RELATION OF SURFACE AREA OF LIMING MATERIALS TO REACTION RATE

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ABSTRACT

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by Gordon Stanley Miner

Four methods of estimating the surface area of calcic limestone, dolomitic limestone, basic oxygen processed slag and open hearth slag were studied. Determination of surface area of liming materials by isotopic exchange did not prove satisfactory. The oxalate titration method was satisfactory for calcic limestone and the nitrogen gas adsorption method was satisfactory for all materials studied. Estimation of surface area by calculation, assuming spherical particles, agreed closely with surface area determined by oxalate titration suggesting that the titration gives a measure of external surface area only. Nitrogen gas adsorption, on the other hand, appears to measure both internal and external surface area.

An acid Warsaw loam surface soil was used in incubation studies to determine the effect of surface area on rate of reaction of liming materials. Treatments for one study consisted of liming materials of different particle size added individually to samples of soil at a calcium carbonate equivalent rate of 5.75 tons per acre of pure calcium carbonate. This produced different surface areas of liming material for each treatment. The second incubation experiment consisted of treatments of liming materials added to the soil at constant surface area as determined by nitrogen gas adsorption. All treatments in incubation studies were replicated three times and incubations carried out at the moisture equivalent and at 20 degrees centigrade.

From an application of experimental data to a proposed theoretical function it appears that the rate of reaction of the dolomite studied is controlled by surface area; however, the reaction of limestone did not appear to be controlled by surface area except during the later stages of incubation.

Microscopic examination indicated that the dolomite studied was uniform and crystalline in nature; whereas, the calcic limestone studied was hetrogeneous containing a portion of slow reacting crystalline material and a faster reacting, porous appearing material.

In general the reaction rate of limestone materials appeared to be more closely related to the external surface area as measured by oxalate titration or estimated by calculation than to total surface area as measured by nitrogen gas adsorption.

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By

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INTRODUCTION

Particle size distribution as determined by sieve analysis has been used extensively for predicting the reaction rate of liming materials applied to acid soils. The finer the composition of the material the greater should be the rate of change of pH and the sooner equilibrium should be reached.

Particle size distribution may give an indication of the expected reaction rate of liming materials; however, it is at best an approximation and not sufficient for quantitative estimation of soil pH changes produced by liming. It reflects no property other than size composition. To accurately predict the reaction rate of liming materials, properties other than particle size and factors within the soil that affect the reaction rate must be taken into consideration.

Many chemical methods using rate of reaction as a standard of comparison have also been used to predict the amount of material needed to rectify undesirable soil conditions and determine the efficiency with which this is accomplished. Limestone activities have been measured by the rate of reaction with ammonium chloride, acetic acid, an oxalate buffer, and disodium ethylenediaminetetraacetate (24, 9). They have been measured by change in pH of an acid soil colloid, liberation of CO_2 from acid soils, and reactions as predicted by an "a" value conceived by Schollenberger (23).

No one method of evaluating the efficiency of liming materials has proven to be totally reliable. Schollenberger and Whittaker made a comparison of methods and found that where the mineral composition varied from pure calcite to pure dolomite the different methods failed to reproduce actual activities of the liming material (24). High correlations were obtained for some of the methods for a few materials that were all calcic or dolomitic but other materials were not so highly correlated.

The efficiency value is defined as the percentage of the limestone applied that should be expected to react with the soil in 3 to 12 months as conditions vary from optimum to average (25). It is difficult to determine in a few minutes with a chemical reaction how much of the total material applied to the soil will react in a definite period of time. The reaction rate may be limited by diffusion of the reaction products away from the lime particles in the soil. In a chemical test the agitated media provides for quick removal of the products from the particles at a more or less constant rate. Amount and movement of water, temperature, and placement of the materials also affect reaction rate. These variables tend to remain constant in chemical tests and thus the measured rate of reaction reflects chemical composition, surface area, degree of crystallinity, and other properties of the liming material.

Since a reliable method for predicting the effectiveness of a liming material has not been developed, additional work is needed to study individual rate determining factors. Reaction rates may be affected by surface area; consequently, the object of this study was to:

1. Determine surface area of some liming materials by different methods.
2. Determine how change in pH is related to surface area.

REVIEW OF LITERATURE

Effects and Practices of Liming

The liming of tillable soils was practiced by the Celts and the Europeans before the time of Christ (8). Despite early use of lime and benefits obtained in the form of increased yield, little was known about the specific effects of lime on soil until modern times.

In our modern era, liming materials have been defined as materials applied to the soil to improve soil conditions by substituting metallic cations for hydrogen ions on the cation exchange complex (8). Many materials such as marl, chalk, pulverized calcic or dolomitic limestone, burnt or hydrated lime, slag, etc., have been used as liming agents (8). They have been applied to counteract the direct and residual acidic effects on soils of fertilizers such as some commonly used nitrogen carriers (31). Most materials are mined but some are by-products of other industries (8).

Electric furnace slag is obtained from the smelting of aluminum ores and from rock phosphate reduction furnaces (8, 28). It has a solubility similar to limestone of the same fineness. The slag is primarily calcium silicate and contains from 0.9 to 2.3 per cent P_2O_5 (28). The neutralizing value is from 65 to 80 per cent.

Basic slag is a by-product of the basic open hearth method of making steel from pig iron (28). It contains 8 to 10 per cent P_2O_5 and has a neutralizing value of 65 to 80 per cent. Basic slag is generally used for its phosphorus content rather than its neutralizing effect.

Blast furnace slag is obtained during the manufacture of pig iron (28). Calcium oxide combines with the molten silica to give a slag that reacts similar to calcium silicate. The neutralizing value is 75 to 90 per cent and field tests indicate that the material is as effective as ground limestones when applied on the basis of equivalent amounts of calcium and magnesium.

A basic oxygenated slag produced as a by-product of a new method of manufacturing steel has shown very definite promises of being a good liming material. It has been demonstrated in a greenhouse experiment that barley responds to basic oxygen processed slag better than to limestone or open hearth slag.[1]

Determining the amount of liming material to apply to a soil has been the subject of considerable research. While liming and increasing the pH will make some cations more available, others such as manganese, iron, zinc, and boron are precipitated into unavailable forms (8, 11). Liming some soils low in potassium may cause potassium

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[1] Personal communication, B. G. Ellis and E. C. Doll.

deficiencies in plants (17, 28). Potassium cannot be adsorbed at a rapid enough rate in the presence of high concentrations of calcium. Phosphorus is made more available by liming to pH 6.5 while aluminum tends to precipitate out with increasing pH (15, 17). In acid soils containing toxic amounts of aluminum this is very beneficial.

Moderate applications of limestone stimulates the process of nitrification (8). This results in the production of nitric acid which causes other plant nutrients to become more available and reduces the need for fertilizers.

Meyer and Volk found that increasing the rate of limestone application, gave a trend toward higher exchangable calcium for soils (16). The trend was higher with calcic limestone than it was with dolomitic limestone. At three tons per acre a 4-8 mesh material gave 4.1 milliequivalents of exchangable calcium as compared to 3.4 for a check while a > 100 mesh material gave 8.6 milliequivalents. The 4-8 mesh material at ten tons per acre gave only 6.1 milliequivalents of exchangable calcium. This would indicate that exchangable calcium is greatly affected by the size composition of the limestone as compared to rate of application.

Work by Bishop demonstrated that crop response to liming depends on the nature of the clay minerals in the soil (4). Two to one type clay colloids need a higher degree of calcium saturation than one to one type colloids to get comparable adsorption of calcium by plants. Below

70 per cent saturation montmorillonite clays have a high energy of adsorption for calcium ions while kaolinite releases calcium with equal ease regardless of the degree of saturation. Soils with a high clay content are conditioned by lime so that they are more tillable (11).

The root systems of some plants respond greatly to zones of liming in the soil. Using Crimson Clover, Longnecker and Merkle demonstrated that fibrous roots developed very extensively in the limed zones of the soil while they were few in number and very small in the unlimed zones (15). Primary roots appeared able to extend through the unlimed zones. The lack of a fibrous root system in unlimed zones would indicate that there is little horizontal movement of the products of lime dissolution. It has been shown that neutralization of soil acidity occurs only near the reacting particle.

Lime moves most rapidly during the first year after its application (22). This movement is in a downward direction and is the result of the leaching effect of infiltrating water. The dissolution products of lime are retained by the subsoil to a great extent. Ririe, et al., found that calcium from $Ca(OH)_2$, CaO, and $Ca(OH)_2$ + MgO moves more rapidly than calcium from carbonates (22). This is probably due to the higher solubility of these materials. Where MgO alone was added to the soil the loss of calcium almost equaled the loss where $CaCO_3$ was used. This would mean that magnesium replaced exchangable calcium. In coarse sands $CaCO_3$ leached away faster than $CaCO_3 \cdot MgCO_3$ and magnesium was lost at a faster rate than calcium where $CaCO_3 \cdot MgCO_3$ was used. The solubility rate of dolomite is about 50 per cent that of limestone (8). The decrease in diameter of like particles of calcite to dolomite is about 3 to 1. For comparable effectiveness dolomitic limestone should be 60-80 mesh compared to 40-50 mesh for calcic limestone (16).

