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Rate of Reaction of Limestone With Soils

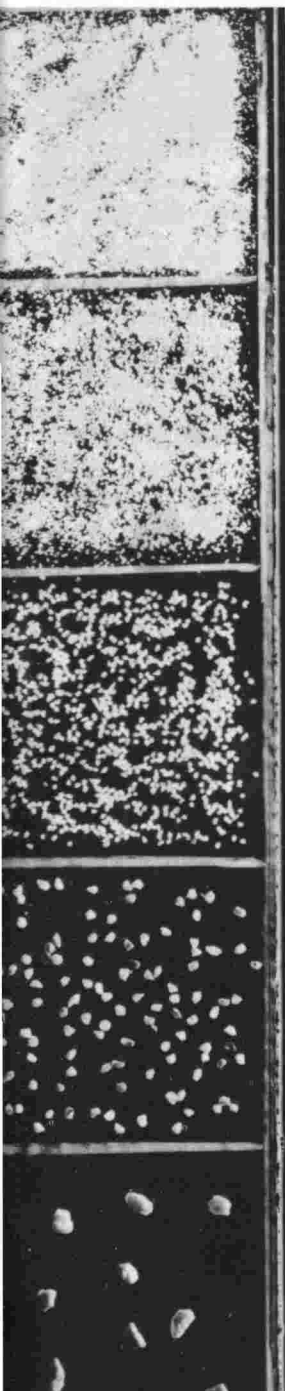
W. M. Shaw

THE UNIVERSITY OF TENNESSEE

AGRICULTURAL EXPERIMENT STATION

John A. Ewing, Director

Knoxville, Tennessee



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Cover illustration is the same illustration that appears on page 4, only natural scale size.

Rate of Reaction of Limestone With Soils

W. M. Shaw

Associate Chemist*

INTRODUCTION

The judicious use of lime is one of the most important practices in a program of profitable agriculture. Lime is especially important for alfalfa and other leguminous crops, and for intensive crop production with heavy use of fertilizers.

Lime may be purchased from dealers in different forms, such as burnt lime, hydrated lime, and ground limestone; and in the vicinity of certain industries by-products are available at low cost that can be utilized as liming materials. Ground limestone, however, constitutes 95 percent of the agricultural lime used in the United States (9).

Important Properties of Limestone

To bring about the expected benefits, lime must enter into reaction with the soil and neutralize soil acidity. Important properties of ground limestone affecting its reaction with soil are: (a) its chemical composition, especially purity, and (b) its physical properties, particularly fineness of grinding.

Chemical Composition

The purity of a liming material is defined by its *neutralizing value*, in terms of percentage of pure calcium carbonate equivalent. It expresses the maximum percentage of the lime that will *eventually* become available for soil reaction. The speed with which this will be accomplished, however, will be determined primarily by the degree of fineness of the material and to some extent by the conditions of contact with the soil.

The composition of high purity limestones may range from nearly 100 percent calcium carbonate to nearly 100 percent dolomite. Pure dolomite is a double carbonate of calcium and magnesium that contains 12.15 percent magnesium¹ and has a neutralizing value of 108.5 percent. In nature, many limestones are composed of mixtures of calcitic and dolomitic minerals. Dolomites do not so readily dissolve in carbonated water as do calcitic limestones (8, 12). In practice, the slower reactivity

*..Retired August 31, 1959.

1. To calculate the percentage of dolomite in the sample, multiply the determined magnesium percentage by 8.23; to calculate the percentage neutralizing value as dolomite, use the factor 8.92.

of dolomites is compensated by finer grinding. In areas of magnesium deficiency, the dolomitic limestone may be of extra value in increasing crop yields.

Neutralizing values of limestone much below 100 percent indicate a considerable proportion of impurities, which usually consist of clay and chert. These materials do not in themselves adversely affect the reactivity of the limestone fraction, but are objectionable on account of the increased cost to the farmer for transporting and spreading inert material. A high proportion of quartz-like material is hard on grinding machinery and may require more power than is required for high purity limestone (2, 15).

Many states have laws requiring that all liming material offered for sale must not fall below a minimum percentage in neutralizing value. In Tennessee, the minimum requirement is 85 percent calcium carbonate equivalent.

Fineness of Grinding

In practice, fineness is expressed by the percentage passing an 8- or 10-mesh and 100-mesh sieves; a 40- or 60-mesh sieve is often added or used instead of the 100-mesh sieve. For special purposes intermediate mesh screens may also be added to give more detailed information on particle size distribution.

A pound of 40-mesh limestone has four times the surface area and 64 times the number of particles as does a pound of 10-mesh limestone (Figure 1). Such an increase in fineness greatly speeds up the rate of solution and brings about a more complete reaction of the limestone with

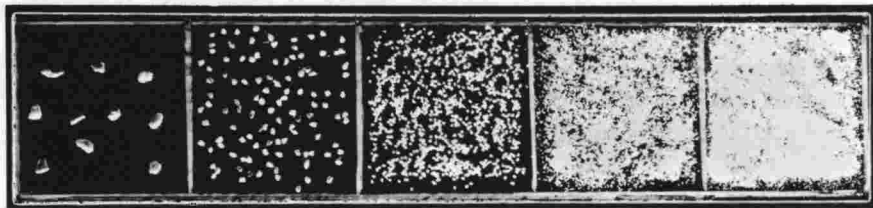


Figure 1. Particle Sizes and Surface Coverages of Different Limestone Sieve Separates When Applied at the Rate of One-Half Ton Per Acre Surface (7/12 Natural Scale).

Sieve Separates:					
Nos.	10-12	18-20	35-40	60-70	120-140
Mean Dia.					
Inches	.0724	.0362	.0181	.0091	.0045
Theoretical Efficiencies:					
Percent	18.0	33.0	58.0	87.5	100

the soil, because of the greater surface for reaction and the more widespread distribution in soil of the greater number of particles (Figure 2).

