

## Specific Surface and Reaction Rate of Calcitic Limestone in Neutralizing Soil Acidity<sup>1</sup>

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The reaction of limestone with acid soils is one of the most important reactions in agriculture. Rapid neutralization of soil acidity is desirable from a practical standpoint and there has been considerable research and education stressing the importance of using limestone having a high per cent of fine particles (3, 5, 6).

Many observations have been made concerning the effect of fineness of limestone on the rate of change of soil pH (5, 8, 9, 10, 11). A screen test is the common method of estimating fineness and the relative surface exposed. Barber (2) has shown that the per cent of limestone finer than 60-mesh is an excellent measure of the neutralizing efficiency of limestones. Barnes (4) proposed the reaction of oxalic acid with limestone as a measure of the relative surface area. He stated that the relationship between the amount of oxalic acid reacting with the limestone and the fineness of the limestone expressed as screen size was a straight line. Thomas and Gross (12) studied this reaction further and modified the procedure of Barnes (4).

It is logical to expect a direct relationship between the rate of reaction of limestone in an acid soil and the specific surface of the limestone particles. It was thought that the oxalic acid method (4) might be used to determine the amount of calcium at limestone surfaces and by consideration of the crystal structure of calcite this could be converted into specific surface values.

### Materials

The limestone used in this study was a calcitic limestone from Bedford, Indiana, and had a neutralizing value of 100 percent. The material was separated into 4-8, 8-10, 10-40, 40-60, 60-100, and <100-mesh fractions and the fractions coarser than 100-mesh were carefully washed on sieves to remove surface dust.

The soil used in studying the rate of reaction of the limestone fractions was a Newton fine sandy loam having an initial pH of 4.8 and a lime requirement of 6.0 tons/acre by an equilibrium calcium hydroxide titration (Fig. 1). The titration curve (Fig. 1) is essentially linear in the pH range of 4.8 to 7.4.

### Methods and Procedures

A slight modification of the method of Thomas and Gross (12) was used in an effort to estimate the surface area of the limestone fractions. One-gram samples of limestone were treated with 10 ml. of 0.1 *N* oxalic acid on the steam plate for one hour. The amount of oxalic acid reacting

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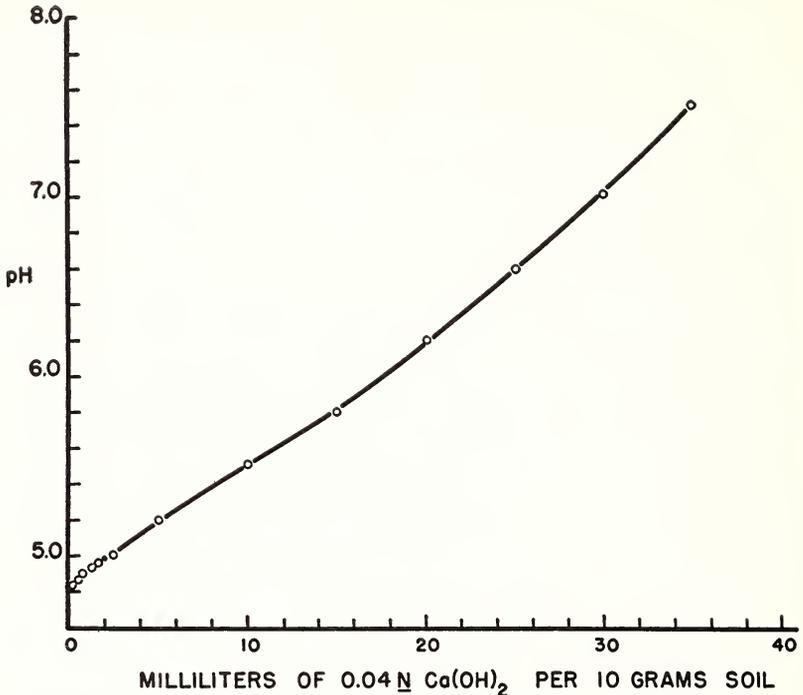


Figure 1. The equilibrium titration curve for Newton fine sandy loam with 0.04 N Ca(OH)<sub>2</sub>.

with the calcium surfaces was determined on an aliquot by titration with 0.05 N potassium permanganate. The calcium reacting with the oxalate was designated as "surface Ca<sup>++</sup>", m.e./gram. Attempts were made to express this in terms of square meters of surface area, but calculations of the ratio of Ca<sup>++</sup> per unit of surface area made on the basis of the unit cell of calcite showed the area to be much higher than that reported for ball-milled calcite by Jurinak and Bauer (7). When one considers the solubility products for calcium carbonate ( $8.7 \times 10^{-9}$  at 25° C.) and calcium oxalate ( $2.57 \times 10^{-9}$  at 25° C.) it can be seen that the solubility of the carbonate is about three times greater than that of the oxalate. Thus, the reaction would affect not only calcium ions at the immediate surface, but would continue until a number of sub-surface layers had reacted.

