# A STUDY OF THE RELATIONSHIP BETWEEN pH, EXCHANGEABLE CALCIUM, PERCENT BASE SATURATION, AND LIME REQUIREMENT IN SOME MICHIGAN SOILS

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# A STUDY OF THE RELATIONSHIP BETWEEN pH, EXCHANGEABLE CALCIUM, PERCENT BASE SATURATION, AND LIME REQUIREMENT IN SOME MICHIGAN SOILS

By

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# A STUDY OF THE RELATIONSHIP BETWEEN pH, EXCHANGEABLE CALCIUM, PERCENT BASE SATURATION, AND LIME REQUIREMENT IN SOME MICHIGAN SOILS

## INTRODUCTION

In soils there are certain general relationships between pH, exchangeable calcium, percent base saturation, and lime requirement which have been examined by a number of investigators (13, 14, 16, 18, 22, 25). However, there is a need for more information concerning the specific aspects of these relationships in Michigan soils. One of the most important of these for successful crop production is the correction and control of soil reaction. This immediately brings up the problem of lime requirement or the amount of lime which must be added to bring the soil to a desired pH value. In the past the most simple of the chemical methods for estimating lime requirement has been the determination of soil reaction. However, on soils of varying cation exchange capacities it is almost impossible to base accurate liming values on the hydrogen ion concentration alone. For example it is commonly known that two soils having the same pH may require considerably different amounts of lime. This variance is largely due to differences in clay and organic matter contents of soils. Likewise, since the percent base saturation is a soil property which is not directly related to the buffering capacity, it would seem that this characteristic would also be limited as a measure of lime requirement.

Since soil pH alone has proven unsatisfactory as an accurate measure of the needs of lime for soils, other chemical methods have been proposed over a period of years. Many of these procedures are based on sound chemical principles and give accurate values for lime requirement. Such methods attempt to take into consideration pH, base exchange capacity, and percent base saturation when determining lime requirement of soils.

It is the purpose of this work to study some of the relationships between pH, percent base saturation, exchangeable calcium, and lime requirement and to compare several methods for the determination of lime requirement.

## REVIEW OF LITERATURE

In order to study the problem of the need for lime in Michigan soils, it is necessary to review the methods for lime requirement as well as the relationships between percent base saturation, lime requirement and pH.

According to Peech and Bradfield (21), lime requirement methods may be listed under the following headings: (a) determination of exchangeable hydrogen; (b) rapid determination of the lime requirement; (c) determination of soil reaction; (d) determination of exchangeable calcium and degree of calcium saturation; and (e) determination of readily soluble aluminum, iron and manganese.

Practically all the rapid methods in determining lime requirement involve the determination of exchangeable hydrogen. The first group of methods to be considered involve the titration of acid soils with a base. Veitch as reported by Truog (27), was one of the first to propose titrating the soil to a phenophthalein endpoint with lime water. This naturally gave high results. Bray and DeTurk (9) used a solution of KCL to replace the hydrogen ions and then titrated the extract with $Na_2CO_3$ using brome thymol blue as an indicator. It has been pointed out, however, (20) that pH values of sodium are higher than those of equivalent amounts of calcium. In the methods using potentiometric titration of the soil, Pierre and Worley (23) have shown that the pH of soils in the laboratory are higher than those in the field when equivalent amounts of lime are added. To correct this they introduced a liming factor of 1.5. Dunn (7) also found that additions of a solution of $Ca(OH)_2$ to the soil gave higher pH readings than did additions of $CaCO_3$ as measured by the glass electrode. Hardy and Lewis (8) developed a method involving titration of the soil with $Ca(OH)_2$ in the presence of $CaCl_2$ to pH 7.00. Peech (20) has shown that the presence of $CaCl_2$ will produce lower pH values even though the equivalence point is unchanged.

A second type of method for lime requirement is a single extraction. Here the exchangeable hydrogen is extracted with a salt solution and the extract titrated with a base. Peech (20) has pointed out that extraction with $KNO_3$, as proposed by Hopkins (27), does not give complete replacement of exchangeable hydrogen. He has also shown that the use of calcium acetate, as first given by Jones (27), tends to give low results on heavier soils because calcium acetate solution is strongly buffered at too low a pH value to effect complete replacement of exchangeable hydrogen. A better suited method would seem to be one using a buffer of p-nitrophenol and lime water which is Schofield's (24) method. The p-nitrophenol is partially neutralized with the $Ca(OH)_2$ and is strongly buffered at pH 7.00. Upon addition of the buffer to an acid soil a measurable amount of the calcium is taken up. Innes and Birch (10) have shown that this method gives low results as compared with the Bradfield and Allison method (1) or Mehlich's method (12).

The method of Bradfield and Allison (1) uses a buffer of $NH_4Cl$ - .01N with respect $NH_4OH$. This is strongly buffered at pH 7.40. The difference in titration values before and after addition of the buffer to the soil gives the values for exchangeable hydrogen. Mehlich's (12) method makes use of barium chloride-triethanolamine buffer. This procedure is essentially the same as that of Bradfield and Allison with the buffer replacing the exchangeable hydrogen. Both the Bradfield and Allison and Mehlich methods have been shown to compare favorably (10).

