestone is essential for effectiveness. Vegetation experiments have shown that limestone which is finer than 100-mesh is equal to hydrated lime in promoting yields on acid soils. Material coarser than 20-mesh has such small surface area that it is very slow to react with the soil and has been found to remain almost unaltered for many months.

Conclusive as the early experiments appear to be, there are some questions not adequately answered by them. Is fineness and chemical analysis sufficient to evaluate limestones or should the relative porosity, crystal form, content of magnesium, and possibly other properties be taken into account? The work here reported was an attempt to devise a procedure which might combine chemical analysis and physical form in a simple expression which might be called "relative effectiveness".

To determine this so-called "relative effectiveness", we have the measurement of available or exchangeable nutrients as affected by different lime products added to the soil, and finally, of course, the influence upon the yield of some lime-loving plants.

## EXPERIMENTAL

A laboratory method for a simple and approximate determination of the "relative efficiency" of liming materials was developed as follows. An amount of the product equivalent to 1 gram of CaCO<sub>3</sub> (on the basis of its neutralizing value) is placed in a 150 ml beaker. To this is added 100 ml of 0.3 N acetic acid having a pH value of 2.6 at 25° C. The contents were stirred for ½ minute after 5 and 10 minutes, and after 15 minutes of reaction 10 ml aliquots were removed and titrated with 0.1 N NaOH to the phenolphthalein end point. The amount of acetic acid neutralized by the lime product was calculated in each case and from this the percentage efficiency of the product was determined (assuming the c.p. calcium

hydrate to be 100% efficient). It is believed that this procedure takes into account particle size porosity, and chemical form insofar as these properties influence the reaction between lime and soil. The relative efficiencies of separates from two limestones and the <100-mesh separates from five different limestones are given in Table 1.

M172, a calcitic limestone from Bellefonte, Pennsylvania, contains 97% CaCO<sub>3</sub> and 1.0% MgCO<sub>3</sub>. Water-washed separates were used.

M174, a dolomite limestone from Devault, Pa., contains 52% CaCO<sub>3</sub> and 44% MgCO<sub>3</sub>. Water-washed separates were used.

M171 is a calcitic limestone from LeGore, Md., containing 90% CaCO<sub>3</sub> and 3.5% MgCO<sub>3</sub>.

M173, a dolomitic limestone from Plymouth Meeting, Pa., contains approximately 54% CaCO<sub>3</sub> and 44% MgCO<sub>3</sub>.

M175 is a calcitic limestone from Thomasville, Pa. It contains approximately 92% CaCO<sub>3</sub> and 4% MgCO<sub>3</sub>.

M176, a calcitic limestone from Anville, Pa., contains approximately 91% CaCO<sub>3</sub> and 2% MgCO<sub>3</sub>.

M177, calcitic limestone from York, Pa., contains 90% CaCO<sub>3</sub> and 7 MgCO<sub>3</sub>.

Only one separate, passing 100-mesh, was used in the case of the last five stones.

## EFFECTIVENESS ON AVAILABILITY OF EXCHANGEABLE NUTRIENT ELEMENTS

In order to determine whether or not the chemical procedure above described simulates the way in which the lime products operate in the soil, an incubation experiment was conducted as follows: a quantity of acid Chester soil was air dried, sieved through a 2 mm sieve, and thoroughly homogenized. Its lime requirement was determined by the method of Merkle (2)<sup>2</sup> and moisture equivalent approximated by the method of Bouyoucos (1). Seven hundred and fifty gram portions were weighed out, sufficient lime of the various sources and finenesses added in equivalent amounts, and the whole brought up to optimum moisture content (25.4%). These were incubated in quart containers having top and bottom ventilation in a cabinet held at 25° C and 90% relative humidity. The initial moisture content was maintained by periodic weighing and watering, distilled water being added with an atomizer. The period of incubation was 10 weeks. Samples were withdrawn every two weeks. These were extracted with 0.5 N. sodium acetate at pH 5.0 and the extract analyzed for Ca, Mg, K, PO<sub>4</sub>, Mn, Al, Fe, NO<sub>3</sub>, and NH<sub>3</sub>, using colorimetric and turbidimetric procedures developed in this laboratory. The pH and lime requirements were also determined periodically. The results of these analyses are shown in Figs. 1 and 2. The average analyses for the 10-

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<sup>2</sup> Figures in parenthesis refer to "Literature Cited", p. 393.

TABLE 1.—Relative Effectiveness of Liming Materials.

Materials used	In Soil						In 0.3 N HAc		
	In decreasing			In increasing			Average	After 15''	After 30''
	H	Al	Mn	Ca Mg	PO <sub>4</sub>	pH			
Calcitic M 172									
20-60 mesh	26	14	40	16	0	16	19	37	49
60-100 "	46	49	88	69	16	34	50	47	61
100-200 "	74	68	98	88	105	77	85	64	76
200 "	85	95	105	110	100	96	99	94	95
Hydrate	100	100	100	100	100	100	100	100	100
Dolomitic M 174									
20-60 mesh	1.8	27	21	9.8	0	6	11	2.0	4.0
60-100 "	5.3	49	59	20	3.2	11	25	3.7	6.0
100-200 "	29	62	95	16	4.9	28	39	5.2	7.2
200 "	53	76	100	35	49	48	60	11	13
Hydrate	84	95	112	67	100	98	93	96	98
M 171 100 mesh	78	81	71	80	25	81	69	53	67
M 173 100 "	45	73	124	12	49	46	58	3.1	4.6
M 175 100 "	81	59	107	88	49	59	74	65	72
M 176 100 "	85	73	107	76	49	81	79	55	68
M 177 100 "	64	68	69	65	33	56	59	52	57

week period were recalculated to show the comparative influence of the particular lime separates or products in increasing or decreasing the pH value or the amount of each ion easily extracted. All of these values are

and pH values. The average influence of the separates in bringing about changes in availability of these nutrient elements in the soil may be compared with the relative effectiveness in rate of neutralizing 0.3 N acetic acid.

