AGRICULTURAL LIMESTONES

Surface Area and Reactivity of Typical Limestones

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The specific total surface areas, determined by gas adsorption, of agricultural limestone particles of the same size but from different limestones varied widely and were, in general, many times greater than the geometric surfaces calculated from gross particle dimensions. When the particle size was varied, the total surface showed relations with the geometric surface varying from nearly linear to markedly curvilinear. The total surface appears to consist of an "interior" surface that has little or no effect on the chemical reactivity of the limestone, and a "reacting" surface that is proportional to the reactivity of the limestone. Percentagewise, both total and reacting surface areas studied increased much less rapidly with particle size reduction (finer grinding) than did the geometric surface, a result that may have an important bearing on the economic fineness of agricultural limestones. The extent of the increase in total and reacting surface with particle size reduction appears to be dependent on the nature of the limestone. The results of the study provide an approach to a better understanding of the factors that influence the quality of agricultural limestones.

INFORMATION on the fundamental properties of agricultural limestones is needed both to understand and predict their action in the soil and to permit the design of scientific methods for evaluating such limestones. That existing evaluation methods for predicting the rate of reaction in the soil are not completely satisfactory is due largely to failure to base such methods on the fundamental properties of the limestone that control its activity in the soil. These methods have been briefly reviewed (8). Underlying many of the methods is the idea that the extent of the reacting surface is an important factor controlling the reactivity. The trouble has been that the nature and extent of the reacting surface itself have not been understood, and that the term "surface" has often been used in different senses.

Back of the usual sieve analysis applied to agricultural limestones is the idea that the rate of reaction in the soil is inversely proportional to the particle size and hence is governed by a surface area derivable directly from particle dimensions. This is the specific geometric surface area, S_g. As applied to a size class (sieve fraction) of agricultural limestone of density ρ, it may be calculated by assuming the individual particles to be smooth solid spheres or cubes, of diameter d, equal to the geometric mean of the diameters of the openings of the two sieves limiting the size class. The relation for either spheres or cubes is expressed by the simple equation

$$S_g = 6/\rho d \qquad (1)$$

For agricultural limestones composed of particles that are statistically cubical, spherical, or of some intermediate shape, Equation 1 would give a useful approximation of the specific surface area, if the extent of that area were governed solely by gross particle dimensions. Large proportions of platy or rodlike particles, however, would cause large errors in such an estimate. In any case, gross particle dimensions are not the sole controlling factor. As limestones tend to be microcrystalline, individual particles obtained on crushing are often aggregates of numerous tiny crystals or elementary particles bonded together. Such individual particles would have rough faces and possess more or less interstitial space between the structural units of the particle, resulting in greatly increased surface area over that computed by Equation 1. If any part of this extra surface is accessible to reacting ions, it is apparent that the sieve analysis gives no satisfactory estimate of either the total or the reacting surface.

Relative surface areas of limestones have been estimated from the coating of calcium oxalate formed on limestone surfaces in contact with oxalate ions (7). This is a direct approach to the reacting surface, in which ions are used to estimate a surface accessible to other ions. The thickness of the oxalate layer, however, appears to be affected by the conditions of the oxalate ion–limestone contact, by any magnesium carbonate in the limestone, and by impurities. Absolute surface areas are not readily obtainable from the results, and surface areas of limestones of different chemical composition are not readily compared.

Apparently no direct means of measuring the reacting surface is available, but it is possible to measure the total surface accurately, and then relate that to reaction rates in an effort to define the reacting surface. The gas-adsorption method of determining surface area, as devised by Brunauer, Emmett, and Teller, measures all the surface that is accessible to the molecules of the gas being absorbed. It is usually taken as the total surface, though surfaces in completely closed off voids are not included. It necessarily includes the reacting surface reached by molecules or ions reacting with the limestone. Surface area measured by gas adsorption is reproducible, can be expressed in absolute units such as square meters per gram, and is one of the fundamental properties of any particular material.