Brown (5) by using normal ammonium acetate and pH determinations developed a simple means of determining lime requirement. By titrating the ammonium acetate with an acid, the number of milliliters added are plotted against pH depression. Then, by adding the ammonium acetate to the soil, the m.e. of hydrogen in the soil can be read directly from the pH depression caused by the addition of the soil to the buffer.

The pH changes in the buffer are small, however, and extreme accuracy must be exercised (20).

The most recent method for determination of lime requirement in the buffer group is the Woodruff procedure (28). In this method the buffer consists of a mixture of p-nitrophenol, calcium acetate and magnesium oxide, which is used to adjust the pH to exactly 7.00. The buffer is compounded so that when mixed with the soil each 0.1 pH unit that the buffer pH is depressed is equivalent to one m.e. of exchangeable hydrogen per 100 gm. of soil or 1000 pounds of $CaCO_3$ per acre.

Two methods involving color intensity have been used to some extent. The earliest is Comber's (6) which uses an alcoholic solution of potassium-thiocyanate to develop a red color with the soluble iron. The more acid a soil is the more intense will be the red color due to soluble iron. This method is much too empirical because of other factors besides pH that influence the solubility of iron in the soil (20). Sieling (25) has developed a colorimetric lime determining method using copper. A solution of cupric acetate - acetic acid is added to the soil sample. The amount of copper left in solution is measured by adding $NH_4OH$ which gvies a deep blue color. This method has been called sufficiently accurate for practical purposes by Lucas (11). However, in his comparisons with other methods it is not always in complete agreement.

There has also been considerable work done on the inter-relationships between pH, percent base saturation, and lime requirment. Hissink (9) was the first to designate the term percent base saturation and point out its importance. Bray and DeTurk (3) did not find a close relationship between pH and percent base saturation in Illinois soils. Below 60% saturation of the soil's exchange capacity there was very little correlation. However, above this point a better correlation was observed. Pierre and Scarseth (22) found that soils of the same reaction may vary considerably in their percentage base saturation. Morgan (16), Peech (18) and Mehlich (13, 14) have all found similar results. These investigators have found a direct relation between pH and percent base saturation. However, it is not a close correlation. Mehlich (13,14) has attributed this variation of percentage saturation at the same pH value to differences in the exchange complex. He has stated that the base unsaturation -- pH relationship is a specific expression of the nature of the base exchange complex present and is therefore not influenced by exchange capacity or buffer activity. According to Sieling (25), indications are that, in general, soils of higher exchange capacity require greater quantities of lime for neutralization than do soils of low exchange capacity at the same initial pH. Lucas (11) has found an excellent correlation between lime requirement and cation exchange capacity.

## EXPERIMENTAL MATERIALS AND METHODS

The soils used in this experiment ranged in texture from sandy soils to clay soils and were taken from twenty-three different counties in Michigan. The majority of these were in the southern half of the lower penninsula. The soils studied, together with their texture, depth, and location by county are given in Table 1. The approximate locations are shown on the map in Figure 1.

All soils were air dried and screened through a 20 mesh sieve before using.

## ANALYTICAL METHODS

Determination of pH -- a 1:1 soil-water ratio was used with a 10 gm. sample of soil. The soil suspensions were stirred at intervals during a 15 minute period and the pH values measured with a Beckman pH meter.

Determination of base exchange capacities -- the ammonium acetate method, as outlined by Peech (10), was employed. In this method a 20 gm. sample of soil was extracted with N, pH 7.0 ammonium acetate, and leached with 95% ethyl alcohol, and the ammonia displaced by sodium. The ammonia was then nesslerized and readings made on a photoelectric colorimeter.

Determination of total bases -- the method given by Bray and Willhite (2) was used. The ammonium acetate leachate from the base exchange capacity procedure was divided exactly in half. One aliquot of leachate was used in the determination of total bases, while the