The agreement between the chemical method and that involving the effectiveness on availability of easily replaceable elements is quite satisfactory for the calcitic separates, M172. The dolomitic hydrate, when used in equivalent quantity, was nearly as effective as the calcitic hydrate by both methods. However, the dolomitic limestone separates (M174) used in equivalent quantities were not as effective as the calcitic stones in decreasing the replaceable H or Mn, nor were they as effective in increasing the replaceable Ca and Mg, the pH value, or the extractable PO<sub>4</sub>. Furthermore, the chemical method for measuring effectiveness did not agree well with the effectiveness of the dolomitic products in the soil. Dolomitic stone, even if extremely finely ground, is very slowly soluble in 0.3 N acetic acid.

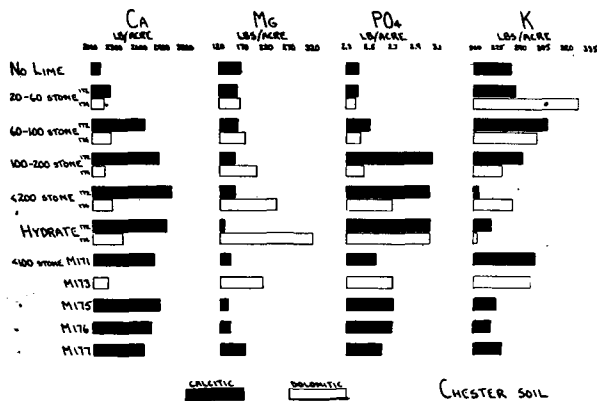


FIG. 1.—The influence of form and fineness of lime compounds upon the correction of acidity and nutrient status of soils.

referred to the effects of the calcium hydrate (M172 Hydrate) taken as 100 (Table 1).

## DISCUSSION

Table 1 gives the relative efficiency of the different lime products and separates in neutralizing 0.3 N. acetic acid in 15- and 30-minute periods. The calcitic stone M172 decreases in effectiveness as the size increases. The 200-mesh material is nearly as rapid as the hydrate while the 100-200 mesh material is 65-75% as effective as the hydrate. These may be compared with the influence of the same product in decreasing replaceable H, Al, and Mn or increasing the replaceable Ca, Mg, PO<sub>4</sub>

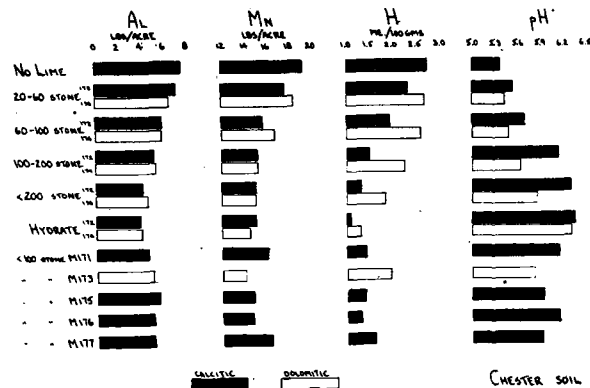


FIG. 2.—The influence of form and fineness of lime compounds upon the correction of acidity and nutrient status of soils.

Limestone samples M171, M173, M175, M176, and M177 are 100-mesh sievings from different limestones as described previously. M173 is from a dolomitic stone, the others are calcitic. Both chemical and soil tests were made on chemically equivalent amounts. The dolomitic product M173 is, in some respects, slower and less effective with respect to its influence in the soil than the other 100-mesh calcitic products. However, the chemical measurement would give it a value much lower than its efficiency in the soil, as in the case of the other dolomitic stone M174.

Comparing the 100-mesh screenings from limestones of different origin one with another, there is not much evidence thus far secured to indicate that the geological mode of formation makes much difference. Morgan and Salter (3) likewise found little or no apparent relationship between the rate of solubility of limestones in acid soils and any physical property of the rock. The 100-mesh material from samples M171, 175, 176, and 177 gave values around 55 to 70 as compared with calcitic hydrate by both methods. The presence of magnesium in considerable quantity, however, lowers the speed of action. A vegetation experiment is in progress to test this matter more fully.

#### SUMMARY

The neutralizing values of ground limestones and hydrated lime were determined by their reaction with

0.3 N acetic acid having a pH value of 2.6 acting over 15 and 30 minute intervals.

For calcitic limestones the 200-mesh material is nearly as effective as the corresponding hydrate. The 100-200 mesh material is definitely slower. Material coarser than 20-mesh is less than one third as effective as hydrate in neutralizing this weak acid.

The neutralizing value in 0.3 N acetic acid agreed quite closely with the activity of calcitic limestones of varying degrees of fineness in influencing availability of soil nutrient elements. This was revealed by their effect in decreasing the replaceable H, Al, and Mn and in increasing the Ca, Mg,  $\text{PO}_4$ , and pH.

Dolomitic limestones are slower to act biologically and chemically but the chemical measurement of their relative effectiveness does not agree with the response in soil. Further work is needed on these products.

#### LITERATURE CITED

1. BOUYOUCOS, G. J. A comparison between the suction method and the centrifuge method for determining the moisture equivalent of soils. *Soil Sci.*, 40: 165-170. 1935.
2. MERKLE, F. G. Soil testing. Operation, interpretation, and application. *Penna. Agr. Exp. Sta. Bul.* 398. April, 1940.
3. MORGAN, M. F., and SALTER, R. M. Solubility of limestones as related to their physical properties. *Soil Sci.*, 15: 293-304. 1923.