A study was therefore undertaken of the total surface areas of some typical agricultural limestones, as related to their kind, particle size, and other features. In an attempt to measure and define the reacting surface, the total surfaces were also studied in relation to the chemical activity of the limestones. It is recognized, of course, that the extent of the total surface area, or even that of the "reacting surface," does not fully delimit the reactivity of the limestone. The quality of such a reacting surface will also play a part, and that quality may depend on both the physical structure and chemical composition of the limestone, including the amount and kind of impurities. Such factors would not be fully or directly reflected in the simple physical extent of the reacting surface.

Method of Measurement

Surface areas were measured by the generally accepted and widely used physical adsorption procedure of Brunauer, Emmett, and Teller (BET method, 4). According to the theory of multilayer gas adsorption proposed by these workers, the volume, V_m, required to form an adsorbed monolayer of gas molecules on the surface being measured is related to the total volume of gas, V, adsorbed at any pressure, P, and to the vapor pressure, P_o, of the gas at the temperature of adsorption, by the equation:

$$\frac{P}{V(P_o - P)} = \frac{1}{V_mC} + \frac{C-1}{V_mC} P/P_o \quad (2)$$

where C is a constant.

Experience with many materials has shown that the equation holds best in the relative pressure range $P/P_o = 0.05$ to 0.35. In this range for most materials, when $P/V(P_o - P)$ is plotted against P/P_o, a straight line results (the BET plot). The volume of gas in the monolayer, V_m, is calculated from the intercept, $1/V_mC$, and the slope, $(C-1)/V_mC$, of the line. From this the total number of molecules in the monolayer can be computed, and the total surface area obtained by multiplying this number by the area occupied by a single adsorbed molecule.

Apparatus and Procedure

Details of the BET apparatus and manipulation have been described many times (2, 6). Only certain variations peculiar to the present investigation are discussed here. Sample surfaces were cleared of moisture and adsorbed gases by heating at 200° C. for 4 hours at a pressure of less than 10^{-5} mm. of mercury. Increasing the time to 8 hours gave area values for limestone surfaces only about 5% higher. At room temperature even extended evacuation failed to produce a straight-line BET plot.

Krypton was chosen as the gas to be adsorbed because it has been found suitable for relatively small surface areas, such as those expected in the present work (3, 5). Space in the sample bulb and connecting tubing (dead space) not occupied by the sample was measured by the nonadsorbed gas helium. Both

gases were supplied in spectroscopically pure form by the Air Reduction Sales Corp.

The adsorption measurements were made at the temperature of a liquid nitrogen bath (−195.8° C. at 760 mm. of mercury for pure nitrogen). The actual bath temperatures were regularly determined with an oxygen vapor pressure thermometer and used in the calculations. Krypton is a solid at such temperatures, but the P_o value used was that of the liquid extrapolated to bath temperatures by the equation of Meihuizen and Crommelin (7). Use of the liquid vapor pressure is recommended by Beebe, Beckwith, and Honig (3) and by Davis, DeWitt, and Emmett (5). For the area occupied by the adsorbed krypton molecule these workers found, respectively, values of 19.5 and 20.8 sq. A. to give the most consistent results. An intermediate value of 20.0 was used in the present work.

The mercury manometer customary in surface area work was replaced, because of the low pressures incident to the use of krypton, by a McLeod gage having a range of 0.05 to 2.4 mm. of mercury. The surface area values were corrected for a sample bulb surface of 0.004 square meter calculated roughly from the bulb dimensions. This value is below the range of accurate measurement with the equipment used.

Thermal transpiration sometimes results in false readings of very low gas pressures. When, however, corrections for thermal transpiration were applied to the krypton pressures in test calculations, the surface area obtained differed from that obtained without corrections by amounts well within the usual experimental uncertainty. Helium was used at pressures above the range where ther-
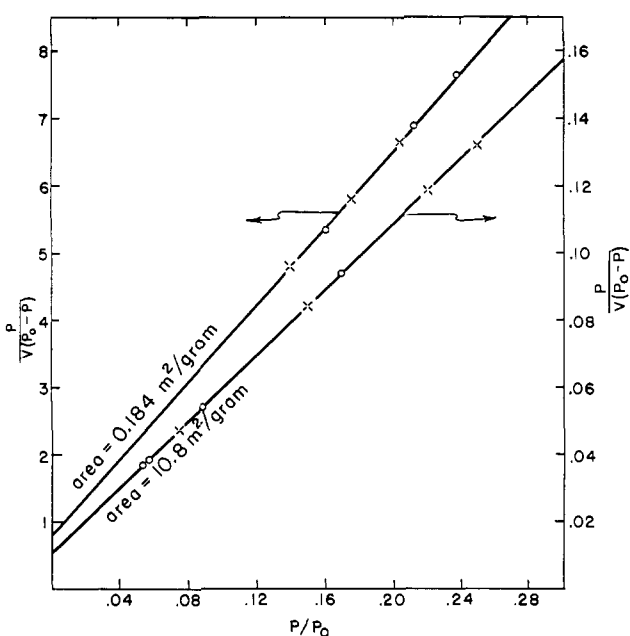