TABLE 1

THE LOCATION, DEPTH OF SAMPLING AND TEXTURE OF SOIL TYPES USED

| Soil No. | Soil Type | Location County of Mich. | Depth or Layer |
|---|---|---|---|
| 1 | Mancelona Sandy Loam | Kalkaska | 6-34 inch |
| 2 | Bellfontaine Sandy Loam | Cass | 8-18 inch |
| 3 | Plainfield Sandy Loam | Cass | 6-22 inch |
| 4 | Kalkaska Sand | Benzie | 0-6 inch |
| 5 | Plainfield Sandy Loam | Cass | 0-6 inch |
| 6 | Bellfontaine Sandy Loam | Cass | 7-14 inch |
| 7 | Mancelona Sandy Loam | Kalkaska | 0-6 inch |
| 8 | Kalkaska Sand | Benzie | 6-24 inch |
| 9 | Bellfontaine Sandy Loam | Cass | 0-7 inch |
| 10 | Warsaw Loam | Kalamazoo | Surface |
| 11 | Fox Sandy Loam | St. Joseph | Surface |
| 12 | Bellfonatine Loam | Kalamazoo | Surface |
| 13 | Plainfield Sandy Loam | St. Joseph | Surface |
| 14 | Hillsdale Sandy Loam | Ingham | Surface |
| 15 | Plainfield Sandy Loam | Clinton | Surface |
| 16 | Waukesha Sandy Loam | St. Joseph | Surface |
| 6AS | Fox Loam | Branch | Subsoil |
| 7AS | Fox Loam | St. Joseph | Subsoil |
| 10AS | Miami Clay | Calhoun | Subsoil |
| 31AS | Arenac Sand | Saginaw | Subsoil |
| 75AS | Napanee Clay | Macomb | Subsoil |
| 30AS | Macomb Fine Sandy Loam | Saginaw | Surface |
| 101AS | Kent Silt Loam | Oceana | Subsoil |

TABLE 1 - Cont'd.

THE LOCATION, DEPTH OF SAMPLING AND TEXTURE OF SOIL TYPES USED

| Soil No. | Soil Type | Location County of Mich. | Depth or Layer |
|---|---|---|---|
| 71AS | Miami Loam | Lapeer | Surface |
| 59AS | Isabella Silt Loam | Isabella | Surface |
| 15AS | Berrien Sand | Lenawee | Surface |
| 21AS | Miami Clay Loam | Clinton | Subsoil |
| 97AS | Isabella Clay | Ottawa | Subsoil |
| 4AS | Hillsdale Loam | Branch | Subsoil |
| 2AS | Hillsdale Loam | Hillsdale | Subsoil |
| 14AS | Conover Silt Loam | Lenawee | Subsoil |
| 98AS | Berrien Sand | Ottawa | Surface |
| 100AS | Kent Clay | Oceana | Subsoil |
| 1B | Conover Loam | Calhoun | Surface |
| 53AS | Napanee Silt Loam | Sanilac | Subsoil |
| 26AS | Brady Sandy Loam | Ingham | Surface |
| 3AS | Hillsdale Loam | Branch | Surface |
| 96AS | Conover Loam | Ionia | Surface |
| 42AS | Coloma Sand | Livingston | Surface |
| 5AS | Fox Loam | Branch | Subsoil |
| 1AS | Conover Loam | Calhoun | Subsoil |
| 27AS | Coloma Loamy Sand | Ingham | Surface |
| 8As | Miami Silt Loam | Cass | Subsoil |
| 89AS | Onaway Loam | Alcona | Surface |

**FIG. 1 APPROXIMATE LOCATIONS OF SOILS USED**

other portion was required for the determination of exchangeable calcium.

Determination of exchangeable calcium -- The above mentioned aliquot of ammonium acetate leachate was used for the determination of exchangeable calcium. It was evaporated to a volume below 100 ml. and brought back to a 100 ml. volume with distilled water. The flame photometer used was a Perkin-Elmer flame photometer, model 52A. The procedure followed was that outlined by Toth and Prince (26).

Methods for Determination of Lime Requirement -

1- Calcium carbonate method - additions of precipitated $CaCO_3$ were made to 100 gm. samples of soil. On light textured soils these additions were made at rates varying from 1000 to 8000 pounds per acre. On the heavier soils the applications of $CaCO_3$ ranged from 2000 pounds to 12000 pounds per acre. These soils were incubated in a moist condition for three months. After incubation the soils were air dried and the pH measured.

2- Method of Bradfield and Allison (1) - Two-gram samples of soil were thoroughly mixed with 100 ml of ammonium chloride buffer solution. The buffer consists of N ammonium chloride - .01 N with respect to ammonium hydroxide and with a pH of 7.4. The mixture of soil and buffer was allowed to stand for one hour and filtered. Twenty-five milliliters of the filtrate were then titrated with .01 N HCL using methyl red as an indicator. A blank of twenty-five milliliters of buffer solution was titrated to the same end point and exchangeable hydrogen measured by difference between the two titration values.

3- Woodruff buffer method (28) - Woodruff's buffer solution consists of a mixture of 8 gm. of p-nitrophenol, 40 gm. of calcium acetate, and 0.62 gm. of magnesium oxide per liter of solution. It is adjusted to exactly pH 7.00 with MgO or dilute HCl as required. Ten gm. soil samples were mixed with 20 ml of buffer solution and allowed to stand for 30 minutes. A pH determination was then made on the sample. From this pH reading the lime requirement was determined by observing how much the addition of the soil to the buffer had lowered its pH value. This is called the pH depression. The buffer is so compounded that when mixed with the soil each 0.1 pH depression below pH 7.0 is equivalent to one m.e. of hydrogen or to 1000 pounds of $CaCO_3$ per acre.

4- Bouyoucos Hydrometer Method (4) - This method was used for the mechanical analyses of selected soils. In this most recent method, as outlined by Bouyoucos, a dispersing agent of sodium hexametophosphate is used and only two readings taken, 40 seconds and two hours. Other steps in the procedure are, in general, the same as have been in practice for a number of years in making mechanical analyses with the hydrometer.

