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LIMING MATERIALS IN SOILS

Radiochemical Measurement of Reaction Rates

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This investigation was intended to demonstrate the usefulness of radiocalcium in evaluating liming materials, and to develop a radiochemical method applicable to the study of natural materials, yet subject to fewer obvious errors than those associated with commonly used techniques. It was found that reaction rates of liming materials could be followed by tagging the calcium of the exchange complex of a soil, incorporating the liming material, and determining the specific activity of the calcium in successive crops grown on the system. A second successful method involved measurement of calcium-45 and calcium-40 concentrations in dilute calcium nitrate solution before and after equilibration with a sample of soil previously treated with limestone or slag. The methods developed provide a more direct means of evaluating limestones and slags than was previously available. The equilibration technique shows promise as a means of determining exchangeable calcium, and should be particularly valuable when applied to calcareous soils or those containing residual limestone.

THE EFFECTIVENESS of a limestone or slag as a soil amendment depends mainly upon two properties of the material: its potential capacity to neutralize soil acidity, and the rate at

which the material will react in the soil to accomplish the neutralization.

Of these properties, the reaction rate is the more difficult to measure. No one of the numerous methods that have been

developed for its determination is entirely satisfactory. In greenhouse or field experiments, some of the measurements involved are questionable. Soil pH is subject to natural fluctuations over

a period of time, and the precise measurement of soil pH is difficult, particularly when the soil has been recently limed. Determination of exchangeable calcium in the presence of residual limestone is complicated by the solubility of calcium carbonate in the ammonium acetate leaching solution (4). Analysis for residual carbonate, a method capable of a high degree of precision, cannot be applied to studies of materials such as slags. Laboratory methods, such as sieve analyses, treatment of the material with oxalic acid for estimation of surface area or reaction rate (1, 12), and distillation in boiling ammonium chloride (11), are more quickly and easily carried out, but are empirical, and are often capable of yielding worth-while information only when interpreted in the light of accompanying soil or plant experiments.

Consideration of the possible applications of radiotracers as research tools led to the belief that techniques involving the use of calcium-45 could be employed for evaluating liming materials, and that these methods would have certain advantages over those previously employed. Two such schemes have been investigated and are reported here.

Isotopic Analyses of Plants Grown On Ca⁴⁵-Labeled Soil

In an acid soil, essentially all of the calcium is in the exchangeable form. The addition of limestone or slag results in a soil that contains two forms of calcium: exchangeable calcium and unreacted solid calcium compounds. This condition exists until all of the added liming material has been decomposed. The exchangeable calcium is generally accepted as being easily available to plants; the calcium of the limestone or slag is either unavailable or has a lower degree of availability. If either the original exchangeable calcium or the calcium of the added material has been labeled with radiocalcium, the decomposition can be followed by isotopic analysis of plants grown on the system, as their Ca⁴⁵/Ca⁴⁰ ratios will change as the reaction proceeds.

From the standpoint of the analytical procedures, tagging of either the liming material or the soil would be equally useful. However, direct tagging of natural materials or slags would probably be unsatisfactory, both because of the probability that elements other than calcium would be made radioactive and because of the possibility that the calcium-45 formed would not be equally distributed within the particles (8). Fortunately, the calcium of the soil exchange complex can be satisfactorily labeled (2).

Methods and Materials. A Sassafras loam from eastern Maryland with an exchange capacity of 5 meq. per 100 grams, a pH of 5.3, and an exchangeable calcium content of 2.0 meq. per 100 grams was pre-

pared for the experiment. One per cent of the total batch of soil to be used was withdrawn, made to a thin paste, and treated with calcium-45 at a rate of about 500 μ c. per gram of exchangeable calcium. The suspension was thoroughly stirred and allowed to dry at room temperature. This procedure was repeated twice, and finally the dry tagged soil was passed through a 20-mesh sieve.

No. 10 cans, cut off at a height of 5 inches, were used as pots. Treatments were prepared in quadruplicate by mixing together in a twin-shell dry blender (for each pot) 22.7 grams of tagged soil, 2247 grams of inactive soil, sufficient potassium dihydrogen phosphate, ammonium nitrate, and magnesium sulfate to provide per acre (weight basis) 100 pounds of potassium, 79 pounds of phosphorus, 75 pounds of nitrogen, and 50 pounds of magnesium, and an amount of liming material equivalent to 2000 pounds per 2,000,000 pounds of soil. Table I lists the limestones and slags used.