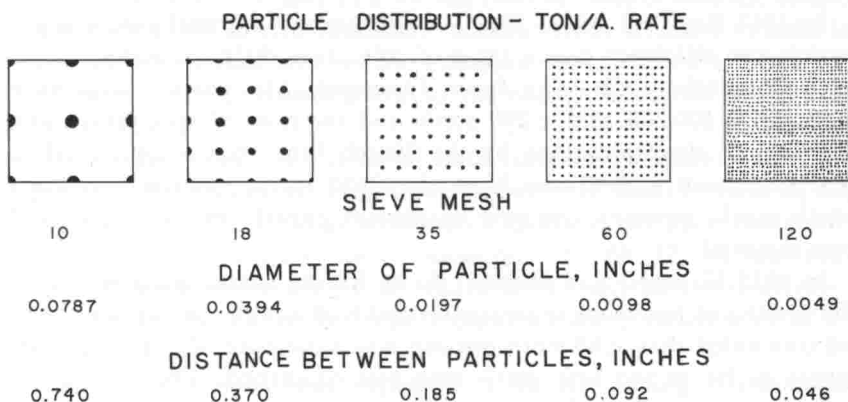


Figure 2. Distances between Different Sized Particles of Limestone when Uniformly Mixed with the Soil at the Rate of 1 Ton per Acre 6-2/3 inches deep.

The importance of particle size was recognized at the turn of the century soon after the widespread recommendation of ground limestone. Despite the numerous studies on particle size efficiency during the past 50 years, general agreement is lacking on minimum fineness requirement for ground limestone. Specifications differ in the various states; in Tennessee the law requires that 85 percent of ground limestone must pass a standard 10-mesh sieve and 50 percent must pass a standard 40-mesh sieve.

Climatic conditions, type of soil, and cropping system may play an important part in deciding on the minimum fineness requirement. It is, therefore, important to determine experimentally the rate of reaction of different-sized particles of limestone under Tennessee conditions. Such a study has been under way during the past 12 years, and the results are presented in this bulletin.

REVIEW OF PREVIOUS WORK

One of the earliest publications on limestone fineness was that by Thomas and Frear in 1912 (21). The first appreciable increase in the growth of clover on a strongly acid Hagerstown silt loam was from the 40-60 mesh limestone, with a further significant increase from the 60-80 mesh fineness.

In a more comprehensive study by White in 1917 (22) different degrees of fineness of limestone were evaluated by crop yield and carbonate dissolution at the end of 3 years. The results with calcitic limestone were:

Sieve separates, mesh	8-12	20-40	60-80	<100
Percent dissolution	14.9	46.7	81.5	92.4
Relative growth of plants	5	22	69	100

In 1917 Kopeloff (7) at New Jersey reported a greenhouse study of particle size efficiency on six types of soils from different states, including a Cumberland silt loam from Tennessee. The particle sizes were: 20-40, 60-80, 100-200, and <200 mesh, and the rates of application were according to determinations by the Veitch lime requirement method. Near maximum growth was from the 60-80 mesh material. On Portsmouth muck, however, the near maximum growth was from the 20-40 mesh material.

In 1919 Hartwell and Damon (6) at Rhode Island reported on the effectiveness of limestone separates on yields of alfalfa, carrots, and beets, and concluded that <80-mesh portion was a measure of the limestone's activity as far as the first year's crop was concerned. The 20-40 grade was only one-fourth as effective.

MacIntire and Shaw (11) in 1925 reported lysimeter experiments with size separates of calcitic and dolomitic limestones on a Cumberland silt loam. Lime incorporations were in the upper or lower half of the soil column. The residual carbonate was determined at the end of 4 years. Much greater limestone dissolution took place in the lower zone. This was particularly evident with the coarser grades of limestone and with most size grades of dolomite. The greater moisture content in the lower zone is considered the cause for these differences.

In 1930 Pierre (16) reported on the effectiveness of several size grades of limestone. The relative neutralizing efficiencies at the end of 3 months were:

Sieve size-mesh	>20	20-60	60-100
Cecil Sandy loam	17	76	99
Susquehanna clay	9	86	88

In 1930 MacIntire and Shaw (13) reported on the rate of reaction of calcitic and dolomitic limestone size separates with a Cumberland silt loam as affected by season of the year. The soil was contained in 2-gallon pots, placed outdoors in a trench. The dissolutions of the calcitic material during April-September months were 55 percent for the 20-40 mesh, and about 70 percent for the 60-100 mesh. The dissolutions during October-March months were: 35 percent for the 20-40 mesh and 50 percent for the 60-100 mesh. The dolomitic limestone was only about one-half to two-thirds as reactive as the calcitic material.

More recently, Beacher, Longenecker, and Merkle (1) evaluated calcitic and dolomitic limestone size separates of 20-40, 60-80, 100-200 and <200 mesh on a Westmoreland silt loam having a lime requirement

of 7,000 pounds calcium carbonate equivalent and a pH of 4.0. The yields of crimson clover seeded 3 weeks after liming, in grams per pot were: 0, 0, 10.9, 12.9, and 15.1 for the no-lime control and the respective finenesses of the calcitic limestone. Alfalfa yields, seeded 6 months later, were for the control and calcitic materials: 0, 1.2, 4.7, 5.9, 6.5. The pH values of the calcitic-treated soils at the ends of 6 months were: 4.0, 4.7, 5.9, 6.5, 6.5.

Meyer and Volk (14) evaluated different sized particles of calcitic and dolomitic limestones by their effects on soil pH and the yield of alfalfa and soybeans. The yield of alfalfa on a Canfield silt loam indicated the following efficiencies for calcitic limestone: 16, 60, 72, 99, and 100 for the size separates of 4-8, 20-30, 40-50, 60-80, and 100, respectively. By the decrease in acidity the same separates showed efficiencies of 7, 51, 76, 90, and 100.

Davis (3) carried out experiments on the liming effectiveness of different sized particles of limestone. The evaluation was done by the growth of crimson clover and Sudangrass, and the annual determination of pH values. It was concluded that agricultural limestone for Alabama should all pass through a 10-mesh sieve and 50 percent of it through a 60-mesh sieve.

MATERIALS AND METHODS

The experimental work of this study consisted of three parts: (I) the reaction of limestone with soils contained in outdoor lysimeters, exposed to natural weather conditions, (II) reaction of limestone with soil in the greenhouse, and (III) limestone-soil reactions carried out in the laboratory under controlled moisture and temperature conditions.