## EXPERIMENTAL

For each soil the pH, cation exchange capacity, percent base saturation, and exchangeable calcium was determined according to the methods previously given. These basic soil chemical data are presented in Table 2.

The values for the determination of lime requirement by the Woodruff method for all soils are given in Table 3 along with the pH depression.

In Table 4 is listed the increments of $CaCO_3$ in pounds per acre added to 15 selected soils, some fine and some coarse textured. Six treatments were carried out for each soil. The additions of lime for both light and heavy soils are given along with the pH value, recorded after a three months moist incubation period, with that particular increment. From these data the lime requirement value was considered to be the increment of $CaCO_3$ which brought the soil sample closest to a pH of 7.0. By using the lime requirement data obtained with the carbonate method and plotting them against exchangeable hydrogen obtained by the difference between the cation exchange capacity and total base content of the soils, a definite relationship was found. This is shown in Fig. 2 where it is observed that the lime requirement increases regularly with the exchangeable hydrogen in the soil. This would probably indicate that an accurate determination of exchangeable hydrogen leads to an accurate evaluation of the lime needs of soils. In Fig. 3 curves are plotted to represent the rise in pH with increasing

TABLE 2

THE RELATIONSHIP BETWEEN SOIL pH AND CATION EXCHANGE CAPACITY, PERCENT BASE SATURATION, AND EXCHANGEABLE CALCIUM IN SOME MICHIGAN SOILS

| Soil No. | Soil Type | Soil pH | Cation Exchange Capacity* m.e./100gm. | Total Bases* m.e./100gm. | Base Saturation Percent | Dial Read. Exch. Ca Flame Photo.* | Exch. Ca.* m.e./100gm |
|---|---|---|---|---|---|---|---|
| 1 | Mancelona Sandy Loam | 6.50 | 2.50 | 2.16 | 86.40 | 22.7 | 1.95 |
| 2 | Bellfontaine Sandy Loam | 5.40 | 4.81 | 3.32 | 69.02 | 28.2 | 2.60 |
| 3 | Plainfield Sandy Loam | 5.63 | 2.53 | 1.55 | 61.26 | ---- | ---- |
| 4 | Kalkaska Sand | 6.00 | 2.82 | 1.81 | 64.16 | 17.0 | 1.42 |
| 5 | Plainfield Sandy Loam | 5.80 | 3.75 | 2.49 | 66.40 | 28.9 | 2.70 |
| 6 | Bellfontaine Sandy Loam | 5.39 | 6.44 | 3.78 | 58.70 | 34.7 | 3.12 |
| 7 | Mancelona Sandy Loam | 5.80 | 6.44 | 3.37 | 52.33 | ---- | ---- |
| 8 | Kalkaska Sand | 6.26 | 2.14 | 1.17 | 54.67 | 12.8 | 1.05 |
| 9 | Bellfontaine Sandy Loam | 6.25 | 6.35 | 4.40 | 69.21 | ---- | ---- |
| 10 | Warsaw Loam | 5.59 | 20.45 | 9.81 | 47.96 | 79.3 | 7.85 |
| 11 | Fox Sandy Loam | 5.80 | 3.75 | 1.90 | 50.67 | ---- | ---- |
| 12 | Bellfontaine Loam | 4.85 | 8.31 | 2.71 | 32.61 | ---- | ---- |
| 13 | Plainfield Sandy Loam | 5.47 | 6.06 | 2.78 | 45.87 | 31.0 | 2.70 |
| 14 | Hillsdale Sandy Loam | 5.20 | 7.49 | 3.33 | 45.40 | 34.4 | 3.10 |
| 15 | Plainfield Sandy Loam | 5.58 | 4.19 | 2.25 | 53.70 | 24.0 | 2.10 |
| 16 | Waukesha Sandy Loam | 5.11 | 14.70 | 7.49 | 50.90 | 70.1 | 6.82 |
| 6AS | Fox Loam | 5.33 | 5.00 | 1.55 | 31.50 | 17.1 | 1.45 |
| 7AS | Fox Loam | 5.12 | 14.21 | 8.95 | 62.77 | 72.2 | 7.05 |

* Average of duplicate samples

TABLE 2 - Cont'd.