The degree of fineness of a limestone also determines the rate of solution in a particular soil. The finer the material the greater the rate of solution and consequently the greater the rise in pH (16). Meyer and Volk found that material of 4-8 mesh size had little value correcting soil acidity regardless of rate of application or time after application. It took 18 months at a 10 ton rate for 20-30 mesh limestone material to reach equilibrium. Twenty mesh material gave an initial rise in pH but after 2 weeks the pH decreased. This was thought to be caused by the presence of dust on the coarser particles that gave the initial rise in pH. Fifty to sixty mesh material took 12 months to reach equilibrium and finer than 60 mesh material took 6 months. At the same rate of application and particle size, calcic limestone gave higher pH values than dolomitic limestone during the first 6 to 9 months after application (16). After 9 months, however, dolomitic limestone produced higher pH's than calcic materials. The yield of alfalfa was increased with 3 ton calcic limestone applications where the degree of fineness was increased up to 60 mesh. Finer grades than 60 mesh did not give further increase in yield at this rate.

Meyer and Volk used increase in exchangable calcium as a measure of the amount of material reacted with the soil at any given time (16). They determined that 18 months after applying limestone at a 3 ton per acre rate, 13.4 per cent of the 4-8 mesh material, 72.5 per cent of the 40-50 mesh material, and 94.5 per cent of the finer than 100 mesh material had reacted.

It is generally agreed that a large portion of the limestone should pass a 40 mesh sieve to be effective (16). Particles finer than 40 mesh are approximately equal in their ability to change pH. Unless maximum effects are desired within one year there is little advantage in having limestone ground finer than 100 mesh due to the increased cost of grinding. Since these particles are effective only in their immediate vicinity, liming materials must be mixed well with the soil or their efficiency in correcting soil acidity may be very low.

Methods of Area Determination

There are three general methods of determining surface area of solids (3). These are calculation from particle size, determination of adsorption isotherms, and the relation of some special property which depends in some known manner on available area.

Area by Calculation

Area can be calculated arithmetically if the general shape and density of the particles is known. Determining shape is the greatest source of error due to geometrical irregularities of the particles (29). Motto and White examined calcic limestone particles microscopically and suggested that spheres would give a close approximation to the shape (18). The diameter was obtained as the average of the openings of the larger and smaller screens for each size class. Areas determined by particle size would be the lowest possible because internal area in porous materials would not be considered (3). Small particles also tend to aggregate into larger particles so that they appear as a single particle.

Area by Radioactive Isotopic Exchange

As cited by Brunauer (6) and Wang (29) the radioactive tracer method of determining surface area was first applied by Paneth and Vorwerk. They determined the surface area of lead sulfate using a lead isotope, Thorium B, as the tracer. This method is based on the assumption that a constant kinetic exchange occurs between ions in solution and ions on the surface of the solid. After exchange at the surface, the tracer is transported within the solid by recrystallization and self-diffusion. If the rates of self-diffusion and recrystallization are small in comparison to surface exchange, a pseudo-equilibrium state is reached.

The following formula gives the relationship between the tracer and the other ions (29):

$$\frac{N_s'}{N_s} = \frac{N_1'}{N_1} \qquad (1)$$

where

N_s' = number of tracer atoms on the surface,

N_s = total number of this species of atoms on the surface,

N_1' = number of tracer atoms in the bulk of solution, and

N_1 = total number of this species of atoms in the bulk of solution.

The total number of atoms on the surface can be calculated by measuring the other three unknowns and the area can be determined if the cross-sectional area of one of the atoms is known.

Paneth and Vorwerk suggested three minutes as the length of time needed for the Thorium B-lead sulfate exchange reaction to reach equilibrium. The tracer was absorbed on the solid surface at a rapid rate up to this time and then absorption occurred at a slower rate. Kolthoff and Rosenblum concluded that the absorption of Thorium B at the lower rate was from penetration of the ion into the lattice due to recrystallization of the lead sulfate (14).

Kolthoff and Eggertsen studied the kinetics of the reaction for a period of several hours and extrapolated the time-adsorption curve back to zero time (13). This value was used as the quantity of ions absorbed on the surface of the solid.

There are many difficulties with the surface exchange method. Adsorption of the tracer without exchange sometimes occurs which would necessitate using a correction factor (13). One lattice ion may exchange at a faster rate than others. The time for equilibrium to be reached may be different in each case and consequently a point of uncertainty (29). In new precipitates the rate of diffusion and recrystallization is rapid and not constant (6, 29).

Area by Oxalate Titration

Barnes proposed a method of determining surface area by liming materials by reacting them with saturated oxalic acid (1). The calcium oxalate formed on the surface of the particles is dissolved with sulfuric acid and the oxalate titrated with 0.1 N potassium permanganate. Barnes' data showed the volume of permanganate used to be directly proportional to the particle size. Motto and White disputed this on the grounds that the volume of oxalate used should be related to surface area which is a function of diameter squared (18). Particle size is a function of the first power of the diameter.

Thomas and Gross proposed using 0.1 N oxalic acid instead of a saturated solution because magnesia limestone continued to react on the steam bath with the saturated oxalic acid as long as free acid or lime particles were present (27). They found that the concentration of Mg ions in solution increased while the oxalate gradually dissolved from the surface of the particle exposing more calcium ions to react with the excess oxalate ions.

Motto and White were unable to express area as square meters per gram because the area they determined using the number of Ca ions from a unit cell of calcite was much higher than the area reported for a ball milled calcite (18). They suggested that the reaction affected the subsurface layers as well as the calcium ions on the surface because the solubility of the carbonate (8.7×10^{-9} at 25°C) is about three times greater than that of the oxalate (2.57×10^{-9} at 25°C). In determining surface area all the calcium that reacted would be designated as surface calcium.

Motto and White plotted change in pH for one week against surface area of the particles determined by assuming particles to be spheres (18). The plot was a curve with an increasing slope from which the surface of the finer particles appear to be more reactive than the surface of the coarser particles. They made an analogy comparing small drops of liquid having higher vapor pressures than big drops to fine material having higher vapor pressure, greater solubility, and a lower melting point than coarse crystals. Greater reactivity was suggested to be the result of an increase in the surface energy of a crystal with a decrease in particle size.

Motto and White also proposed that the presence of a "Beilby" layer on particles gives a surface of greater reactivity and solubility (18). This is an amorphous layer produced by grinding. They cited where Beilby had found this layer up to 50 Å thick on calcite crystals, with effects to a depth of 5,000 to 10,000 Å produced by grinding action. Finer particles would have this layer to a greater degree than coarser particles because of the increased grinding required to reduce the particle size.

Area by Gas Adsorption

The physical adsorptive properties of solids have led to other methods of determining surface area. Brunauer, Emmett, and Teller derived the relationship between the volume of polymolecular layers of gas adsorbed on the surface of a solid and the relative pressure of the gas (7). This relationship produces a curve called an adsorption isotherm that is concave to the abscissa at lower relative pressures and convex to the **abscissa** at higher relative pressures with a linear portion between (3, 6, 7). The beginning of the linear portion corresponds to the first layer of gas adsorbed. Brunauer found there was a sharp decrease in the net heat of adsorption at this point when using nitrogen as the adsorbate (6). It was assumed the higher values were due to the interaction between the gas molecules of a monolayer and the solid surface while the lower values were due to the interaction between gas molecules as more layers were adsorbed. He also obtained better agreement in calculating surface area from this point than from other points on the adsorption isotherm.

The relationship derived by Brunauer, Emmett, and Teller is known as the BET equation and is expressed by (20):

$$\frac{P}{V_{ads}\,(P_o - P)} = \frac{C-1}{V_m C}\,\frac{P}{P_o} + \frac{1}{V_m C} \qquad (2)$$

where

V_{ads} = total volume of adsorbed gas on surface of adsorbent,

V_m = volume of adsorbed gas covering entire adsorbent surface with a complete monomolecular layer,

P_o = saturation pressure of the adsorption gas at the temperature of the coolant,

P = partial pressure of the adsorption gas,

C = constant expressing net adsorption energy, and

P/P_o = relative pressure of the adsorbate.

A plot of $\frac{P}{V_{ads}\,(P_o - P)}$ versus $\frac{P}{P_o}$ gives a curve that is linear in the range of relative pressure values from 0.05 - 0.30 (3, 7, 10, 19, 20).

Adsorption occurs upon cooling the sample to low temperatures (6, 7, 19, 20, 30). Where nitrogen gas is used as the adsorbate, liquid nitrogen is usually used as the coolant (6). Brunauer suggested that perhaps adsorption is closely related to condensation if condensation can occur at pressure far below the vapor pressure of the liquid in capillaries of molecular dimensions (7). He stated that the convex portion of isotherms at higher pressures may be due to condensation.

Nelsen and Eggertsen developed the continuous flow method to determine the variables of the BET equation (19). This method is faster and does not require the skill or fragile high vacuum apparatus needed to measure pressure-volume relationships by the volumetric method. The adsorbate mixed with an inert gas carrier moves by the sample in a continuous flow. Cooling the sample causes adsorption of nitrogen and the change in flow rate of nitrogen is indicated by an output signal from thermal conductivity cells monitoring the gas stream. This output signal is proportional to the change in flow rate of the adsorbate gas and is recorded as a curve by a potentiometric recorder. Warming the sample causes desorption which is recorded in the same manner. A known volume of adsorbate is introduced into the gas stream and the output signal is recorded. The area from the known volume of adsorbate is compared with the area produced by desortpion to determine the volume of adsorbate adsorbed. The desorption peak area is used in calculations because most of the effects of tailing are eliminated (19, 20). This procedure is repeated at different flow rates of adsorbate to determine the adsorption isotherm.