Figure 1. BET plots

mal transpiration would have any significant effect.

Precision and Accuracy

The precision of the measurements can be judged roughly from Figure 1, which shows typical BET plots of data on two limestones differing widely in chemical composition, hardness, particle size, and surface area. Circles are points obtained in the first run on each sample; crosses, those in a second run on the same sample after re-evacuation at room temperature. Circles and crosses fall closely on the same straight line. Duplicate measurements of areas of about 0.2 square meter per gram usually differed by less than 5%. Values below 0.05 were uncertain to 10% or more. The determined surface (0.10 square meter per gram) of a check sample agreed within 3% of the value obtained in another laboratory.

Limestones

The five limestones and Iceland spar used in this study are listed in Table I. Numbers 1, 2, and 4 have been described in more detail by Schollenberger and Whittaker (8).

Size classes or sieve fractions of the first five materials were prepared by machine crushing and dry sieving on a Ro-Tap machine, using the following sieve pairs of the U. S. series: 7–8, 14–16, 25–30, 45–50, 80–100, 170–200, and 200–325. The Iceland spar was hand crushed and sieved because of the small amount available. Two other size classes of two of the samples were prepared on the Roller analyzer. These were composed of particles 10 to 44 and 0 to 10 microns in diameter as calculated from

Table I. Limestones

Sample No.	Name	Type	Origin	CaCO₃, %	MgCO₃, %
1	Upper Columbus	Dolomitic	Bellevue, Ohio	74.8	23.6
2	Niagara (Guelph)	Dolomite	Woodville, Ohio	55.2	43.9
3	Mosheim	High-calcium	Stephens City, Va.	99.3	0.22
4	Vanport	High-calcium[a]	Lawrence Co., Pa.	90.5	Trace
6	Goodland	High-calcium	Idabel, Okla.	95.9	1.6
7	Iceland spar	Massive calcite	Chihuahua, Mexico	[b]	

[a] Mixture of soft and hard limestones from overlying strata in quarry.
[b] High grade calcite.

Table II. Surface Areas of Size Classes of Different Limestones

(Square meters per gram)

Sample No.	Type of Limestone	U. S. Sieve Nos.							Diameters, Microns[a]	
		7–8	14–16	25–30	45–50	80–100	170–200	200–325	10–44	0–10
					Total Surface Area					
1	Dolomitic	0.303	0.293	0.315	0.354	0.400	0.375	0.425	0.412	2.52
2	Dolomite	0.136	0.175	0.238	0.301	0.442	0.586	0.679	0.530	3.80
3	High calcium	0.149	0.237	0.277	0.332	0.479	0.506	0.765	...	...
4	High calcium mixture[b]	1.73	...	2.38	...	3.31	3.09	...	...	...
6	High calcium	11.77	...	11.54	12.23	12.10	12.63	12.85	...	...
7	Iceland spar	0.008	...	0.031	...	0.079	0.171	0.213	...	...
					Geometric Surface Area[c]					
	All samples	0.00085	0.0017	0.0034	0.0069	0.0137	0.0275	0.0389	0.1059	...

[a] Diameters in microns as calculated from Roller analyzer calibration and checked by microscope.
[b] Mixture of hard and soft limestone from overlying strata in same quarry.
[c] Based on particle size.

the analyzer calibration and checked microscopically. These nine separates represent a fair sampling of the size classes encountered in agricultural limestones.