THE RELATIONSHIP BETWEEN SOIL pH AND CATION EXCHANGE CAPACITY, PERCENT BASE SATURATION, AND EXCHANGEABLE CALCIUM IN SOME MICHIGAN SOILS

| Soil No. | Soil Type | Soil pH | Cation Exchange Capacity* m.e./100gm. | Total Bases* m.e./100gm. | Base Saturation Percent | Dial Read. Exch. Ca Flame Photo.* | Exch. Ca.* m.e./100gm |
|---|---|---|---|---|---|---|---|
| 10AS | Miami Clay | 5.43 | 15.40 | 12.54 | 81.43 | 97.3 | 9.97 |
| 31AS | Arenac Sand | 4.75 | 5.91 | 0.59 | 10 | 10.9 | 0.85 |
| 75AS | Napanee Clay | 5.50 | 19.00 | 13.95 | 73.68 | 83.2 | 8.30 |
| 30AS | Macomb Fine Sandy Loam | 5.70 | 6.00 | 4.03 | 67.16 | 37.2 | 3.42 |
| 101As | Kent Silt Loam | 7.50 | 12.62 | 17.43 | 100 | 97.0** | 12.32 |
| 71As | Miami Loam0 | 5.32 | 15.93 | 10.31 | 64.72 | 78.8 | 7.80 |
| 59AS | Isabella Silt Loam | 6.28 | 7.50 | 5.66 | 75.45 | ---- | ---- |
| 15AS | Berrien Sand | 7.30 | 12.25 | 14.06 | 100 | 96.1** | 9.75 |
| 21AS | Miami Clay Loam | 4.95 | 11.70 | 8.04 | 68.72 | 61.5 | 6.17 |
| 97AS | Isabella Clay | 5.46 | 19.60 | 15.60 | 74.38 | 93.1 | 9.45 |
| 4AS | Hillsdale Loam | 6.16 | 5.00 | 4.07 | 81.40 | 36.4 | 3.30 |
| 2AS | Hillsdale Loam | 5.15 | 2.94 | 1.59 | 54.08 | 16.0 | 1.35 |
| 14AS | Conover Silt Loam | 7.50 | 12.25 | 18.46 | 100 | ---- | 150 |
| 98AS | Berrien Sand | 5.45 | 1.98 | 1.03 | 52.02 | 11.7 | 0.95 |
| 100AS | Kent Clay | 6.20 | 18.74 | 16.00 | 85.38 | ---- | ---- |
| 1B | Conover Loam | 6.01 | 8.31 | 5.45 | 65.58 | 51.9 | 4.85 |
| 53AS | Napanee Silt Loam | 5.10 | 9.80 | 4.77 | 48.67 | 42.4 | 3.90 |
| 26AS | Brady Sandy Loam | 6.46 | 3.42 | 3.36 | 98.24 | 32.5 | 3.02 |
| 3AS | Hillsdale Loam | 5.90 | 4.81 | 2.03 | 42.2 | 25.6 | 2.25 |
| 96AS | Conover Loam | 6.40 | 7.69 | 10.78 | 100 | 97.6 | 9.95 |
| 42AS | Coloma Sand | 5.80 | 2.54 | 1.78 | 59.60 | 15.7 | 1.30 |
| 5AS | Fox Loam | 6.10 | 3.31 | 2.10 | 63.44 | 22.5 | 1.92 |
| 1AS | Conover Loam | 5.44 | 8.31 | 5.55 | 66.78 | 52.0 | 4.92 |
| 27AS | Coloma Loamy Sand | 6.34 | 1.46 | 1.42 | 56.80 | 15.2 | 1.27 |
| 8AS | Miami Silt Loam | 6.18 | 15.93 | 11.98 | 75.34 | 92.1 | 9.25 |
| 89AS | Onaway Loam | 5.68 | 7.35 | 3.22 | 43.81 | 33.7 | 3.02 |

* Average of duplicate samples
** A separate curve used for very high readings

TABLE 3

DETERMINATION OF LIME REQUIRMENT BY WOODRUFF METHOD

| Soil No. | Soil Type | pH depression | lbs. $CaCO_3$ /Acre | Soil No. | Soil Type | pH depression | lbs. $CaCO_3$ /Acre |
|---|---|---|---|---|---|---|---|
| 1 | Mancelona Sandy Loam | 0.080 | 800 | 71AS | Miami Loam | 0.295 | 2950 |
| 2 | Bellfontaine Sandy Loam | 0.125 | 1250 | 59AS | Isabella Heavy Soil | 0.150 | 1500 |
| 3 | Plainfield Sandy Loam | 0.100 | 1000 | 15AS | Berrien Sand | ——— | ——— |
| 4 | Kalkaska Sand | 0.100 | 1000 | 21AS | Miami Clay | 0.300 | 3000 |
| 5 | Plainfield Sandy Loam | 0.170 | 1700 | 97AS | Isabella Clay | 0.285 | 2850 |
| 6 | Bellfontaine Sandy Loam | 0.160 | 1600 | 4ASS | Hillsdale Loam | 0.140 | 1400 |
| 7 | Mancelona Sandy Loam | 0.140 | 1400 | 2AS | Hillsdale Loam | 0.190 | 1900 |
| 8 | Kalkaska Sand | 0.030 | 300 | 14AS | Conover Silt Loam | ——— | ——— |
| 9 | Bellfontaine Sandy Loam | 0.155 | 1550 | 98AS | Berrien Sand | 0.150 | 1500 |
| 10 | Warsaw Loam | 0.540 | 5400 | 100AS | Kent Clay | 0.200 | 2000 |
| 11 | Fox Sandy Loam | 0.110 | 1100 | 1B | Conover Loam | 0.200 | 2000 |
| 12 | Bellfontaine Loam | 0.400 | 4000 | 53ASS | Napanee Silt Loam | 0.300 | 3000 |
| 13 | Plainfield Sandy Loam | 0.215 | 2150 | 26AS | Brady Sandy Loam | 0.500 | 5000 |
| 14 | Hillsdale Sandy Loam | 0.300 | 3000 | 3AS | Hillsdale Loam | 0.290 | 2900 |
| 15 | Plainfield Sandy Loam | 0.185 | 1850 | 96AS | Conover Loam | 0.150 | 1500 |
| 16 | Waukesha Sandy Loam | 0.700 | 7000 | 42ASS | Coloma Sand | 0.090 | 900 |

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TABLE 3 - Cont'd.