Molecules are held to the surface of solids either by chemical binding known as chemisorption or by physical forces known as Van der waals forces (3, 6, 10, 19, 20, 30). The theory of the BET equation is based on physical adsorption; therefore, the adsorbate and sample must not react in any way other than with Van der waals forces (7). Berl lists the characteristics an adsorbate must have as follows (3):

1. Must not react with the sample. This changes the surface and other products may be formed either on the surface or by complete reaction.
2. Must not dissolve with the solid. The gas moves into the solid and may or may not form interstitial compounds. This gas would not desorb.
3. Chemical nature of the gas must not be changed by the solid acting as a catalyst.
4. Gas should be pure.

Chemisorbed air and molecules held by Van der waals forces must be removed from the surface of the solid before areas are determined (3, 6, 19, 20, 30). Wise and Lee removed impurities by outgassing in a helium stream at 250°C to 300°C for one hour (30). Nelsen and Eggertsen outgassed at 500°C with helium at a 20 ml per min flow rate for one hour (19).

The boiling points of pure compounds are best for cooling temperatures to be used (3). These temperatures remain quite constant so that the equilibrium pressure of the adsorbed gas will also remain constant.

Most workers agree that the area covered by one nitrogen molecule is about 16.2 $Å^2$ (3, 6, 19). This area is determined by assuming the packing to be the same as for liquid nitrogen (3). The area varies with the temperature as does the saturation pressure; therefore, the temperature of the liquid nitrogen must be measured (19).

The thermal conductivity of a nitrogen-helium mixture is not linear for different concentrations of the gases (20). The volume of nitrogen used for calibration should be about the same as the amount adsorbed on the sample (19, 20). Errors in determining volume adsorbed result otherwise but they should be small (20).

Small surface areas require the use of a calibration gas made up of 10 to 20 per cent nitrogen in helium (20). The effective volume of nitrogen introduced gives an area comparable to the desorption area. Samples with large areas require smaller samples to be used (20). Care must be taken so that variability of sample does not enter the calculation.

The continuous flow method has been found to give results comparable to the volumetric method (19, 20, 30). Wise and Lee compared the two methods and found the following areas (30):

Material	Adsorp. Method	Vol. Method
activated charcoal	1372.0 m^2/g	1360.0 m^2/g
activated alumina	218.0	195.0
red chromosorb	4.6	4.8

EXPERIMENTAL PROCEDURES

Liming Materials

Bellevue calcic limestone, dolomite obtained from the L. Hill Co., open hearth slag, and basic oxygen processed slag obtained from Levy & Co., were dry sieved to produce five particle size fractions, 20-40, 40-60, 60-80, 80-100 and > 100 mesh material. All materials were placed in Erlenmeyer flasks and repeatedly washed with distilled water to remove fine material adhering to the surface. The supernatant liquid was decanted until it was clear. The materials were then dried in an oven at 105°C. The calcium carbonate equivalent of each size range was determined for each material and is given in Table 1.

Table 1. Calcium carbonate equivalent of liming materials studied.[1]

Materials	Particle Size				
	20-40	40-60	60-80	80-100	> 100
Calcic Limestone	91.1	77.7	65.7	67.4	80.6
Dolomitic Limestone	105.9	107.1	106.6	106.6	99.5
Open Hearth Slag	59.9	56.4	57.2	57.9	60.4
Basic Oxygen Processed Slag	73.0	79.5	81.1	80.7	80.1

[1] Determined by titration method as described by Jackson (12).

Incubation at Constant Calcium Carbonate Equivalent

Soil from the surface layer of a Warsaw loam was air-dried and screened through a one-fourth inch screen. Each treatment in the incubation consisted of one particle size of a particular liming material added in sufficient quantity to be equal to 5.75 tons of pure $CaCO_3$ per acre. The material was thoroughly mixed with 900 grams of soil and the moisture content was brought to the moisture equivalent with distilled water. Each size fraction and a check with no lime added were replicated three times. The rates added to the soil are as shown in Table 2. The soils were incubated in a constant temperature room at 20°C. Soil samples were obtained at 1, 2, 4, 6, and 8 weeks.

Table 2. Quantity of material added to 900 gm of soil to produce constant calcium carbonate equivalent of liming materials.

Particle Size	Materials (gms)			
	Calcic Limestone	Dolomitic Limestone	Basic Oxygen Processed Slag	Basic Slag
20-40	6.00	5.16	7.39	9.20
40-60	7.03	5.10	6.87	9.68
60-80	8.32	5.13	6.73	9.55
80-100	8.11	5.13	6.77	9.43
$>$ 100	6.78	5.49	6.82	9.05

Constant Surface Area Incubation

This incubation study was conducted similar to the previous study. Eight hundred fifty grams of soil and five size fractions of calcic limestone were used. The amount of $>$ 100 mesh material required was determined on a $CaCO_3$ basis as in the previous incubation study. Other size fractions were added in sufficient quantities to give surface areas equal to the surface area of the $>$ 100 mesh material. Rates added to the soil are shown in Table 3.

Table 3. Quantity of calcic limestone added to 850 gm of soil to produce constant surface area of liming material.

Particle Size	Grams Added
20 - 40	15.87
40 - 60	14.25
60 - 80	16.48
80 - 100	16.75
$>$ 100	6.40

METHODS OF ANALYSIS

Soils

Soil pH was measured immediately after sampling of moist soils with a Beckman (Model G) potentiometer using a 4:5 soil to water ratio.

Lime requirement of the soil as determined by the buffer method of Shoemaker, _et al_. (26) was 6 tons per acre.

Moisture equivalent of the soil as determined by the method of Briggs and McLane (5) was 25 per cent.

Liming Materials

Calcium carbonate equivalence of the liming materials was determined by the official A.O.A.C. method as described by Jackson (12).

Limestone density as determined by water displacement in a pycnometer was 2.75.

Surface areas were determined by four methods:

1. Arithmetically calculated.
2. Oxalate method as described by Barnes (1).
3. Dynamic physical adsorption method as described by Nelsen and Eggertsen (19). The volume of gas adsorbed as a monomolecular layer can be determined from the slope and intercept of the BET equation as follows:

$$m = \frac{C-1}{V_m C} \qquad (1)$$

$$b = \frac{1}{V_m C} \qquad (2)$$

From (2) substitute the value of C into equation (1) to obtain:

$$m = \frac{1}{V_m} - b \qquad (3)$$

and solve for V_m,

$$V_m = \frac{1}{m + b} \qquad (4)$$

where

m = slope,

b = intercept,

V_m = volume occupied by monomolecular layer, and

C = constant expressing net adsorption energy.

The specific surface is obtained by multiplying V_m by the area covered by one unit of this volume and dividing by the sample weight.

Areas were determined using a Perkin-Elmer Shell Model 212B sorptometer. Four point adsorption isotherms were determined on materials outgassed at 160°C for 10-12 hours with helium. The areas of calcic limestone are the average of 3 different samples while 2 different samples were averaged for all other materials. Liquid nitrogen temperatures were measured with an oxygen thermometer.

4. Radioactive isotopic exchange method. Samples of material from 1 to 8 gm were placed in 100 ml of

water until saturation equilibrium was reached. One ml of a Ca^{45} solution giving approximately 4,000 counts per minute in 100 ml of water was added to the sample. Ten ml aliquots were taken at 2, 5, 10, 15, 20, and 25 minutes. These were centrifuged immediately and a 2 ml portion placed on counting plates. Water was evaporated and counts taken to determine the loss of Ca^{45} from solution. Amount absorbed versus time was plotted and the curve extrapolated back to 0 time to determine amount absorbed on the surface of the material.

Radioactive measurements were made on a Nuclear Measurements Corp. Model DS-1 scalar with a Geiger-Mueller tube having a mica window of 1.4 mg per cm^2 density.

Ca^{45} was obtained from the Oak Ridge National Laboratory as $CaCl_2$ in HCl. The concentration was 4.30 ± 10 per cent mc per ml. The specific activity of the solid $CaCl_2$ was 14,144 mc per gm.

RESULTS AND DISCUSSION

Determination of Surface Area of Liming Materials

Four methods were studied to determine their applicability in determining the surface area of liming materials. Each of the methods will be discussed individually in the following paragraphs.

Calculation and Oxalate Titration

Table 4 shows the comparison of calculated area to area determined by oxalate titration. The area determined increases with decreasing particle size for both methods but the calculated area increases at a faster rate than the area determined by titration. The 20-40 or 40-60 mesh titrated area is greater than the corresponding calculated area for spheres while the reverse is true for the 60-80 and 80-100 mesh material. The calculated area and the area determined by titration are about the same magnitude which would indicate that only external surface area is measured by the titration method.

Figure 1 supports Motto and White's proposal that the volume of permanganate used is not directly proportional to the diameter of the particle for the calcic limestone studied (18).

Table 4. Surface area of calcic limestone as determined by oxalate titration and calculation.

Particle Size	Area (cm^2/gm)	
	Oxalate Titration[1]	Calculated (spheres)[2]
20 - 40	51.3	34.9
40 - 60	71.0	65.6
60 - 80	91.2	102.6
80 - 100	106.4	135.9
$>$ 100	422.4	--

[1] Area determined by method of Barnes (8 cm^2/ml of .1 N $KMnO_4$).

[2] Diameter based on the average of two sieve sizes for each range.