Total Surface

Results for the total surface area (Table II) range from 0.008 to 12.85 square meters per gram from the coarsest fraction of the Iceland spar to the finest fraction of the Goodland limestone. Differences between materials are far more prominent than those between size classes. Thus, the surface area results for the sieve separates of the first three materials range under 1 square meter per gram, those of the fourth from 1.7 to 3.1, and those of the fifth from 11.5 to 12.9.

Obviously, surface area differences between limestones cannot be compensated by fine grinding.

There is a drop in total surface area, instead of the expected increase, in passing from the sieve-graded size classes to the Roller-analyzer separates theoretically containing particles smaller than those in the finest sieve-graded separates. The two methods of grading do not appear comparable so far as surface area is concerned, a fact which renders the subsieve data of little value for present purposes. Whittaker, Rader, and Zahn (9) found a similar discontinuity in the citrate solubility–particle size relation of dolomite particles when passing from sieve to Roller-analyzer separates.

Because of the prominence of the sieve analysis in the evaluation of agricultural limestones, the relationship between the sieve analysis and the total surface requires further comment. For this it will be convenient and meaningful to express the particle size in terms of the geometric surface area (Table II, bottom). For the samples studied, the BET surface was usually enormously greater than the geometric surface area. Even the Iceland spar had a BET surface that was 5 to 10 times the geometric surface. The relation between the two surfaces ranged from linearity to marked curvilinearity (Figure 2), but the BET surface always tended to increase as the geometric surface increased (particle size decreased). The rate of increase, however, was highly variable and characteristic of each limestone.

In general, the BET surface area increased, percentagewise, much less rapidly with particle size reduction than did the geometric surface area. This suggests that the usual resort to finer grinding to increase surface area is not as effective as is commonly supposed and that its relative effectiveness varies from limestone to limestone.

The wide variation in surface area of particles of the same size from different limestones may be partly due to variation in the average size and degree of bonding of the elementary particles in the aggregates making up the sieve-size particles. If the elementary particles are lightly bonded together, exposing their surface, uniform in size and structure, and small relative to the smallest fragments studied, one would expect that the total surface would be large, owing to the contribution of such particles, and that the geometric–total surface relation would be essentially linear, with the size of the aggregates having little effect on total surface. The extremely fine-grained and soft Goodland limestone, No. 6 in Figure 2, exhibits these relationships. Nonuniform elementary particles would cause a similar behavior, provided the crushing did not result in

Figure 2. Relation of BET or total surface area to calculated geometric surface area of size classes of four limestones
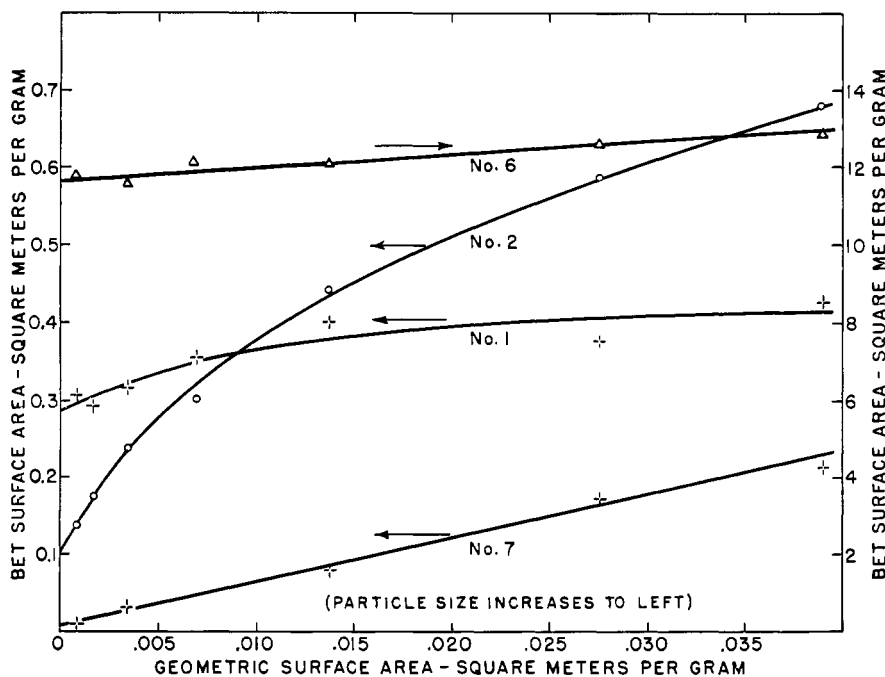
the segregation in certain size classes of particular kinds or sizes of such particles.