I. The lysimeters were 1/20,000 acre in area and accommodated 100 pounds of soil. They were constructed of 14-gauge galvanized ingot iron 20½ inches in diameter, 12 inches deep with concave bottom sloping 1½ inches towards a central opening. A 0.5 inch block tin tubing soldered to this opening carried the rainwater leachings into receptacles housed 4 to 5 feet below. All were painted with two coats of asphalt paint before installation. The drainage opening in the tank was covered with fine brass screening. The soil was underlain by a 6-mesh lower and 18-mesh upper layer of quartz sand filter about 2½ inches thick. An asphaltum-coated wire screen separated the soil from the quartz.

The lime addition was mixed in a large bowl with about one-half gallon of soil which was in turn mixed with the remainder of the soil for 10 minutes in a end-over-end mixing machine provided with baffles. The soil was deposited in four equal portions and each tamped down thoroughly in turn. At the end of each annual period the soil was

taken up, mixed and sampled for carbonate determination. The mixed soil was then returned to its original receptacle. At the time of mixing and sampling the soil was in a crumbly moist condition. The soils in the lysimeters were kept free of vegetation.

The lysimeter experiments were carried out in three phases: one year in 1947-48 with a Hartsells and a Claiborne soil; one year in 1949-50 with Hartsells soil; five years, 1951-55, with a Hartsells soil. Although Hartsells sandy loam was used in each phase, the three samples differed in chemical properties as shown in Table 1.

II. The greenhouse experiment was with a Hartsells soil that had an exchange acidity of 6,000 pounds calcium carbonate equivalent per acre. Calcitic and dolomitic limestone of different particle sizes were applied to 3.2 kilograms of soil in gallon tin cans lined with polyethylene bags and incubated at optimum moisture for 3 weeks before seeding to alfalfa. Samples for pH and carbonate determination were taken at the end of 6 months.

Table 1. Chemical Properties of Soils Used

Soil Type	Experimental Period	Cation Exchange Capacity ¹	Exchange ² Acidity	Reaction	Organic Matter Content
		me.	me.	pH	%
Lysimeter Experiments:					
Hartsells f. s. loam	1947-49	10.2	8.7	4.7	4.21
Claiborne s. loam	1947-49	10.9	5.5	5.5	3.35
Hartsells f. s. loam	1949-50	11.6	10.7	4.7	—
Hartsells f. s. loam	1951-55	13.0	11.6	4.5	4.83
Greenhouse Experiment:					
Hartsells f. s. loam	1959	7.2	6.0	4.8	—
Laboratory Experiments:					
Hartsells f. s. loam		10.2	8.7	4.7	4.21
Fullerton s. loam		5.6	3.5	5.6	2.40
Talladega cl. loam		9.7	8.3	4.9	3.90
Cumberland clay subsoil		8.0	7.4	4.8	0.17
Susquehanna subsoil		30.0	26.4	3.8	0.10
Portsmouth s. muck		52.0	60.0	3.8	28.0

1. Cation exchange capacity by ammonium acetate.

2. Exchange acidity by calcium acetate method (20).

III. The laboratory experiments were conducted to determine the effects of temperature and moisture conditions, which cannot be controlled conveniently in outdoor experiments. Also, it was desired to test the reaction characteristics of samples of different types of soil that were in limited supply. One hundred grams of air-dry soil was mixed with each lime treatment and placed in 150-ml. beakers. The Portsmouth and Susquehanna soil samples required 250-ml. beakers to keep the

rapidly expanding reaction mixtures from over-flowing. The moisture conditions were expressed as percentage water saturation of the soil as determined by the Hilgard cup method (10). The weight of each beaker with the initial moisture was recorded; on alternate days each beaker was brought up to original weight. The wetted soil mixtures were incubated at constant temperatures, generally at 88° F. At the end of the contact period the soil was spread on a clean sheet of paper for air drying and ground to pass a 35-mesh sieve. The residual carbonate determination was usually made on a 10-gram soil sample, using the steam distillation procedure of Shaw and MacIntire (19). Smaller samples were taken of soils of high carbonate content. The small and variable error due to carbon dioxide evolution from organic matter was corrected for by a blank determination on the unlimed soil.

The liming materials were a high grade calcitic marble and a high grade dolomite whose neutralizing values were 99.0 and 105.8 percent and magnesium contents 0.15 and 11.57 percent, respectively. The crushed materials were sifted through a series of U. S. standard sieves. The crushed materials were sifted through a series of U. S. standard sieves. The size groups were those collected between standard sieve Nos.: 10-12, 18-20, 35-40, 60-70, and 120-140; the average particle diameter of these separates are: 0.0724, .0362, .181, .0091, and .0045 inch. All sieve separates were washed free from adhering dust with tap and then distilled water.

RESULTS

For sake of brevity, the following simplified expressions will be used; calcite, for high calcitic limestone; dolomite, for high dolomitic limestone; lime, for either type of limestone when distinction is not essential. The rate of application in pounds will represent the pounds of calcium carbonate equivalent per acre, or 2,000,000 pounds of soil.

The limestone separates will be identified by the sieve mesh (actually No.) of the larger opening of each pair; thus, size separates will be referred to as 10, 18, 35, 60, and 120 mesh. The "percentage dissolution" refers to the percentage of the lime material that is found no longer in the form of carbonate. A part of the reacted limestone may have leached from the soil; a part may have been taken up by the growing plant; the largest part, however, is that used in the neutralization of soil acidity.

I. (a) Two-Year Lysimeter Experiment, 1947-49.

Hartsells fine sandy loam and Claiborne silt loam received a 5,000-pound per acre rate of lime application, which was equivalent to only 40 percent of the exchange acidity (20) of the Hartsells but nearly 100 percent of that of the Claiborne soil.