Isotopic Tracer Exchange

Data from the isotopic tracer exchange method of determining surface area was inconsistent and did not permit determination of surface areas. Figure 2 is an illustration of data obtained for Ca^{45} lost from solution as a function of time of exchange. The curves for the 20-40 and 40-60 mesh range show a decrease in loss of Ca^{45} from solution after an initial increase. The same characteristic can be detected slightly for the 60-80 mesh material. This is in contrast to what should be expected. An initially fast removal of Ca^{45} with a distinct slower rate of removal should occur which would correspond to surface exchange and incorporation of Ca^{45} within the internal structure respectively.

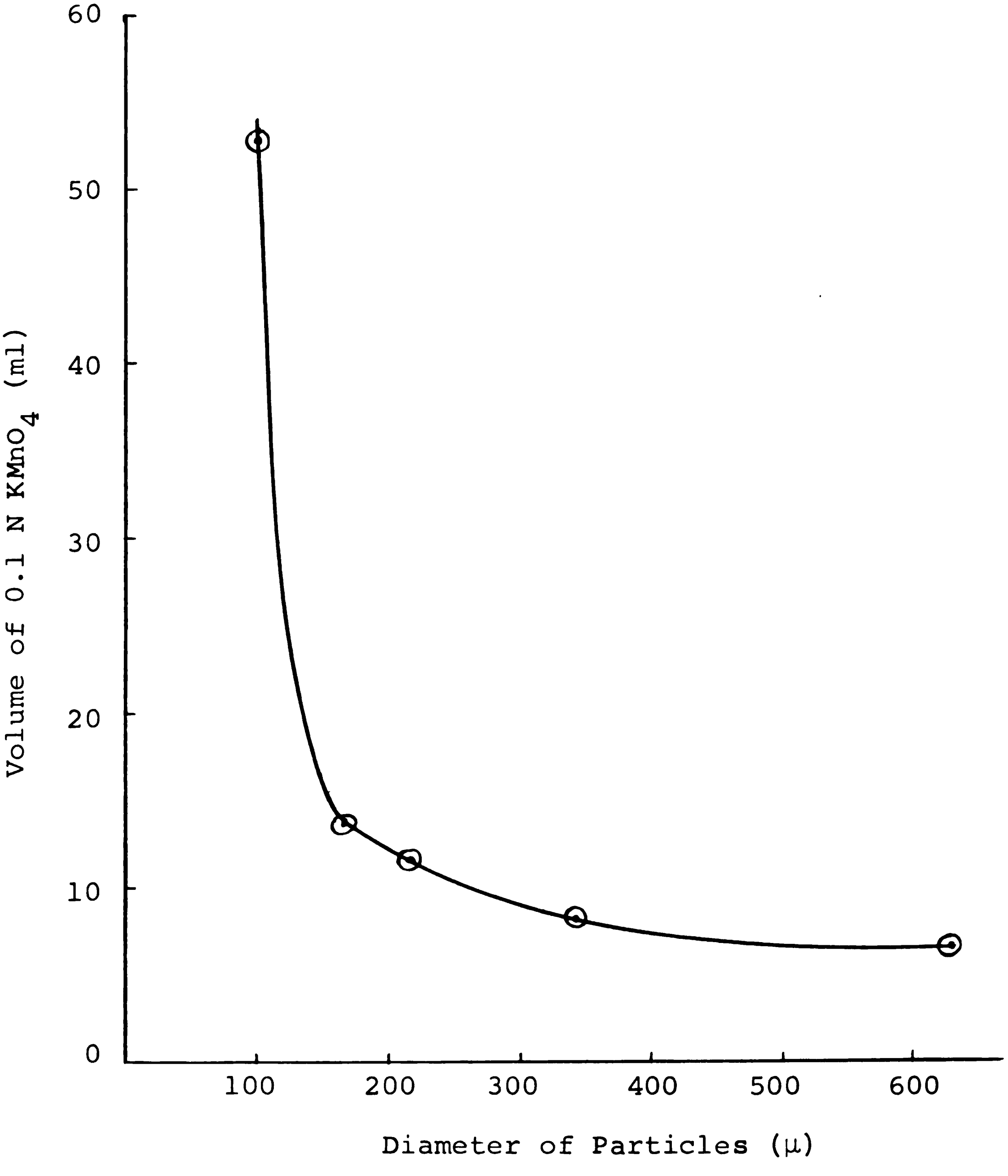

Figure 1. Relationship between particle diameter and quantity of 0.1 N $KMnO_4$ used for titration of oxalate on calcic limestone.

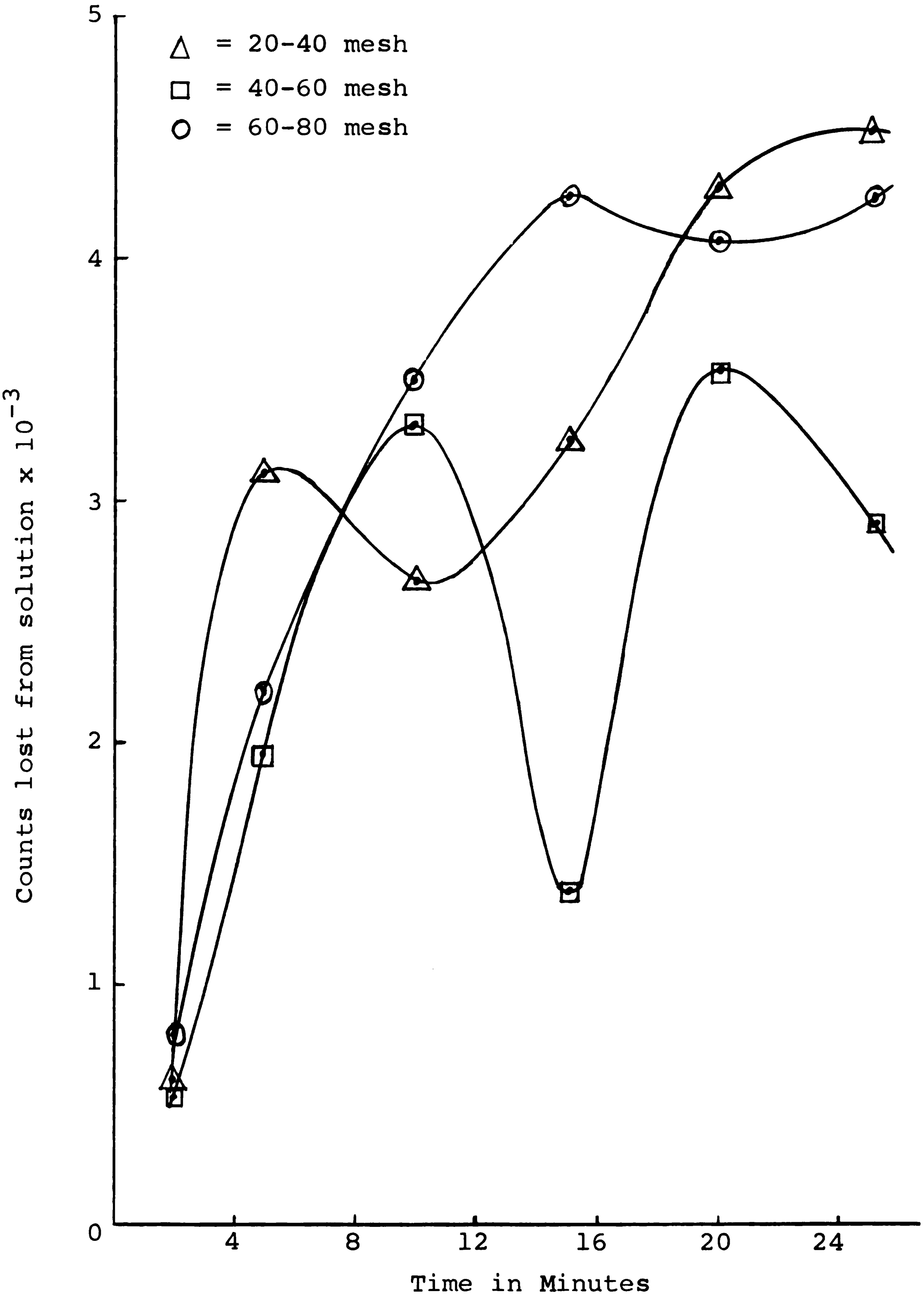

Figure 2. Loss of Ca^{45} from solution as a function of time.

Different limestone samples varying from 1 to 8 grams in weight were run without a significant change in amount of Ca^{45} exchanged. This would suggest that the loss of Ca^{45} was by a mechanism other than surface exchange.

It is difficult to explain why this method gave variable results. The equilibrium of the system may have been disrupted by addition of the tracer and co-precipitation may have taken place. Ions of Ca^{45} would have been removed from solution as part of the precipitated material. The subsequent increase in Ca^{45} ions found in solution may be the result of exchange of newly precipitated Ca^{45} ions with calcium ions in solution. This would cause an increase in the Ca^{45} count at a later time. The reason for a fast initial uptake of Ca^{45} ions not occurring was perhaps caused by impurities on the surface of the limestone particles. These impurities may have masked the exchange and caused exchange at a slower rate. As cited by Wang (29), Paneth obtained initial uptake in about one minute for lead chromate and lead sulfate. These materials were pure salts, however. The time of initial uptake on the limestone samples was in the range of 5 to 15 minutes.