DETERMINATION OF LIME REQUIREMENT BY WOODRUFF METHOD

| Soil No. | Soil Type | pH depression | lb. $CaCO_3$ /Acre | Soil No. | Soil Type | pH depression | lbs. $CaCO_3$ /Acre |
|---|---|---|---|---|---|---|---|
| 6AS | Fox Loam | 0.180 | 1800 | 5AS | Fox Loam | 0.080 | 800 |
| 7AS | Fox Loam | 0.370 | 3700 | 1AS | Conover Loam | 0.215 | 2150 |
| 10AS | Miami Clay | 0.260 | 2600 | 27AS | Coloma Loamy Sand | 0.060 | 600 |
| 31AS | Arenac Sand | 0.305 | 3050 | 8AS | Miami Silt Loam | 0.200 | 2000 |
| 75ASS | Napanee Clay | 0.300 | 3000 | 89AS | Onaway Loam | 0.190 | 1900 |
| 30AS | Macomb Fine Sandy Loam | 0.180 | 1800 | | | | |
| 101AS | Kent Silt Loam | ——— | ——— | | | | |

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TABLE 4

EFFECT OF ADDITION OF LIME ON pH OF SELECTED SOILS

Light or Coarse Textured Soils, pH after addition of $CaCO_3$ (lbs./Acre)

| Soil No. | Soil Type | Original pH | 1000 | 2000 | 3000 | 4000 | 6000 | 8000 |
|---|---|---|---|---|---|---|---|---|
| 9 | Bellfontaine Sandy Loam | 6.25 | 6.60 | 7.00 | 7.05 | 7.10 | 7.25 | 7.28 |
| 13 | Plainfield Sandy Loam | 5.47 | 5.45 | 6.50 | 6.42 | 7.10 | 7.30 | 7.40 |
| 4 | Kalkaska Sand | 6.00 | 7.20 | 7.20 | 7.50 | 7.62 | 7.72 | 7.80 |
| 14 | Hillsdale Sandy Loam | 5.20 | 5.25 | 5.70 | 6.00 | 6.38 | 6.95 | 7.30 |
| 31AS | Arenac Sand | 4.75 | 5.70 | 6.00 | 6.28 | 6.70 | 6.98 | 7.50 |
| 98AS | Berrien Sand | 5.45 | 6.75 | 7.35 | 7.65 | 7.79 | 7.80 | 7.95 |
| 42AS | Coloma Sand | 5.80 | 7.25 | 7.50 | 7.68 | 7.83 | 7.98 | |

Heavy or Fine Textured Soils, pH after addition $CaCO_3$ (lbs./Acre)

| SOIL No. | Soil Type | Original pH | 2000 | 4000 | 6000 | 8000 | 10000 | 12000 |
|---|---|---|---|---|---|---|---|---|
| 9 | Warsaw Loam | 5.59 | 5.55 | 5.94 | 6.40 | 6.80 | 7.10 | 7.40 |
| 10AS | Miami Clay | 5.43 | 6.70 | 7.27 | 7.60 | 7.72 | 7.78 | 7.80 |
| 16 | Waukesha Sandy Loam | 5.11 | 5.42 | 6.30 | 5.90 | 6.52 | 7.00 | 7.00 |
| 97AS | Isabella Clay | 5.46 | 6.50 | 7.15 | 7.55 | 7.78 | 7.80 | 7.86 |
| 75AS | Napanee Clay | 5.50 | 6.30 | 6.83 | 7.15 | 7.55 | 7.65 | 7.70 |

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TABLE 4 - Cont'd.