Table 2. Dissolution of Calcitic and Dolomitic Limestone Separates in Mixtures with Hartsells Fine Sandy Loam and Claiborne Silt Loam under Lysimeter Conditions (June 16, 1947-1949)

Liming Material	Fineness		Carbonate Dissolution and pH at Periods in Months									
	Sieve separate	Av. dia.	Hartsells Fine Sandy Loam					Claiborne Silt Loam				
			pH					pH				
			3	12	24	12	24	3	12	24	12	24
	mesh	mm.	%	%	%			%	%	%		
Calcitic limestone	18/20	0.917	26	80	86	6.0	6.2	25	62	86	6.4	6.4
	35/40	.458	40	92	100	6.3	6.2	43	86	100	6.7	6.4
Dolomitic limestone	60/70	.229	38	70	98	6.2	6.4	37	80	98	6.4	6.6
	120/140	.115	64	89	100	6.3	6.3	65	94	100	6.6	6.6

Table 3. One-Year Dissolution of Calcitic and Dolomitic Limestone Separates in Mixtures with Hartsells Fine Sandy Loam under Lysimeter Conditions

Fineness Sieve separates	CaCO ₃ equiv.	Calcitic Limestone		Dolomitic Limestone	
		Dissolution, percent of applied	Reaction	Dissolution, percent of applied	Reaction
			pH		pH
18/20	5,000	86	5.6	58	5.4
35/40	5,000	96	5.9	86	5.6
60/70	5,000	100	5.8	100	5.9
18/20	10,000	74	6.2	50	5.9

The limestone dissolutions for the 3-month period were very similar in both soils (Table 2). The values for the two calcite particle sizes (18 and 35-mesh) were about 26 and 42 percent; for the smaller dolomite particle sizes (60 and 120-mesh) about 38 and 64 percent. These three-month results agree with those obtained in New Zealand (4 & 5) but are higher (150 percent) than those obtained in Ohio (17).

At the end of 1 year the two particle sizes of calcite in the Hartsells soil had undergone 80 and 92 percent dissolution; in the Claiborne soil, 62 and 86 percent. The dolomite dissolutions in the Hartsells soil were 70 and 89 percent; in the Claiborne soil, 80 and 94 percent. At the end of 2 years all but the 18-mesh calcite separate had completely dissolved. The maximum pH value of the Hartsells soil was 6.3 and that of the Claiborne soil, 6.6 to 6.7.

I. (b) One-Year Lysimeter Experiment, 1949-50

The 5,000-pound rate of liming was 47 percent of the exchange acidity (20) of the Hartsells fine sandy loam used. The 18-, 35-, and 60-mesh calcite separates at the 5,000-pound rate was dissolved 86, 96, and 100 percent, while the 18-mesh separate at the 10,000-pound rate was dissolved 74 percent (Table 3). The corresponding dissolutions of dolomite separates were 58, 86, 100, and 50 percent. The highest pH attained by the 5,000-pound rate was 5.9; that by the 10,000-pound rate was 6.2.

I. (c) Five-Year Lysimeter Experiment, 1951-55.

Calcite and dolomite were applied at the rate of 12,000 pounds, which was about equal to the exchange acidity (11,600 pounds) of the Hartsells fine sandy loam used. The 1-year calcite dissolutions of the 10-, 18-, and 35-mesh separates were 43, 63, and 90 percent (Table 4.) The cor-

Table 4. Percent Dissolution of Calcitic and Dolomitic Limestone Separates in Mixtures with Hartsells Fine Sandy Loam under Lysimeter Conditions, September 16, 1951-1955.

Liming Material	Sieve Separate Nos.	Carbonate Dissolution, in Years:			
		% of Applied $\pm$ Av. Dev.			
		1	2	3	4
Calcitic limestone	10/12	43 $\pm$ 3	61 $\pm$ 6	58 $\pm$ 3	71 $\pm$ 2
	18/20	63 $\pm$ 1	87 $\pm$ 2	95 $\pm$ 2	96 $\pm$ 1
	35/40	90 $\pm$ 1	97 $\pm$ 0	99 $\pm$ 1	98 $\pm$ 1
Dolomitic limestone	10/12	35 $\pm$ 7	35 $\pm$ 1	38 $\pm$ 4	51 $\pm$ 7
	18/20	40 $\pm$ 2	67 $\pm$ 2	83 $\pm$ 3	93 $\pm$ 2
	35/40	60 $\pm$ 3	95 $\pm$ 1	98 $\pm$ 1	100 $\pm$ 1

* Applied at the rate of 12,000 lbs./A.; approximately equal to the exchangeable acidity of the soil. Each value is the average of triplicate lysimeter experiments.

responding dissolutions for the dolomite separates were 35, 40, and 60 percent. The time required for practically complete dissolution of the calcite separates was 2 years for the 35-mesh and 3 years for the 18-mesh separate; only about 71 percent of 10-mesh dissolved in 4 years. In 4 years the 10-mesh dolomite separate was 51 percent dissolved; 18-mesh, 93 percent; and 35-mesh, 100 percent.

Summary of Calcite-Soil Reaction Under Lysimeter Conditions

The data for calcite dissolution in lysimeter soils are summarized in Table 5.

The 5,000 and 10,000 pound applications of the 18-mesh calcite separate in the 1949-50 season resulted in absolute dissolutions of 4300 and 7,400 pounds per acre, whereas the percentage dissolutions were 86 and 74 percent. The 10-mesh calcite particles were present only in the 1951-55 experiment and were dissolved 43 percent in the first year. The 60-mesh particles in the 1949-50 season were completely dissolved in the 12-month period.

For a 1-year complete calcite dissolution under Ohio conditions, a particle passing a 120-mesh was required, whereas in the present experiment a 60-mesh particle sufficed.

II. Limestone-Soil Reaction in the Greenhouse

Alfalfa was seeded April 12, 1958. All treatments came to a good stand and were thinned to 10 alfalfa plants per can. Three cuttings were obtained: June 28, July 21, and September 12. Alfalfa yields and calcium and magnesium uptake will be reported elsewhere.

Residual carbonate contents and pH values for soil samples from each treatment are given in Table 6. Calcite dissolution varied from 18 to 93 percent of the amount added, depending on particle size. For dolomite the range was 12 to 62 percent. Calcite dissolution values were intermediate between those obtained for the 3- and 12-month periods in lysimeters (Table 5).

Soil samples were leached with distilled water before determining their pH value. These values closely reflect the differences in the reactivities of calcite and dolomite as reported in Table 6.