Gas Adsorption

Materials were obtained from Professor Fripiat of the University of Louvain, Belgium, that have had surface areas determined by several laboratories. Table 5 compares the accepted areas[1] with areas determined by gas adsorption on samples of two different weights.

Table 5. Calibration of sorptometer with standard clay materials of known surface area.

Materials	Sample Weight (gms)	Accepted Area (M^2/gm)[1]	Area by Sorptometer (M^2/gm)
Kaolinite	.0396		45.5
(yangambi)	.5530	42.0	50.2
Kaolinite	.2212		20.7
(zettlitz)	.3032	20.2	20.4
Gel	.0314		282.9
	.1455	--	344.0
Gibbsite	--	<1	<1

[1] Surface areas by Professor Fripiat, Louvain, Belgium.

Gibbsite had such a low surface area that adsorption was hardly detectable. The area found agreed at least qualitatively with the accepted area. The areas for Zettlitz kaolinite compared very well with the accepted area. The area of Yangambi kaolinite deviated from the accepted area but the deviation was not large. The differences may have been due to experimental error or to variability between samples. All of these samples gave good adsorption isotherms.

The areas of the liming materials determined by gas adsorption are given in Table 6. Preliminary work was done to determine the best procedure on the sorptometer to obtain

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[1] Personal communication from Professor Fripiat, Louvain, Belgium.

reproducibility. Warming the sample with room air gave slow desorption. The slow desorption did not appear to be reproducible and areas under the curves were inconsistent. The sample holder was immersed in water at room temperature immediately after cooling to produce more rapid desorption. Although this improved the appearance of the desorption curves, areas determined on the same samples were not very consistent.

Table 6. Surface area of liming materials as determined by gas adsorption.[1]

	Particle Size				
Materials	20-40	40-60	60-80	80-100	> 100
Calcic Limestone	3.24	3.43	3.13	3.08	8.06
Dolomitic Limestone	.25	.22	.22	.23	.77
Open Hearth Slag	3.10	4.41	4.83	4.65	4.08
Basic Oxygen Processed Slag	.41	.47	.69	.68	.62

[1] Expressed in square meters per gram of material.

The final method tested and the one found to give most reproducible results was to immerse the sample holder in water heated to 60°C to produce a rapid desorption. Repeated determinations on the same sample using this method gave very reproducible results.

All liming materials studied except dolomite gave smooth, rapid desorption curves. Curves produced by desorption of nitrogen from dolomite were quite different from those of other liming materials. For dolomite the desorption curve would drop below the base line indicating that adsorption was occurring. The curve would remain below the base line for approximately two minutes and then return to the base line. No logical explanation could be conceived for this behavior. Areas were determined for dolomite using the point where the desorption curve crossed the base line and neglecting the portion that fell below the base line. Consequently, the areas reported for dolomite are subject to large experimental errors.

Calcic limestone was found to have a surface area of 10 to 15 times the corresponding size fraction of dolomitic limestone. Except for the $>$ 100 mesh size there was little difference in surface area for different particle sizes of the same material. The finer than 100 mesh fraction has from 2.5 to 3 times larger area than fractions larger than 100 mesh.

Comparing the external area of the four coarser fractions of calcic limestone by the titration and calculation method with the total area suggests that the ratio of external area to internal area increases with decreasing particle size while the total area remains constant. This would be expected if the material in these size fractions had the same composition and porosity. The higher area of the $>$ 100 mesh material suggests that the smaller particles of this class may be primary particles with little internal surface area. Larger particles may be aggregates of these primary particles.

The surface area of all dolomite particles studied was less than one square meter per gram. Relative differences between size fractions probably mean very little because of the large error in determination of surface areas less than one square meter per gram. The areas are approaching that calculated assuming solid spheres which suggest that the dolomite studied contained very little internal pore space and may be more crystalline than the calcic limestone studied.

The two slags appeared to have a large difference in surface area. Open hearth slag was similar to calcic limestone while the basic oxygen processed slag compares with dolomite. Washing the basic oxygen processed slag with distilled water dissolved a considerable portion of the slag. This may have altered its surface area as well as its composition. Except for the 20-40 mesh fraction the areas are approximately the same for all size fractions. Most of the open hearth slag less than the 100 mesh size is just slightly less than 100 mesh consequently the area is about the same as for coarser fractions.

Incubation Studies

Constant Calcium Carbonate Equivalent

The surface areas of the liming materials added to produce a constant calcium carbonate equivalent as estimated by three methods for calcic limestone and two methods for other liming materials are given in Table 7. The change in pH resulting from liming with each of the materials for 1, 2, 4, 6, and 8 week periods is given in Table 8. Even though the same calcium carbonate equivalent was added for each treatment, it is obvious that another factor is controlling the rate of reaction.

Table 7. Surface areas of liming materials applied to the soil as determined by three methods.

Materials	Particle Size	Weight Added (gms)	Methods of Determining Area		
			Cal. (cm^2)	Adsorp. (M^2)	Titration (cm^2)
Calcic Limestone	20-40	6.00	210	19.4	308
	40-60	7.03	461	24.1	499
	60-80	8.32	691	26.0	758
	80-100	8.11	1094	25.0	863
	> 100	6.78	--	54.7	2864
Dolomitic Limestone	20-40	5.16	180	1.3	
	40-60	5.10	335	1.1	
	60-80	5.13	526	1.1	
	80-100	5.13	691	1.2	
	> 100	5.49	--	4.2	
Basic Oxygen Processed Slag	20-40	7.39	257	3.0	
	40-60	6.87	451	3.2	
	60-80	6.73	691	4.7	
	80-100	6.77	913	4.6	
	> 100	6.82	--	4.2	
Open Hearth Slag	20-40	9.20	321	28.5	
	40-60	9.68	635	42.7	
	60-80	9.55	980	46.1	
	80-100	9.43	1272	43.9	
	> 100	9.05	--	36.9	

If surface area controls the rate of reaction of liming materials, the rate of disappearance of liming material as a function of surface area may be expressed

Table 8. Soil pH as a function of time after addition of liming materials at constant neutralization equivalence.

Materials	Particle Size	Time of Incubation				
		1 week	2 week	4 week	6 week	8 week
Calcic Limestone	20-40	5.85	5.87	6.03	6.08	6.16
	40-60	6.10	6.25	6.45	6.55	6.66
	60-80	6.39	6.64	6.90	6.99	7.08
	80-100	6.61	6.83	7.15	7.21	7.30
	> 100	7.21	7.32	7.49	7.45	7.50
Dolomitic Limestone	20-40	5.63	5.66	5.75	5.70	5.79
	40-60	5.73	5.74	5.90	5.95	5.99
	60-80	5.79	5.86	6.05	6.10	6.20
	80-100	5.85	5.93	6.19	6.25	6.42
	> 100	6.68	6.79	6.95	6.98	7.04
Basic Oxygen Processed Slag	20-40	5.83	5.94	6.08	6.14	6.20
	40-60	6.15	6.33	6.57	6.61	6.65
	60-80	6.51	6.59	6.85	6.89	6.94
	80-100	6.57	6.86	7.04	6.99	7.03
	> 100	7.04	7.11	7.15	7.08	7.09
Open Hearth Slag	20-40	5.81	5.86	5.95	5.91	5.94
	40-60	6.02	6.07	6.22	6.24	6.26
	60-80	6.27	6.27	6.45	6.45	6.50
	80-100	6.32	6.40	6.58	6.69	6.62
	> 100	6.92	6.83	6.92	6.89	6.88
No Lime		5.55	5.59	5.58	5.52	5.46

by the following differential equation:

$$\frac{dP}{dt} = - kS \tag{1}$$

where

P = quantity of liming materials present,

t = time,

k = proportionality constant, and

S = surface area.

The quantity of lime material will be proportional to volume:

$$P = AV \tag{2}$$

where

A = proportionality constant, and

V = volume.

The volume of a sphere as a function of diameter is as follows:

$$V = \frac{\pi d^3}{6} \tag{3}$$

where

d = diameter of particles.

The surface area of a sphere is given by the following equation:

$$S = \pi d^2 \tag{4}$$

Combining equations (2), (3), and (4) yields:

$$S = \frac{6^{2/3}\ \pi^{1/3}}{A^{2/3}}\ P^{2/3} = BP^{2/3} \tag{5}$$

where

$$B = \frac{6^{2/3}\ \pi^{1/3}}{A^{2/3}}$$

Combining equation (5) and (1) gives the quantity of liming material as a function of time:

$$\frac{dP}{P^{2/3}} = - Bk\ dt \qquad (6)$$

Integrating this equation

$$P^{1/3} = - 1/3\ Bkt + C \qquad (7)$$

At $t = t^{o}$, $P = P^{o}$; therefore $C = P^{o}$. The final equation is:

$$P^{1/3} = - K't + P^{o} \qquad (8)$$

where

$$K' = \frac{1}{3} Bk$$

If it is assumed that the change in the hydrogen ion concentration in the soil system is proportional to the rate of disappearance of liming material P, then a plot of cube root of hydrogen ion concentration against time should produce a straight line. Figures 3, 4, 5, and 6 give the plot of the cube root of hydrogen ion concentration versus time for calcic limestone, dolomite, basic oxygen processed slag, and open hearth slag respectively. The curve for the 20-40 mesh calcic limestone approaches linearity; however, the other size fractions give a linear curve only in the last 4 weeks of incubation. With dolomite the curves appear to be linear for all size fractions.