EFFECT OF ADDITION OF LIME ON pH OF SELECTED SOILS

| Soil No. | Soil Type | Original pH | Heavy or Fine Textured Soils. pH after addition of $CaCO_3$ (lbs./Acre) 2000 | 4000 | 6000 | 8000 | 10000 | 12000 |
|---|---|---|---|---|---|---|---|---|
| 21AS | Miami Clay Loam | 4.95 | 6.25 | 7.00 | 7.43 | 7.53 | 7.72 | 7.88 |
| 100AS | Kent Clay | 6.20 | 7.25 | 7.55 | 7.70 | 7.82 | | |
| 7AS | Fox Loam | 5.12 | 6.50 | 6.93 | 7.38 | 7.50 | 7.62 | 7.74 |

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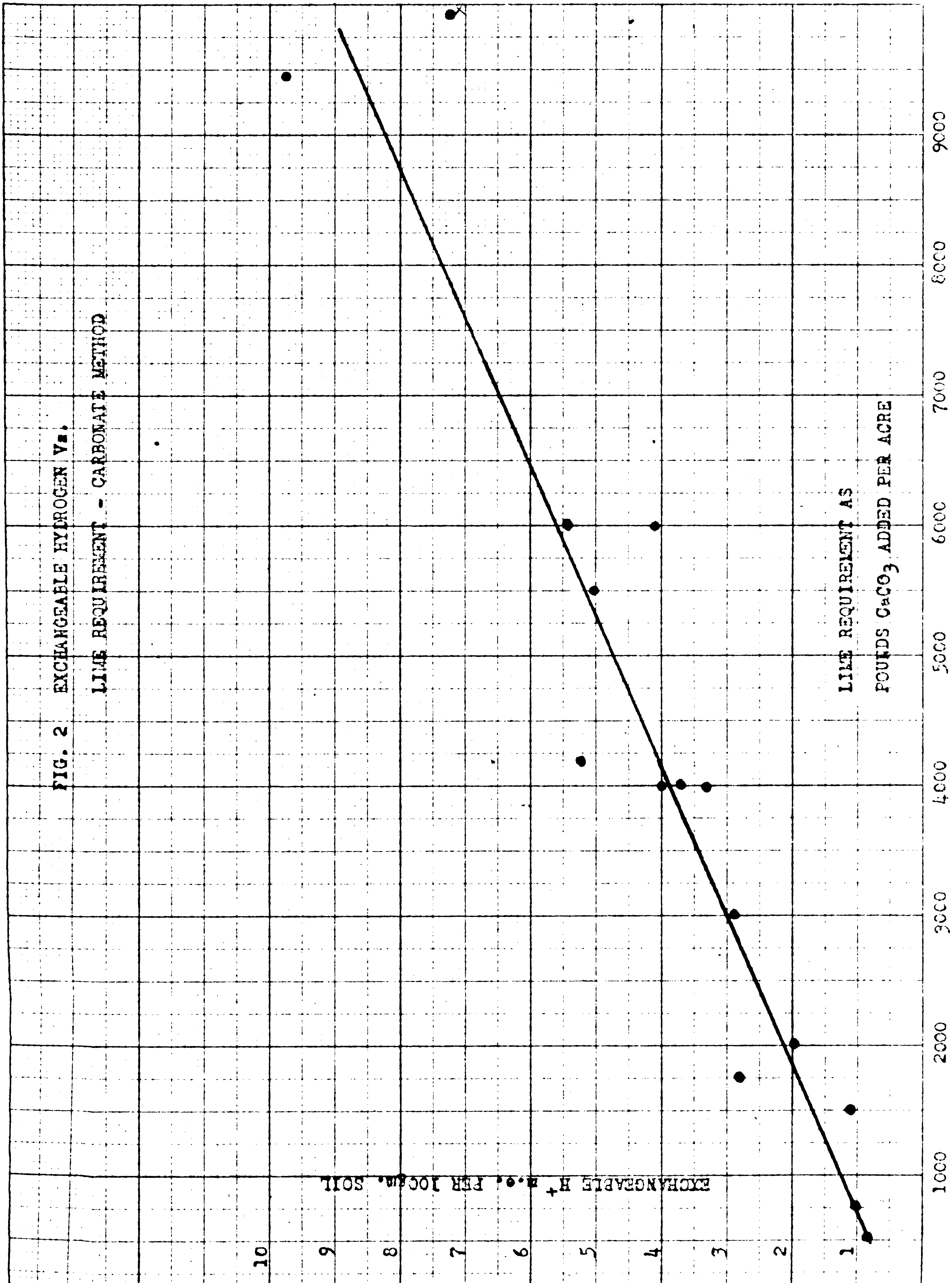