The elementary particles, however, may be of such size that, as subdivision of the limestone progresses, fragments are first composed of clusters of such particles, which may later constitute entire fragments and finally may themselves be broken into. This would result in the gradual disappearance of the interstitial space, with the specific surface area of the finer fractions finally becoming that of the elementary particles or their fragments. The surface areas of such non-aggregate particles would be more closely related to their gross physical dimensions than are those of particles composed of aggregates. The increased curvilinearity and slope of the curves, 1 and 2 in Figure 2, for the Upper Columbus and Niagara limestones, respectively, could be due to the operation of such factors. Present data, unfortunately, do not permit any definitive generalization connecting the type or structure of limestones with their surface area.

Consistent with the foregoing are the observations that the Iceland spar has a relatively very small total surface area that is linearly related to the geometric surface area and is more affected by it than are the surfaces of the limestones (No. 7, Figure 2). The spar tends to break on crushing into relatively smooth, regularly shaped fragments of the original crystals that are without "elementary particles" or interstitial space in the senses used just above.

It is possible that a "shape factor" also plays a part in the geometric–total surface relationship. Variation in particle shape with size, if of sufficient magnitude, could significantly affect the validity of the geometric surface area calculation.

Agricultural limestones are most commonly produced by grinding and sieving in the dry state. This results, as did the laboratory processes used in preparing the separates studied here, in variable quantities of fine limestone dust adhering to particle faces. This dust, particle sizes of which are far in the subsieve range, necessarily has a high specific geometric surface relative to that of the the particle it adheres to. Limited data from initial steps in an investigation of this dust indicate that the proportion of dust, small relative to total particle weight, and characteristic of the limestone, increases as the particle size decreases, and that removal of the dust reduces the total BET surface, thus changing somewhat the geometric–total surface relationship. From a practical standpoint the normal particle with its burden of adhering dust is the one of most interest.

Reacting Surface

Schollenberger and Whittaker studied the rate of reaction in boiling ammonium chloride solution, through which steam was passing to carry off the ammonia as rapidly as possible, of some of the limestone separates included in the present study. Their published (8) and other data on both the ammonium chloride and oxalate reactions afford an opportunity to study the relation of total surface area to the reacting surface. For the ammonium chloride data this was done by examining the relation between total surface area and the rate of reaction.

One would expect the surface area of a limestone to change in extent as attack by any chemical reagent proceeds. In examining the relation between surface area and rate of reaction, therefore, it would seem most logical to use the initial rate of reaction as being the one most affected by the measured initial surface area. Initial reaction rates of the various size classes in the ammonium chloride solutions had not,
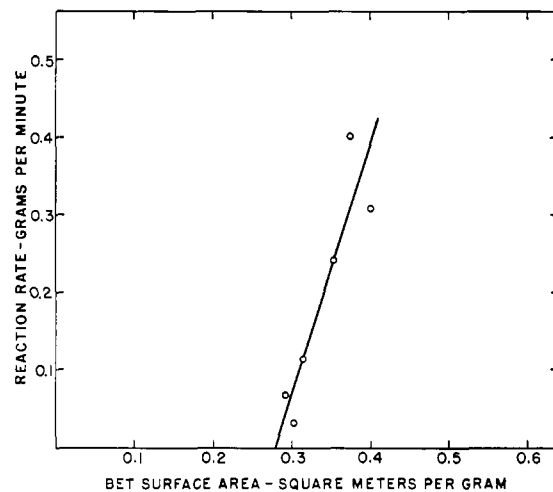

Figure 4. Relation of BET surface areas to average reaction rates of separates of limestone 1 during first 20% decomposition in boiling ammonium chloride solution

however, been directly determined nor could they be satisfactorily estimated by extrapolation of rate curves to zero time. The average amounts decomposed per minute during the first 20% of decomposition in ammonium chloride were therefore used in lieu of true initial rates. Figure 3 shows such rates plotted against the BET surface areas of the various size classes, using the data for limestone 2. The three curves represent different combinations of sample size, concentration of solution, rate of distillation, and other factors in carrying out the ammonium chloride reaction. The details are not important here. Although the average reaction rate varies with the conditions, all three plots appear to be straight lines and all intercept the BET axis at about 0.11 square meter. The reaction rate was thus directly proportional to that portion of the total surface remaining after deducting 0.11 square meter.