Perennial rye grass was planted November 30, 1951, and the pots were placed in a controlled-environment growth room. Three harvests were made at 49, 80, and 111 days. Ammonium nitrate, at the rate of 50 pounds of nitrogen per acre, was applied in solution between cuttings.

After the third harvest the roots and stubble were screened out, and the soil from the four replicates of each treatment was mixed together. The soil was then reappportioned into the individual pots, which were moved from the light chamber to the greenhouse. Plantings of rye grass and of millet were made successively; but growth was unsatisfactory, and the plant material was discarded. A second crop of millet was established June 3, 1952, and harvested 32 days later.

The plant samples were ashed, and calcium was precipitated as the oxalate (10). The precipitate was collected on tared filter rings (9) and was weighed and counted to determine calcium-40 and calcium-45. Results were recorded as counts per second per milligram of calcium (specific activity). From these results, the fraction of the liming material which had decomposed was calculated in the following manner:

$$y = \frac{\text{counts per second per mg. of Ca of plants from limed soil}}{\text{counts per second per mg. of Ca of plants from unlimed soil}}$$

where y is the fraction of the plant's calcium derived from that originally present in the exchange complex.

The amount of calcium from the applied liming material which had become available to the plant could then be found by utilization of the isotope dilution formula as used by Fried and Dean (6):

$$A = \frac{(1 - y)B}{y}$$

where A is the concentration of available calcium derived from the applied liming material (milligrams of calcium per gram of soil) and B is the concentration of exchangeable calcium in the unlimed soil (milligrams of calcium per gram of soil). As the total amount of calcium applied in the liming material was known, the percentage which had become available was readily calculated.

In making the calculations for this experiment, the calcium removed from both soil and liming materials in previous crops was taken into account for all harvests other than the first.

Results and Discussion

The percentages of the liming materials which had become available, as determined by analysis of each of the four crops, are shown in Table II.

The coefficients of variation for the harvests were 15.81, 21.50, 21.84, and 8.47%, respectively. The experimental error increased with each succeeding rye grass harvest, as reduced yields increased the analytical errors of weighing and counting. Also the uncertainty increased as to the quantities of soil and added calcium immobilized in roots and stubble. The lowered experimental error for the millet may be explained in part by the rapid and uniform growth of the crop, but is no doubt due principally to the thorough mixing of all four replicates of each treatment after the last rye grass harvest.

The data on treatments 2 to 7 deal with one limestone ground to different degrees of fineness, and emphasize the well-known effect of particle size upon the speed at which a limestone reacts when applied to soil. The finest particles (170- to 200-mesh) decomposed so rapidly that even the first crop showed them to be completely reacted. The 80- to 100-mesh size became completely decomposed before the end of the growth period of the second crop. At the other extreme, the two coarsest fractions were only slightly reacted (12 and 24%) at the time the last crop was grown.

Treatments 5, 8, 9, 10, and 11 covered applications of various natural carbonates which were all ground to the same sieve size. The data fail to show any great dissimilarity between these five materials, although at the fourth harvest some of the differences are large enough

to be statistically significant. Rather unexpectedly, almost no differences were

found between the reaction rates of calcite and dolomite, or between the rates of the hard, high-calcium limestone and the dolomitic limestone.

Treatments 12 to 16 are slags of different types and sources. The slags differed markedly in their reactivity, although the differences are not correlated with the type of slag. One phosphorus furnace slag was nearly as reactive as the limestone, while the other phosphorus furnace slag was relatively inert. Both the air-cooled blast furnace slag and the basic slag were almost half decomposed by the time the last crop was grown, while only one quarter of the water-cooled blast furnace slag had reacted. MacIntire *et al.* (7) reported

Table I. Liming Materials Investigated

Treatment No.	Liming Material	Mesh Size (U. S. No.)	Ca, %	Source
2 ^a	Limestone, hard, high calcium	170/200	39.40	Stephens City, Va.
3	Limestone, hard, high calcium	80/100	39.40	Stephens City, Va.
4	Limestone, hard, high calcium	45/50	39.40	Stephens City, Va.
5	Limestone, hard, high calcium	25/30	39.40	Stephens City, Va.
6	Limestone, hard, high calcium	14/16	39.40	Stephens City, Va.
7	Limestone, hard, high calcium	7/8	39.40	Stephens City, Va.
8	Limestone, soft	25/30	35.36	Idabel, Okla.
9	Calcite	25/30	39.69	Chihuahua, Mexico
10	Limestone, dolomitic	25/30	30.08	Bellevue, Ohio
11	Dolomite	25/30	22.07	Woodville, Ohio
12	Slag, phosphorus furnace	25/30	32.47	Monsanto Chem. Co.
13	Slag, phosphorus furnace	25/30	33.21	Victor Chem. Works
14	Slag, blast furnace, air-cooled	25/30	31.83	Carnegie Steel Corp.
15	Slag, blast furnace, water-granulated	25/30	30.18	H. T. Williams
16	Slag, basic	25/30	30.69	Tenn. Coal, Iron, and R.R. Co.