Specific surface values for the various size-fractions of limestone were then calculated on the assumption that the particles were spherical in shape with a diameter corresponding to the average sieve opening for the screens used in separating a particular size-fraction. Microscopic observations of the fractions indicated this to be a reasonable assumption. These data are shown in Table 1. It should be noted here that the straight-line relationship between the amount of oxalic acid reacting with limestone surfaces and screen size, as reported by Barnes (4), could not be a valid relationship for true surface area because screen

TABLE. 1. Calculated specific surface values for six size-fractions of a calcitic limestone.

Sieve Size	Average Diameter, cm.	$\Pi D^2$	Average No. of Particles per gram of $\text{CaCO}_3$	Specific Surface, $\text{cm}^2/\text{gram}$
4-8 mesh	0.340	0.3631	18	6.5
8-10	0.220	0.1520	66	10.0
10-40	0.071	0.0154	1,968	30.3
40-60	0.030	0.0028	26,100	73.6
60-100	0.018	0.0010	120,833	120.8
100	0.015	0.00022	208,800	144.0

size is related to the first power of particle diameter,  $D$ , whereas surface area is a function of  $D^2$ .

In investigating the rate of reaction of the limestone fractions with the acid soil, portions of soil were treated with each of the particle-size fractions of limestone at the rate of 11 tons/acre. The samples were kept moist and pH values were measured with a glass electrode pH meter on 1:2 soil-water suspensions at intervals of 2, 4, 8, and 12 weeks.

### Results and Discussion

The changes in soil pH for the various treatments are shown in Figure 2. As a relative measure of the effectiveness of the various

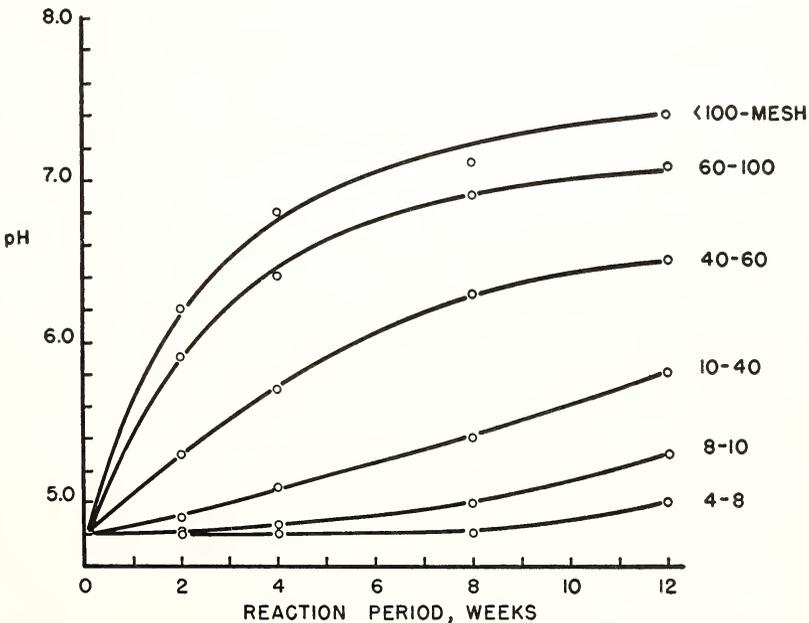


Figure 2. The influence of particle size of limestone on soil pH as a function of time.

size-fractions of limestone we have plotted the time required to produce a change from pH 4.8 to 5.0 (Fig. 3). The material finer than 60-mesh

TIME REQUIRED TO RAISE SOIL pH FROM 4.8 TO 5.0,  
WEEKS

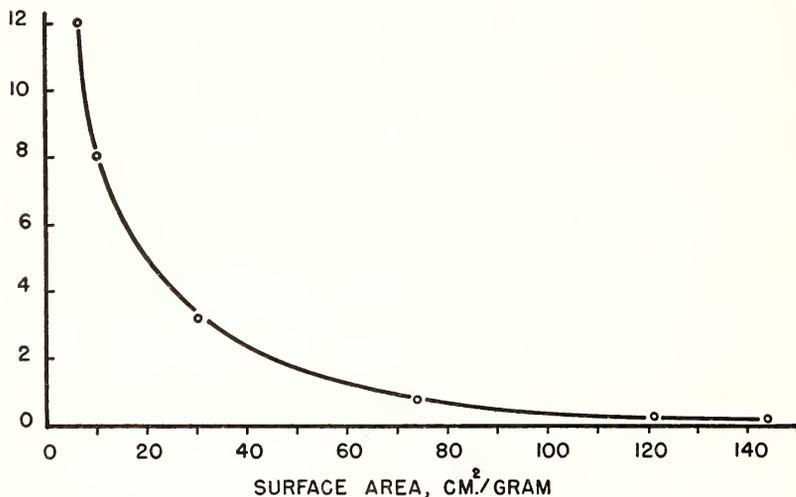


Figure 3. The relationship between specific surface of limestone and the period of time required to raise the soil pH from 4.8 to 5.0.