When the total surface area of each separate of limestone 2 was plotted against its geometric surface area (Figure 2), the curve intercepted the BET axis at 0.10+ square meter. In view of recognized experimental and plotting errors, this is good agreement with the value of 0.11 just obtained. Figure 4 is a plot of similar data for limestone 1. The intercept value of 0.28 square meter agrees well with the intercept of 0.29 obtained for this limestone in Figure 2.

These observations suggest that a portion of the total surface (0.28 and 0.11 square meter for limestones 1 and 2, respectively) plays no part in the reaction and must therefore be inaccessible to the reacting reagent molecules, and that this is the same surface that remains when the geometric surface has approached zero, as it does on the larger particles. Because of its inaccessibility, and because it remains after the cal-

Figure 3. Relation of BET surface areas to average reaction rates of separates of limestone 2 during first 20% of decomposition in boiling ammonium chloride solutions

Lines represent decomposition data obtained under different sets of conditions
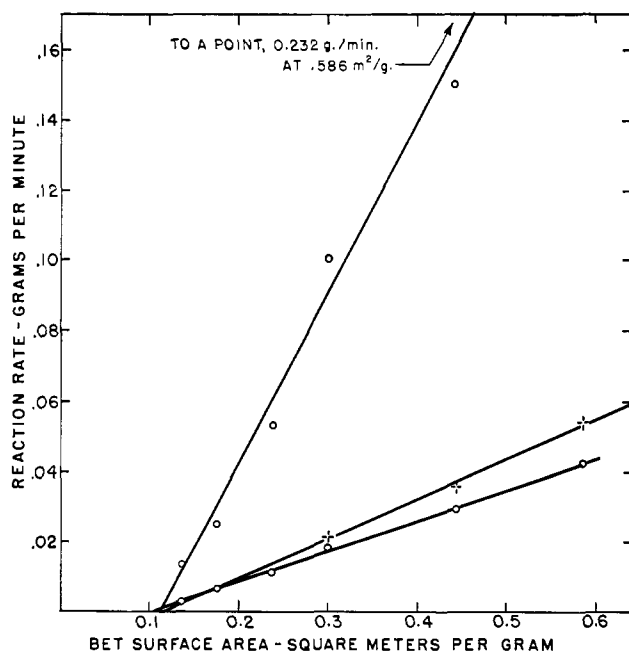
culated exterior surface per gram (the geometric surface) has become zero, this will be referred to as the "interior" surface. At present no information is available as to the nature of this surface. The reacting surface, or that accessible to reagent ions, is apparently the total surface less this interior surface.

Like the total surface, the apparent reacting surface of the two limestones studied with respect to that surface increased much less rapidly with particle size reduction than did the geometric surface. On the basis of the limited data here presented it would appear that the reacting surface, as well as the total surface, is not enhanced in proportion to the fineness of grinding, at least in some cases.

The relation between the total surfaces, S_t, of separates of limestones 1 and 2, and their average reactions rates, R, over the first 20% of decomposition, is expressible by the simple equation:

$$R = k(S_t - C) \qquad (3)$$

where k is a constant characteristic of the limestone for any set of reacting conditions. The constant C, also characteristic of each limestone, may be identified as the interior surface, and the expression $S_t - C$ as the apparent reacting surface. The relation holds within the combined surface area, rate determination, and plotting errors of the data for these two limestones and probably for many others as well.