III. Laboratory Experiment on the Rate of Reaction of Limestone with Soils

(a) Effect of Temperature

The temperatures studied were 50°, 68°, and 86° F, using a Hartsells fine sandy loam and calcite particles of 35, 60, 120, and -325 mesh. The reaction periods were 30, 60, and 90 days. The soil exchange acidity was

Table 5. Summary of Calcite Dissolutions in Soils under Lysimeter Conditions.

Season	Soil Type	Liming Rate-To-Exchange Acidity Ratio	Sieve Separate,	Carbonate Dissolution in Periods of Months			
				3	12	24	48
		%	mesh	%	%	%	%
1947-49	Hartsells	57	18-20	26	80	86	—
	Hartsells	57	35-40	40	92	100	—
	Claiborne	93	18-20	25	62	86	—
	Claiborne	93	35-40	43	86	100	—
1949-50	Hartsells	47	18-20	—	86	—	—
		47	35-40	—	96	—	—
		47	60-70	—	100	—	—
		93	18-20	—	74	—	—
1951-55	Hartsells	103	10-12	—	43	61	71
		103	18-20	—	63	87	96
		103	35-40	—	90	97	98

11,600 pounds calcium carbonate equivalent per acre; liming was at the excessive rate of 20,000 pounds per acre.

The dissolution data for the three size separates at 50° and 86° F are plotted in Figure 3; the data for 68° fall between these two curves and were left out to avoid undue complexity in the graph.

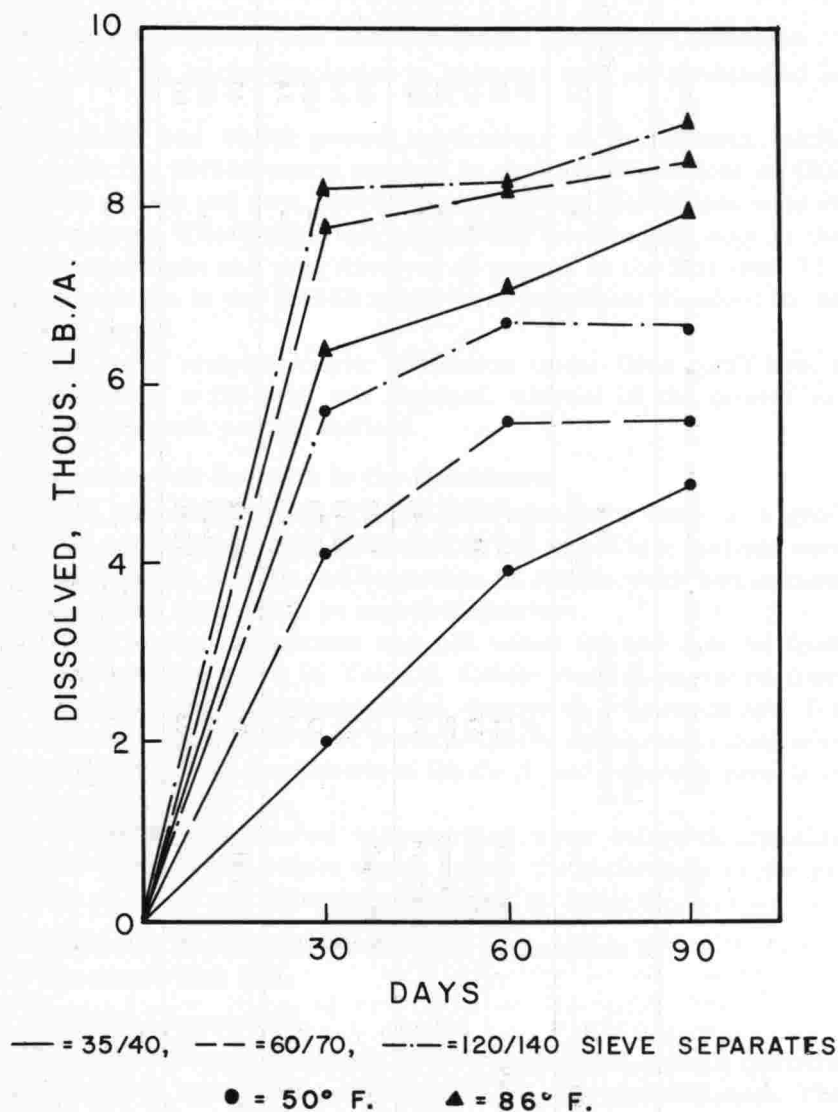


Figure 3. Effect of Temperature on Rate of Dissolution of Calcite with Hartsells Fine Sandy Loam.

Table 6. Dissolution of Different Sized Particles of Limestone and pH of Soils Six Months after a 3 Ton/A. Liming and Growth of Alfalfa

Limestone Sieve Separate	Limestone Dissolution As Of Application	Soil pH*
mesh	%	5.4
—	—	
	Calcitic	
10/12	18	6.0
18/20	30	6.0
35/40	52	6.1
60/70	63	6.3
120/140	93	6.7
	Dolomitic	
10/12	12	5.6
18/20	22	5.6
35/40	45	5.9
60/70	57	6.1
120/140	62	6.3

*Leached with distilled water.

The graph shows that temperature had a greater effect on the dissolution of particles coarser than 100 mesh than on finer particles, and the differences are most pronounced during the 30 days reaction period. The graph also shows that short periods at high temperatures are more effective in advancing the soil-lime reaction than are longer periods at low temperatures. The dissolution of the two coarser particles at 86° F is greater than that of the 120-mesh particles at 50° F for periods of 30, 60 and 90 days of continuous wet contact.

Outdoor pot experiments conducted at the Tennessee Experiment Station showed that the soil-limestone reaction during the winter months proceeded at a very slow rate (13).