^a Treatment 1 consisted of unamended soil labeled with Ca.⁴⁵

dissimilarity in behavior of slags used in greenhouse experiments.

All the materials had relatively rapid reaction rates during the first days of the experimental period, after which each reaction rate became steady. This initial rapid rate of reaction was probably due to the presence of fresh surfaces and to inclusion in each material of some very fine particles which had adhered to the coarser ones throughout the sieving process.

Isotopic Analysis of Equilibration Solution

Borland and Reitemeier (3) found that equilibration of calcium between solution and solid phases of aqueous suspensions of clay minerals was virtually complete in 1 hour of shaking. They did not extend their study to soils, but their work suggests the possibility of determining the exchangeable soil calcium by equilibrating the soil with a solution of known calcium-45 and calcium-40 concentration, followed by analysis of the equilibration solution to measure the dilution in specific activity. The amount of calcium in the soil which enters into equilibration with the calcium of the solution can then be calculated from the specific activity data. Such a procedure appears to be adaptable to reaction rate studies on liming materials.

Methods and Materials The soils previously used for the plant uptake studies were prepared for the equilibration study by screening out the roots and stubble, and mixing the soil of each pot for 10 minutes in a twin-shell dry blender.

A solution containing approximately 100 p.p.m. of calcium-40 (as the nitrate) and 350 μ c. of calcium-45 per gram of calcium-40 was prepared as the equilibration solution. Duplicate 40-gram soil samples

were weighed into 250-ml. glass-stoppered Erlenmeyer flasks. Forty milliliters of the equilibration solution were added, and the flasks agitated on a wrist action shaker for 3 hours at a constant temperature of 26° C. (A previous time study with the same soil had indicated essentially complete equilibration within 1 hour.) The soil material was centrifuged out at 20,000 X G for 5 minutes in an angle head centrifuge, and floating debris was removed from the supernatant liquid by filtering.

Total calcium was determined in a 20-ml. aliquot of the supernatant solution by titrating with disodium Versenate (disodium dihydrogen ethylenediaminetetraacetic acid), according to the method of Cheng and Bray (5). To determine calcium-45, the calcium of 2 ml. of the supernatant solution, together with 25 mg. of carrier calcium, was precipitated as the oxalate, collected on filter paper rings, and counted under the end-window counter. Since the precipitate weights varied only slightly, application of self-absorption correction factors was not necessary. Aliquots of the original equilibration solution were analyzed for calcium-40 and calcium-45 by the same methods employed on the supernatant solutions.

The soil calcium which equilibrated with the solution was calculated by the isotope dilution formula

$$X = \frac{AC}{B} - C$$

where A = original specific activity of equilibration solution

B = final specific activity of equilibration solution

C = calcium added in equilibration solution, mg. of calcium per gram of soil

X = soil calcium equilibrating with solution, mg. of calcium per gram of soil

Subtraction of the value determined for the control soil (the soil which had received no amendment) from the value for a soil which had received a liming material yielded the quantity of exchangeable calcium supplied by the added material. As the amount of calcium added

Table II. Reaction Rates of Limestones and Slags in Soil as Indicated by Plant Uptake of Ca⁴⁶-Tagged Calcium

Treatment No.	Liming Material	Particle Size	% of Liming Material Reacted			
			Rye Grass 0-49 days	Rye Grass 50-80 days	Millet, 81-111 days	Millet, 186-218 days
2	Limestone, hard, high calcium	170/200	102.02
3	Limestone, hard, high calcium	80/100	92.63
4	Limestone, hard, high calcium	45/50	49.08	52.90	65.75	94.35
5	Limestone, hard, high calcium	25/30	20.35	28.90	37.07	59.25
6	Limestone, hard, high calcium	14/16	9.47	14.20	14.31	24.24
7	Limestone, hard, high calcium	7/8	8.72	11.60	11.13	12.00
8	Limestone, soft	25/30	23.38	31.50	37.81	72.04
9	Calcite	25/30	19.71	25.20	33.29	48.28
10	Limestone, dolomitic	25/30	19.56	21.90	34.77	62.14
11	Dolomite	25/30	16.94	24.60	24.18	48.96
12	Slag, phosphorus furnace	25/30	12.82	14.80	11.36	15.46
13	Slag, phosphorus furnace	25/30	28.15	37.10	34.99	54.18
14	Slag, blast furnace, air-cooled	25/30	35.35	41.60	43.71	48.08
15	Slag, blast furnace, water-granulated	25/30	14.94	17.70	18.87	25.11
16	Slag, basic	25/30	20.79	29.23	31.21	48.37
	LSD (0.05)		6.01	8.04	10.43	5.75