Materials of both calcic limestone and dolomite were examined under a petrographic microscope to attempt to explain the differences between materials. Pictures taken through the microscope of 40-60 mesh calcic limestone and 40-60 mesh dolomite are shown in Figures 7 and 8 respectively. The calcic limestone consisted of a heterogeneous mixture

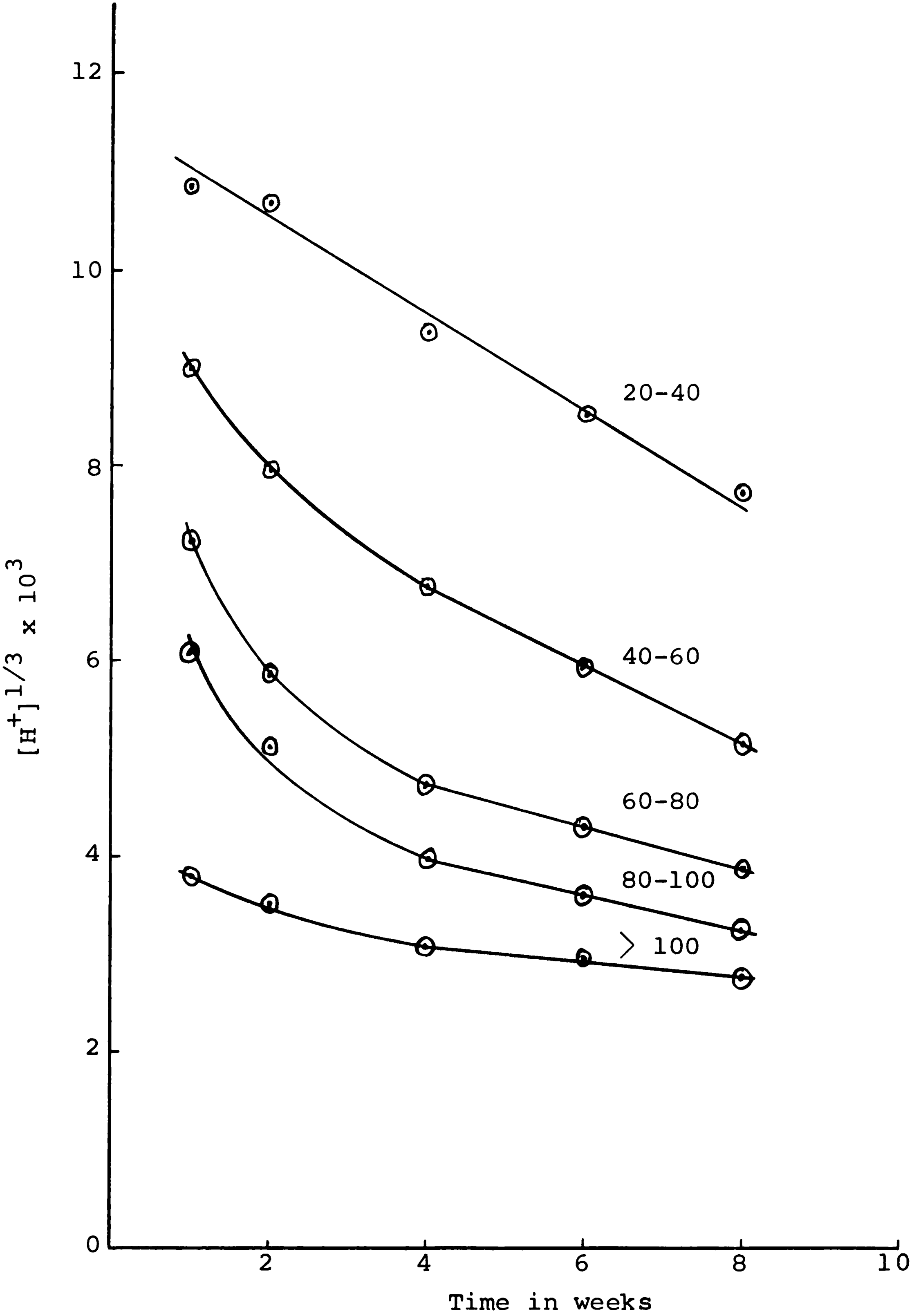

Figure 3. Relationship between cube root of hydrogen ion concentration in a Warsaw loam surface soil and time after addition of calcic limestone.

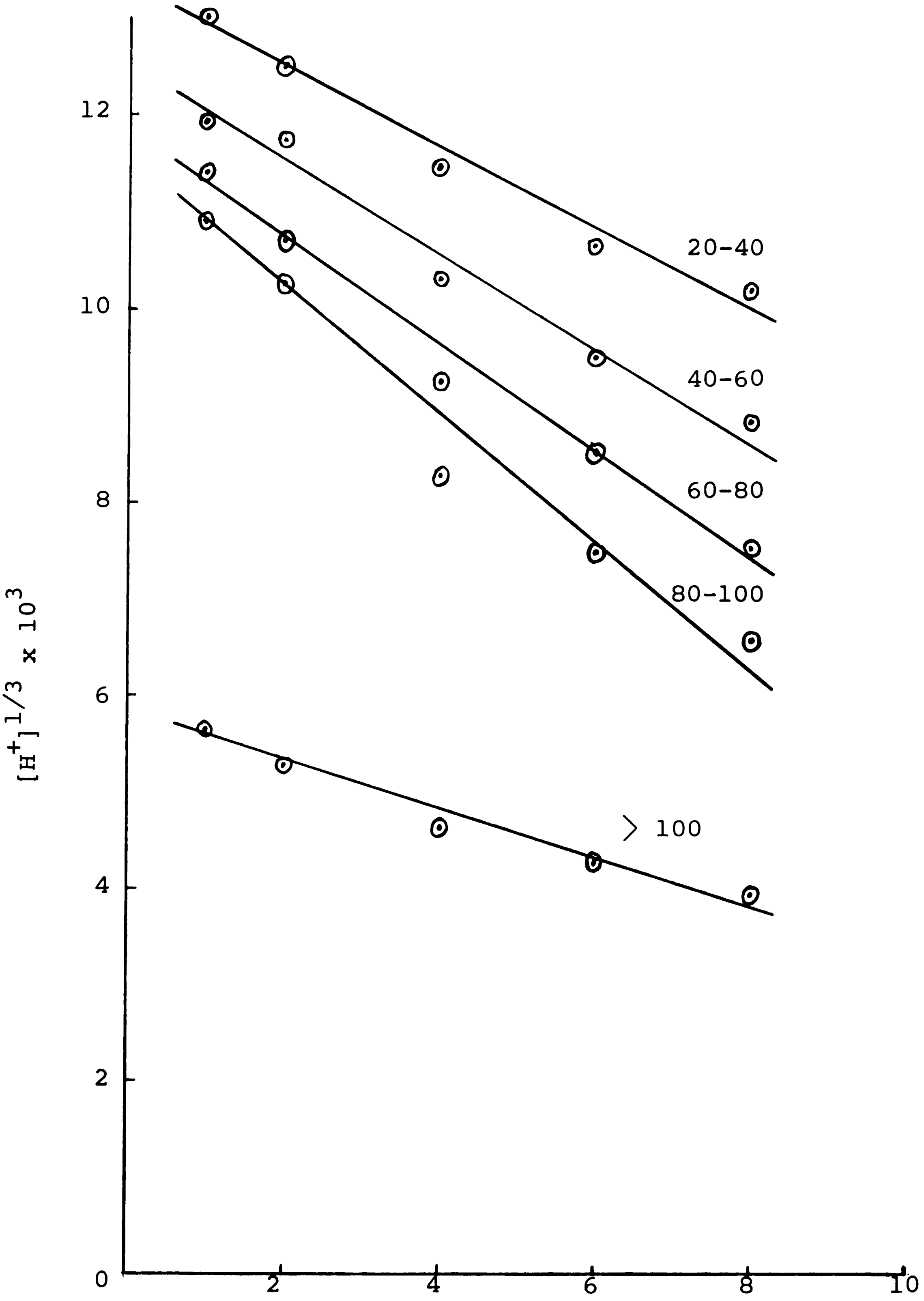

Figure 4. Relationship between cube root of hydrogen ion concentration in a Warsaw loam surface soil and time after addition of dolomitic limestone.