(b) Effect of Soil Moisture Levels

- (1) Calcite was added to Fullerton silt loam samples and the mixtures incubated for 90 days at 86° F, using 2 moisture levels, i.e., 80 and 100 percent saturation. Exchangeable acidity was 3,500 pounds per acre, calcite application rate was 5,000 pounds, and particle sizes were 10, 18, 35, and 60-mesh. The results are presented in Figure 4. The 18 and 35-mesh particles showed a higher percent solution at 100 than at 80 percent saturation. Dif-

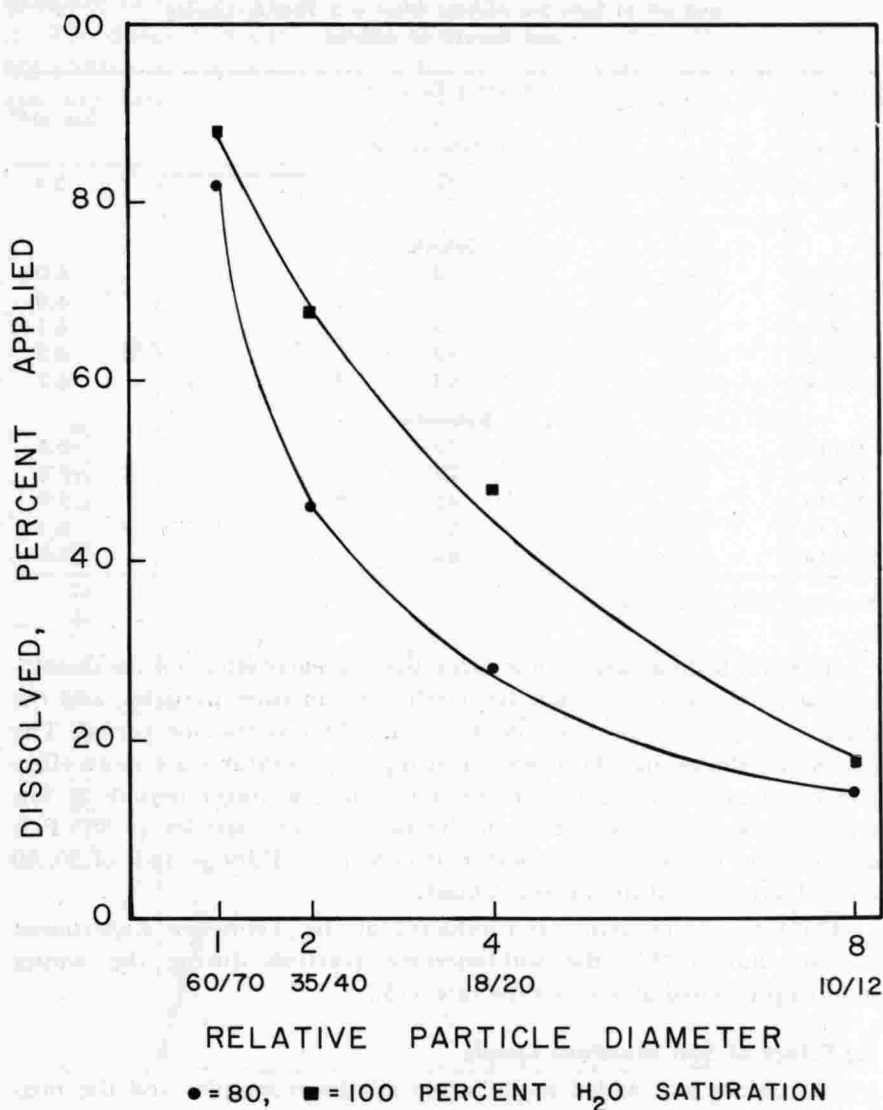


Figure 4. Effect of Soil Moisture Level on Rate of Dissolution of Calcite Particles in Fullerton Silt Loam.

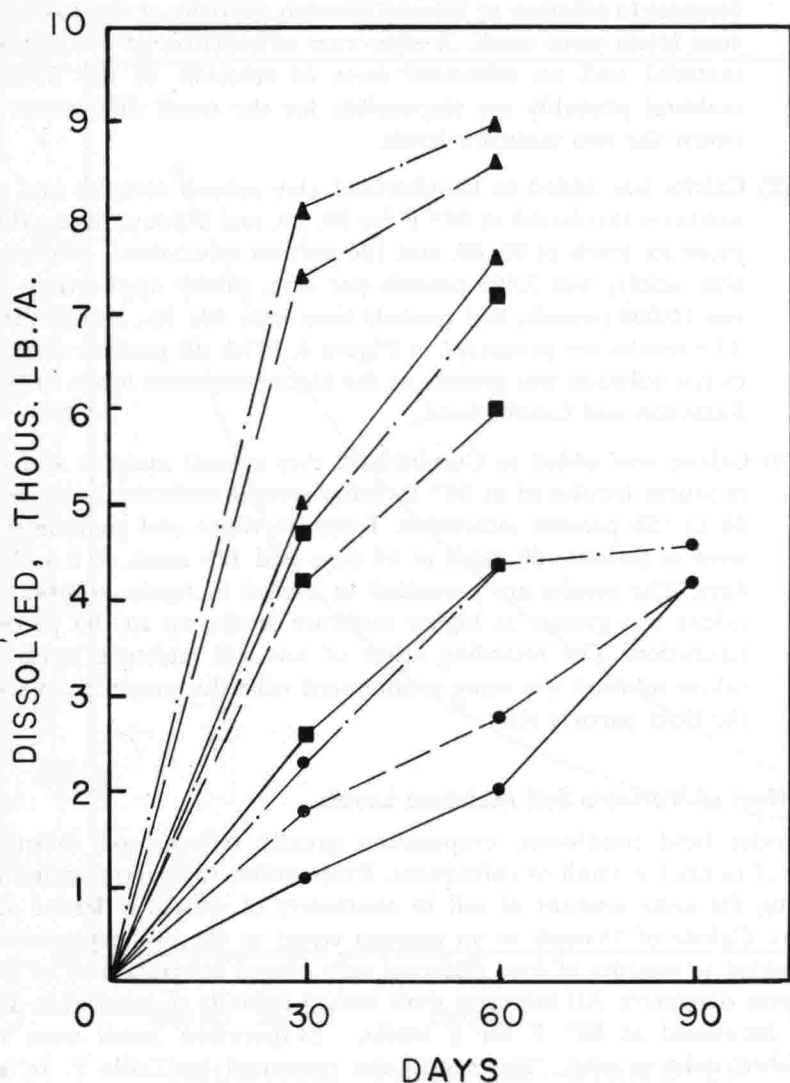
ferences in solution of 10- and 60-mesh particles at the two moisture levels were small. A slow rate of reaction of the 10-mesh material and an advanced state of reaction of the 60-mesh material probably are responsible for the small differences between the two moisture levels.