Table III. Percentage of Added Calcium Reacted

Treatment No.	Liming Material	Mesh Size (U. S. No.)	Percentage Reacted	
			Detd. by plant uptake	Detd. by equilibration
4	Limestone, hard, high calcium	45/50	94.35	83.36
5	Limestone, hard, high calcium	25/30	59.25	56.31
6	Limestone, hard, high calcium	14/16	24.24	25.03
7	Limestone, hard, high calcium	7/8	12.00	12.98
8	Limestone, soft	25/30	72.04	72.80
9	Calcite	25/30	48.28	40.65
10	Limestone, dolomitic	25/30	62.14	51.77
11	Dolomite	25/30	48.96	35.21
12	Slag, phosphorus furnace	25/30	15.46	11.75
13	Slag, phosphorus furnace	25/30	54.18	47.03
14	Slag, blast furnace, air-cooled	25/30	48.08	32.46
15	Slag, blast furnace, water-granulated	25/30	25.11	17.29
16	Slag, basic	25/30	48.37	40.79
	LSD (0.05)		5.75	4.69

in the liming material was known, the percentage that had reacted could be calculated. Actually, the calculations in this particular case were somewhat complicated by the slight corrections necessary to account for the calcium removed from the soil and liming materials during the plant uptake studies. Correction for the relatively small concentration of calcium-45 remaining in the soil from the plant studies was so small that it was ignored.

Results and Discussion

The values for percentage of calcium of various liming materials that had reacted, as determined both by the equilibration technique and by analysis of the final crop of the plant uptake studies, are shown in Table III. The 13 materials compared are ranked in almost the same order by the two methods, although, with but few exceptions, the values determined by equilibration are lower than those obtained through the plant analyses. Actually, if the two methods had measured the same fraction of calcium from the soil-limestone systems, the equilibration results should have been the higher, since the soil samples were taken after the last crop was harvested—i.e., the liming material had slightly more time in which to react. These results may reflect a positive action of plant root growth and associated biological processes on the solubility of the liming materials. They also suggest that part of the plant's feeding may have been directly upon the calcium of the limestones or slags, by roots which were in contact with undecomposed particles.

The two methods do not measure exactly the same fraction of calcium from the systems. The plant method gives an estimate of the calcium that may become available to the plant during its period of growth, while the equilibration method yields results which more nearly approxi-

mate the exchangeable calcium content of the soil.

The equilibration technique offers promise as a method of determining exchangeable calcium in soils. With acid soils which have not recently been treated with slowly soluble calcium compounds, results obtained by equilibration will be the same as the exchangeable calcium content determined by the usual ammonium acetate leaching procedure. When soils have had recent applications of limestone, slag, or rock phosphate, or are naturally calcareous, the equilibration method is subject to possible errors, due to dissolution of limestone during the shaking process, or to isotopic exchange between calcium in the solution and on the surface of particles of calcium compounds. However, it is under just these soil conditions—in which the leaching procedures are known to be seriously in error—that the equilibration technique may be most useful, since its errors appear to be small.

Summary and Conclusions

Two radiochemical methods for evaluating the rate at which liming materials react with soil have been investigated. One technique involved the addition of a limestone or slag to a soil whose exchangeable calcium had been labeled with radiocalcium, followed by isotopic analysis of successive crops grown thereon. The other method involved measurement of calcium-45 and calcium-40 concentrations in a dilute calcium nitrate solution, before and after equilibration with a sample of soil previously treated with limestone or slag. Estimation of the extent of reaction between the liming material and the soil depended, in the first method, upon the decrease in specific activity of the plant samples as compared to the original soil, and in the second method, upon the decrease in

specific activity of the solution during equilibration with the soil sample.

The 13 materials compared were ranked in essentially the same order by the two methods, although estimates of the percentage of the liming materials which had reacted were higher, in most cases, by the plant method. This difference may have been caused by some positive action of the plant roots or associated microorganisms upon the undecomposed particles of limestone or slag.

The reaction of limestones and slags in soil, as measured by the plant method, was comparatively rapid at first and then dropped to a slower rate which depended on the kind of material and the particle size.

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