(surface area greater than 120 cm.<sup>2</sup>/gram) reacted from 24 to 32 times more rapidly than the 8-10 mesh (surface area less than 10 cm.<sup>2</sup>/gram) limestone in producing this change.

The relationship between specific surface and rate of neutralization should be best exemplified in the initial rate of reaction. The change in pH per week for the first two-week period was chosen as the basis for this comparison. Figure 4 shows that the rate of change in pH is very slow for the fractions larger than 40-mesh, but increases markedly for material less than 40-mesh. The increase in the slope of the curve in the smaller particle-size range suggests that the surface of the smaller limestone particles may be more reactive than that of the coarser particles.

It is suggested that this greater reactivity of surface in the finer materials may be explained in part by (1) the presence of a "Beilby" (amorphous) layer, and (2) an increase in surface energy of a crystal with decrease in particle size.

With reference to the formation of a "Beilby" layer, Adam (1, p. 177) states, "The mechanical processes of grinding always result in the formation of a certain amount of the amorphous "Beilby" layer which is obtained by polishing." Adam (1, p. 170) also cites the work of Beilby on the alteration of the structure of calcite by polishing. Beilby observed that an amorphous layer about 50 Å. thick was formed at the surface

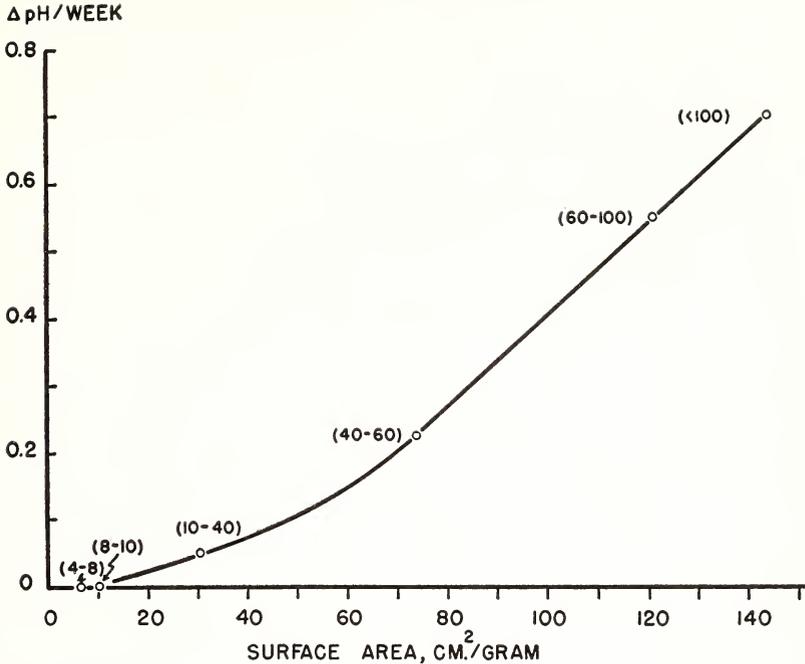


Figure 4. The relationship between specific surface of limestone and rate of change of soil pH for the first two weeks of the reaction period.

and he found traces of the effects of grinding action down to a depth of 5,000 to 10,000 A. The disruption of the structure of the crystal surface to form this "Beilby" layer results in a surface layer of greater reactivity and solubility.

Increase in surface energy with decrease in particle size of crystalline materials is analogous to the fact that the vapor pressure of a liquid in a small drop is greater than that in a large drop. Weiser (13, p. 9) referring to this analogy says, "Similarly, very finely divided particles of a solid might be expected to have a higher vapor pressure, a greater solubility, and a lower melting point than coarse crystals of the material."

### Summary

The specific surface values of six size-fractions of a calcitic limestone were calculated. These values ranged from 6.5 to 144 cm.<sup>2</sup>/gram for the samples studied.

The relationship between specific surface and reaction rate of limestone is neutralizing soil acidity was studied by treatment of an acid Newton fine sandy loam soil with various particle-size fractions of the calcitic limestone. The rate of reaction of the limestone fractions smaller than 60-mesh was from 24 to 32 times more rapid than that of the 8-10 mesh fraction. The relationship between the specific surface and rate of change of pH suggests that the reactivity of the surface of the finer

materials is greater than that of the coarse particles. It was postulated that this greater reactivity of surface may be due to (1) the formation of a "Beilby" (amorphous) layer, and (2) an increase in surface energy with decrease in particle size.

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