- (2) Calcite was added to Cumberland clay subsoil samples and the mixtures incubated at 86° F for 30, 60, and 90 days, using three moisture levels of 60, 80, and 100 percent saturation. Exchangeable acidity was 7,400 pounds per acre, calcite application rate was 10,000 pounds, and particle sizes were 18-, 35-, and 60-mesh. The results are presented in Figure 5. With all particle sizes the calcite solution was greater at the higher moisture levels in both Fullerton and Cumberland.
- (3) Calcite was added to Cumberland clay subsoil samples and the mixtures incubated at 86° F, using several moisture levels from 60 to 150 percent saturation. Reaction times and particle sizes were as follows: 60 mesh at 14 days and 120 mesh at 7 and 14 days. The results are presented in Figure 6. Again, solution of calcite was greater at higher moisture levels, up to 100 percent saturation: The retarding effect of low soil moisture levels on calcite solution was more pronounced with the coarser than with the finer particle sizes.

(c) Effect of Variable Soil Moisture Levels

Under field conditions, evaporation greatly reduces soil moisture levels if rainfall is small or infrequent. Evaporation rates were varied by putting the same amount of soil in containers of widely different diameters. Calcite of 35-mesh in an amount equal to the exchange acidity was added to samples of four different soils placed in containers of five different diameters. All mixtures were wetted initially to saturation and were incubated at 86° F for 2 weeks. Evaporation losses were replenished twice a week. The results are presented in Table 7. In all cases solution of calcite was decreased by increased evaporation. With the Cumberland clay, solution of calcite at the highest evaporation rate was only about one-third that the lowest evaporation rate.

All experiments on moisture effects indicate that calcite solution is highest when soils are approximately saturated with water. It should be noted that water saturation according to the Hilgard method is well above the optimum soil moisture level for most plants.



● = 18/20, ■ = 35/40, ▲ = 60/70 SIEVE SEPARATES

--- = 100, -- = 80, — = 60 PERCENT H_2O SATURATION

Figure 5. Effect of Soil Moisture Level on the Rate of Dissolution of Calcite Particles in Cumberland Clay Subsoil.

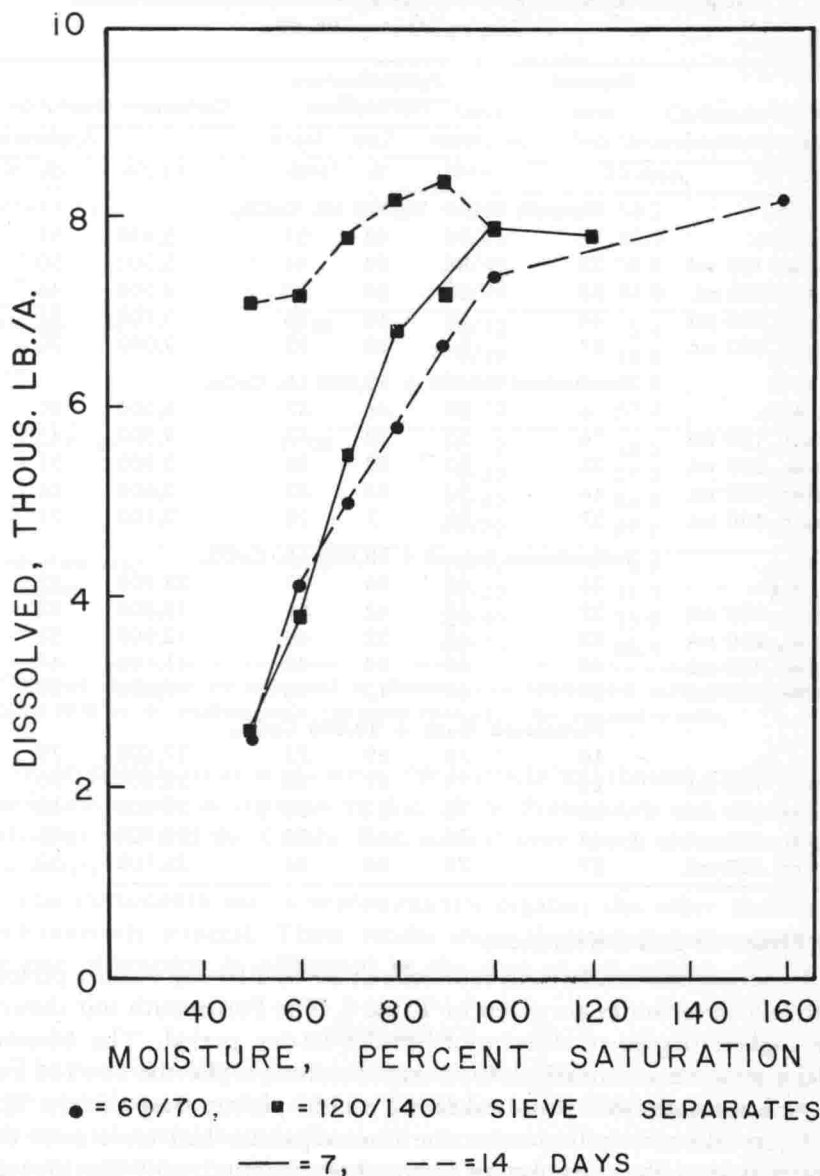


Figure 6. Effect of Soil Moisture Level on the Rate of Dissolution of very fine Particles of Calcite in a Cumberland Clay Subsoil.