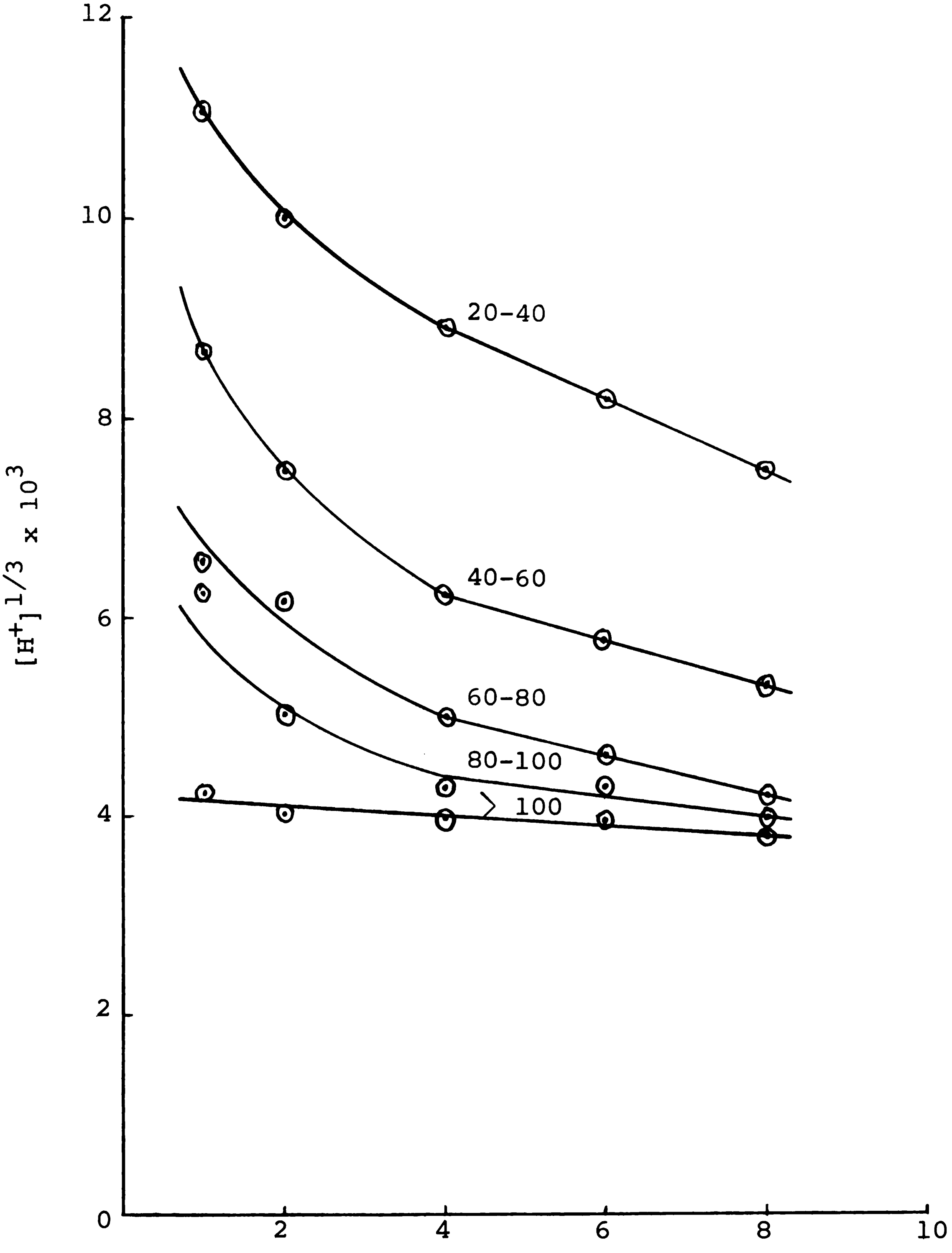

Figure 5. Relationship between cube root of hydrogen ion concentration in a Warsaw loam surface soil and time after addition of basic oxygen processed slag.

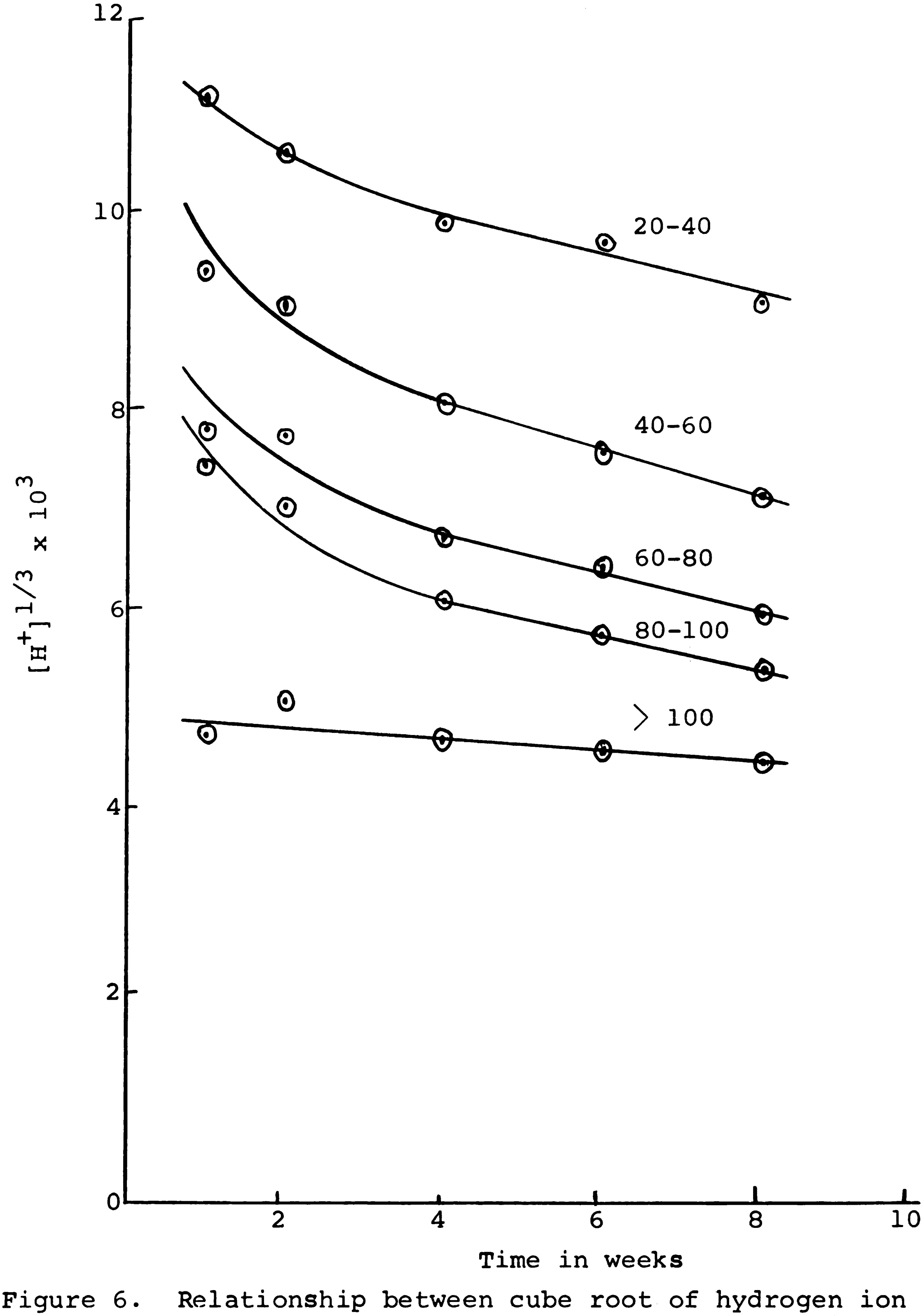

Figure 6. Relationship between cube root of hydrogen ion concentration in a Warsaw loam surface soil and time after addition of open hearth slag.

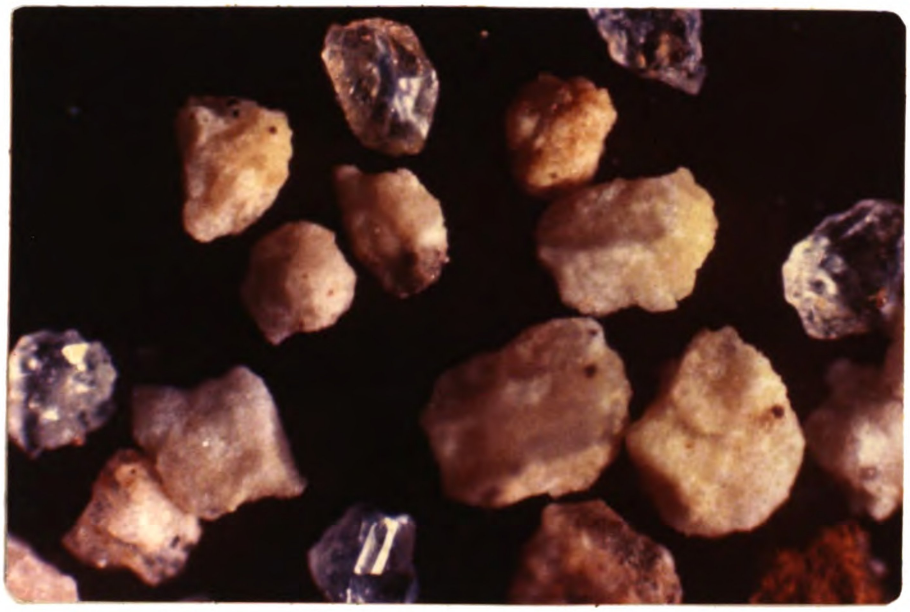

Figure 7. Calcic limestone, 40-60 mesh particles (100 X).