The foregoing was based on the average rate of reaction over the first 20% of decomposition. In Figure 5 the average rates of reaction over the first 10, 30, 50, and 80% of decomposition of

Figure 5. Relation of BET surface areas to average reaction rates of separates of limestone 2 during decomposition in boiling ammonium chloride solutions
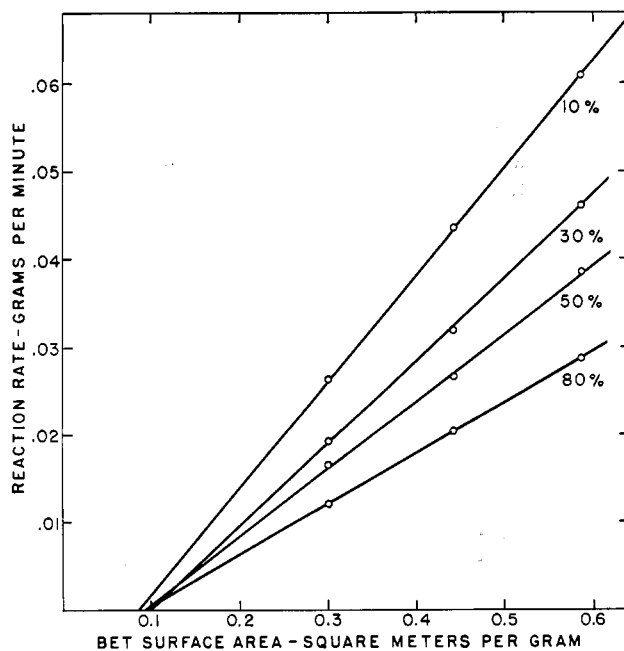
limestone 2 have been plotted against the BET surface. These data, more precise than some of the other rate data because they represent four replicates, show a linear relation to the same reacting surface as did the rate data based on 20% of decomposition. Each of the four curves intercepts the BET axis at about 0.10 square meter, as do the curves for the average rate for the first 20% of decomposition and that for the relation of BET to geometric surface. These data for 10, 30, 50, and 80% decomposition suggest that for this limestone, at least, Equation 3 holds throughout the decomposition.

Relative surface areas of some of the limestone separates were determined by C. J. Schollenberger by allowing them to react with a mixture of sodium oxalate and oxalic acid and titrating the insoluble calcium oxalate formed with potassium permanganate. The number of milliliters of this reagent required to react with the calcium oxalate was then used as a relative surface value. Conditions, details of which are unimportant here, were standardized throughout.

In Figure 6 such relative surface areas of several size classes of limestones 1 and 2 have been plotted against the BET areas of the separates. As in the ammonium chloride reaction, there is a linear relation between the relative oxalate surface and that part of the BET surface remaining after deducting the portion represented by the intercept. The intercepts at 0.27 and 0.10, moreover, closely agree with those previously obtained for limestones 1 and 2. For these two limestones, at least, the effective reacting surface for the oxalate reaction is the same as that for the ammonium chloride reaction, which in turn is the
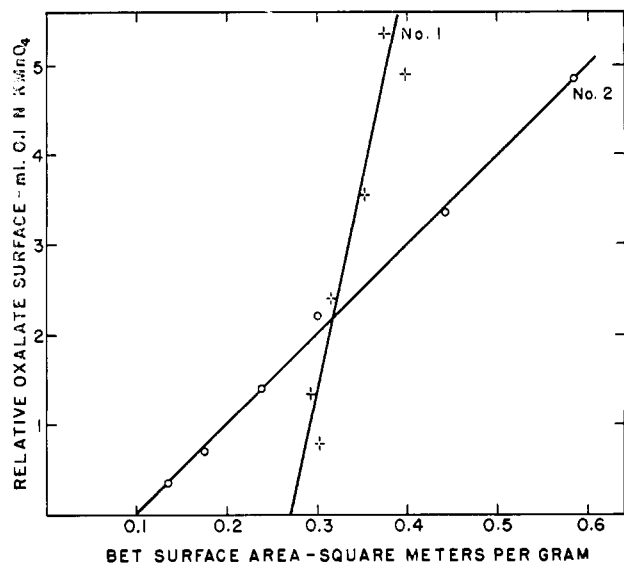

Figure 6. Relation of BET surface areas of separates of limestones 1 and 2 to relative surface areas measured by oxalate procedure

difference between the total BET surface and that residual when the geometric surface approaches zero.

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