Table 7. Dissolution in 14 Days of 35/40 Mesh Calcite in 4 Soils at Varying Moisture Levels

Container Description	Exposed area cm²	3-day Moisture Fluctuations			Carbonate dissolution	
		High	Low	Mean	Application	
		%	%	%	Lb./A.	%
Hartsells Soil + 10,000 Lb. CaCO₃						
Jar, 4 oz.	16	54	48	51	5,400	54
Beaker, 150 ml.	22	54	34	44	5,000	50
Beaker, 250 ml.	33	54	24	39	4,300	43
Beaker, 400 ml.	44	54	18	36	3,700	37
Beaker, 600 ml.	57	54	10	32	3,000	30
Cumberland Subsoil + 10,000 Lb. CaCO₃						
Jar, 4 oz.	16	50	44	47	6,000	60
Beaker, 150 ml.	16	50	32	41	4,500	45
Beaker, 250 ml.	33	50	22	36	3,300	33
Beaker, 400 ml.	44	50	14	32	2,600	26
Beaker, 600 ml.	57	50	7	28	2,100	21
Susquehanna Subsoil + 25,000 Lb. CaCO₃						
Jar, 4 oz.	16	60	54	57	22,900	92
Beaker, 150 ml.	22	60	42	51	15,800	63
Beaker, 250 ml.	33	60	32	46	12,900	52
Beaker, 400 ml.	44	60	24	42	11,100	44
Beaker, 600 ml.	57	60	12	36	9,800	39
Portsmouth Muck + 50,000 CaCO₃						
Jar, 4 oz.	16	75	69	72	37,600	75
Beaker, 150 ml.	22	75	61	68	35,000	70
Beaker, 250 ml.	33	75	52	65	30,000	60
Beaker, 400 ml.	44	75	43	59	27,900	56
Beaker, 600 ml.	57	75	34	54	26,100	52

(d) Effect of Soil Differences

Experimental results with four soils at 30- and 90-day contact periods with calcite separates are given in Table 8. The Portsmouth soil showed the highest degree of dissolution in the 90-day period. The 60-mesh calcite separate was nearly 100 percent dissolved, while the 10-, 18-, and 35-mesh separates were dissolved 48, 67, and 96 percent, respectively. The 30-day results also indicate that the finer separates had undergone the greater part of their dissolution in the shorter period; only the 10-mesh separate showed approximately equal dissolution rates in the two periods. Without the 30-day results on the Portsmouth soil one could have mistakenly concluded that the 60-mesh separate required 90 days for its complete dissolution.

Table 8. Dissolution of Calcite Sieve Separates in Mixtures with Different Soils at 68° F.

Soil type	Rate*	Liming	Carbonate Decomposition, -%	
		Sieve separates,	30 days	90 days
		Nos.		
Hartsells f.s.l.	7.26	10/12	13.2	28.4
"		18/20	22.9	51.8
"		35/40	55.9	86.2
"		60/70	84.8	97.2
Talladega clay l.	6.38	10/12	5.4	16.4
"		18/20	18.0	24.3
"		35/40	40.0	57.4
"		60/70	57.4	71.6
Portsmouth sa. 1.	37.00	10/12	23.5	48.0
"		18/20	51.3	67.0
"		35/40	84.0	96.1
"		60/70	97.7	98.8
Cumberland clay subsoil	4.06	10/12	3.9	11.3
		18/20	11.3	21.2
		35/40	35.9	53.1
		60/70	65.4	90.0

* The rates of liming are expressed in thousands of pounds per acre and represent about 80% of the exchangeable hydrogen content of the respective soils.

In proportion to its application, the Hartsells soil showed a carbonate dissolution nearly as vigorous as that of the Portsmouth soil. Both the Talladega soil and the Cumberland subsoil were much slower in their reactivities.

The Portsmouth soil is predominantly organic; the other three are predominantly mineral. These results show that among other factors the rate of reaction is influenced by the type of soil colloid.

SUMMARY

The present study was undertaken to determine the rate of reaction of ground limestone with certain Tennessee soils. Field lysimeters were employed as reaction containers for the outdoor experiments; supplementary greenhouse and laboratory experiments were conducted to study the effects of temperature and moisture variations on the limestone-soil reaction. The limestone-soil reactivity was gauged principally by the residual carbonate method and to some extent by the determination of pH values at certain intervals.

In lysimeter experiments (1947-1951) calcitic limestone particles passing a 60-mesh sieve dissolved in 1 year when the rate of application approximated the exchange acidity of the soil. The 1-year results are twice as high as those found in Ohio. A 35-mesh particle size of calcite required about 2 years for complete dissolution; an 18-mesh particle, 3 to 4 years.

For dolomitic limestone to be equal in effectiveness to calcitic limestone, it must be ground twice as fine. The relative efficiencies of the two types of limestone, however, will depend upon the stage of dissolution at which the comparison is being made. The shorter the period of reaction the smaller will be the relative dissolution of the slower reacting material. When the calcitic material had run its full course, the dolomite of equal fineness had reached 75 to 85 percent dissolution.

The carbonate dissolution in the 6-month greenhouse experiment with growing alfalfa showed a somewhat slower rate of reaction of calcite than was indicated in the lysimeter study. The slower reactivity may be attributed to a lower moisture content of the limestone-soil mixture in the greenhouse.

Reactions between calcite particles and a Hartsells soil were conducted at 50°, 68°, and 86° F. At 50° F the 35-mesh particles dissolved at the rate of 2,000 pounds per acre in 30 days, whereas at 86° F these particles dissolved at the rate of 6,400 pounds per acre. For finer particles the differences in dissolution rate at the two temperatures narrowed, but for particles of intermediate size the dissolution ratios were about 1 to 3 for the 50° and 86° F temperatures. The increased rate of diffusion of the calcium bicarbonate molecules is considered partly responsible for the greater reactivity at the higher temperature.

The results with different-sized particles of calcite have shown that limestone-soil reaction is speeded up by increasing the soil moisture level from 50 to 100 percent saturation. The 60-day dissolutions of 35-mesh calcite with Cumberland subsoil at moisture saturations of 60, 80, and 100 percent were 44, 60, and 72 percent of the application.

Very fine calcite particles (120-mesh) made good reaction progress at low moisture levels, as shown by the 14-day results. However, in 7 days, the fine particles also show increased solution with increased moisture.

According to present findings, calcitic limestone particles passing a 60-mesh sieve may be expected to completely react with the soil in the first year; those passing a 40-mesh sieve, in 2 years. The coarser particles may be expected to show 1-year efficiencies of 93, 81, 85, 33 and 18 percent for particles of 40, 30, 20, 10, and 8-mesh. The 1-year efficiencies of 60, 40, 30, 20, and 10-mesh dolomite are estimated as 87, 66, 51, 39, 17, and 10 percent.

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