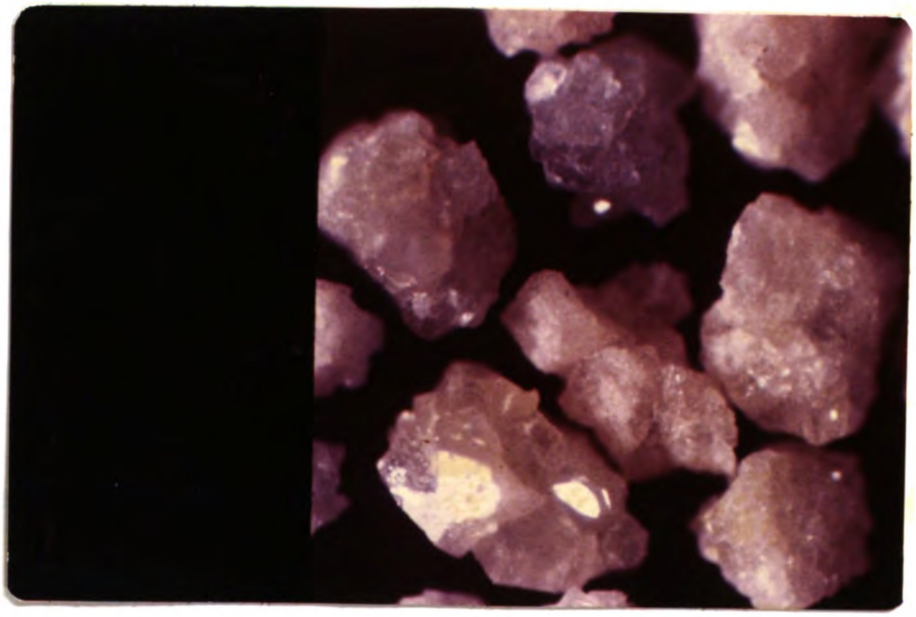

Figure 8. Dolomitic limestone, 40-60 mesh particles (100 X).

of clear crystalline particles and darker, porous appearing particles. Ten particles were obtained of each type and the time necessary for complete reaction with 5 N HCl determined. The crystalline material took approximately 50 seconds per particle to completely react while the porous appearing material took approximately 35 seconds. The different reacting rates of the material may mean that the observed plots were the result of these two types of material. The faster reacting particles may give a linear relationship with a large negative slope during early incubation while the slower reacting particles may give a linear relationship with less negative slope during the latter part of incubation. The change in soil pH produced would be a function of the two types of particles. Although experimental data are not sufficient during the first four weeks of incubation to determine the exact nature of the curve, the experimental points may be the resultant of two linear curves. The curve for 20-40 mesh material of calcic limestone was more linear than other fractions. From microscopic observation it appeared that this fraction contained very few crystalline particles as compared to other fractions, thus giving a more homogeneous material.

Dolomite was found to be very uniform in composition as shown in Figure 8 and appeared to be rather crystalline.

Although the analysis just presented would indicate that the rate of reaction of liming material is a function of surface area, it does not distinguish between external or the combination of external and internal surface area.

If soil pH at any sampling time is plotted against surface area estimated by calculations based on particle size, a relationship is obtained that is nearly linear at least for the smaller size fractions. As an example, the eight week sampling for calcic limestone is shown in Figure 9. On the other hand, there appears to be no correlation between total surface area and change produced in soil pH (see Table 8). This would indicate that external surface area is much more important than internal surface area in controlling reaction rate.

Constant Surface Area

Table 9 shows the pH change that occurred when calcic limestone was applied at constant total surface area as determined by nitrogen gas adsorption.

Table 9. Soil pH as a function of time after addition of different particle size calcic limestone at quantities to give constant total surface area.

Particle Size	Time of Incubation			
	1/2 week	1 week	2 weeks	4 weeks
20-40	6.36	6.38	6.38	6.55
40-60	6.69	6.73	6.90	7.09
60-80	6.95	7.06	7.20	7.43
80-100	7.19	7.33	7.49	7.67
> 100	7.35	7.46	7.49	7.62
No lime	5.70	5.62	5.57	5.59

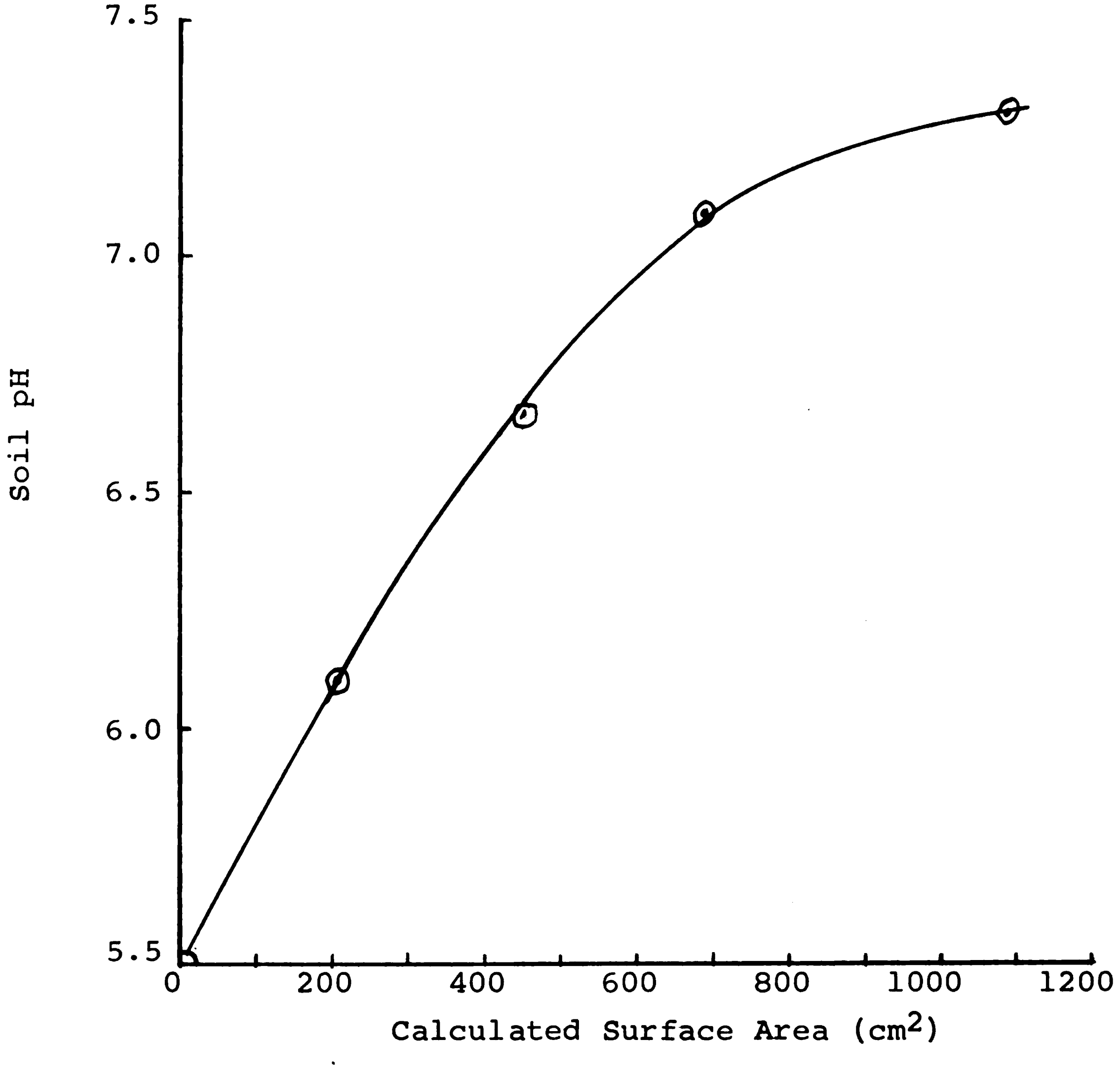

Figure 9. Relationship between calculated surface area of calcic limestone and pH of a Warsaw loam surface soil eight weeks after lime application.

The 80-100 and $>$ 100 mesh material gave similar rates of reaction in the soil even though about three times as much material had been applied for the 80-100 mesh material. The coarser fractions, however, did not react as fast even though they were applied to give the same total surface area. This lends evidence to the theory that internal surface area is not as important as external surface area in controlling reaction rate, particularly in the coarser fractions.

SUMMARY AND CONCLUSIONS

Methods of determining surface area of liming materials were studied. Two laboratory studies were conducted by incubating liming materials with an acid Warsaw loam surface soil to determine the effect of surface area on rate of reaction of liming materials. The first incubation study consisted of various size fractions of liming materials added to the soil at a calcium carbonate equivalence rate equal to 5.75 tons per acre of pure calcium carbonate to give different surface areas. The second incubation experiment consisted of treatments of liming materials added to the soil at constant surface area as determined by nitrogen gas adsorption.

The results of these studies are summarized as follows:

1. Determination of surface area of liming materials by isotopic exchange is not satisfactory.
2. Determination of surface area by the oxalate titration method suggested by Barnes (1) agrees at least qualitatively with surface areas estimated by calculations assuming spherical particles. This would indicate that both methods give an indication of external surface area only. Surface area determined by nitrogen gas adsorption

appear to measure both internal and external surface area.

3. Total area of calcic limestone studies appeared to be constant for particle sizes coarser than 100 mesh while the ratio of external area to internal area increases with decreasing particle size.
4. A plot of diameter of particle versus volume of $KMnO_4$ used for titration of oxalate is not a linear function as suggested by Barnes (1).
5. Rate of reaction of liming materials studied appears to be largely dependent upon the external surface area of the material. However, internal surface area may also influence reaction rate to some extent.
6. A function was derived which indicated that the cube root of the hydrogen ion remaining in the soil system would be a linear function of time if surface area of the liming material is controlling the rate of reaction. Reaction of dolomite appeared to follow this function; however, the reaction of limestone followed this function only during the latter stages of incubation.
7. Microscopic examination indicated that the dolomite studied was uniform and crystalline in nature; whereas, the calcic limestone studied was hetrogeneous containing a portion of slow reaction crystalline material and a faster reacting, porous appearing material.

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