FIG. 2 EXCHANGEABLE HYDROGEN Vs.
LIME REQUIREMENT - CARBONATE METHOD

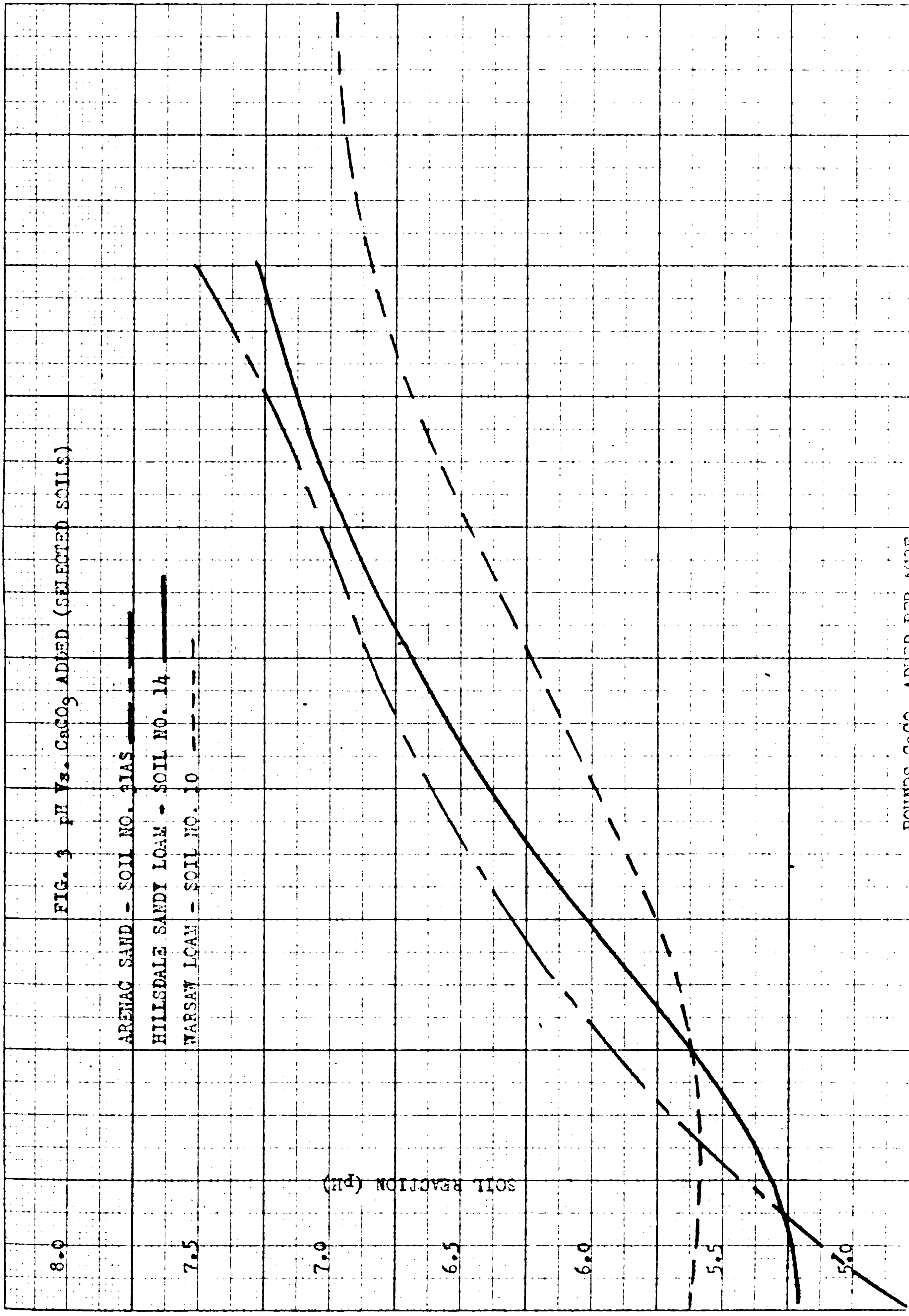


FIG. 3 pH Vs. $CaCO_3$ ADDED (SELECTED SOILS) increments of $CaCO_3$ for three selected soils. From this graph it can readily be seen that the original pH value is a poor indicator for the estimation of lime requirement. Soil no. 10 has the higher original pH, but it also exhibits the higher lime requirment. This soil is the finest textured of the three samples and also has the highest cation exchange capacity (17.21 as compared to 7.49 and 5.91 m.e. per 100 gm. soil). This high lime requirement is to be expected, since it would require considerably more lime to saturate the higher capacity even though the original pH was greater.

A comparison of the carbonate, Woodruff, and Bradfield and Allison methods, is shown in Table 5. Although the agreement of lime requirement values by the two methods is good for a few soils, there appears to be a real difference in the values given by the two buffer procedures. On the other hand, the $CaCO_3$ method for obtaining lime requirement values checks more consistently with the Woodruff values than it does with the method of Bradfield and Allison. However, there are instances where the carbonate method also checks fairly well with the results of the Bradfield and Allison procedure.

Several scatter diagrams showing the relationships between the lime requirement, pH, percent base saturation, base exchange capacity, and soil texture are presented in the following pages.

As shown in Fig. 4 there is a definite relationship between pH and percent base saturation. However, it is not one which can be relied upon to give accurate information concerning the percent base saturation of a specific soil complex at a certain pH value. At any

TABLE 5

LIME REQUIREMENT VALUES OF MICHIGAN SOILS BY THREE DIFFERENT CHEMICAL METHODS

| Soil No. | Soil Type | Carbonate Method lbs. $CaCO_3$/Acre | Bradfield & Allison Method m.e.H /100 gm.* | Bradfield & Allison Method lbs. $CaCO_3$/Acre* | Woodruff Method lbs. $CaCO_3$/Acre |
|---|---|---|---|---|---|
| 9 | Bellfontaine Sandy Loam | 2000 | 2.58 | 2580 | 1600 |
| 13 | Plainfield Sandy Loam | 4000 | 3.70 | 3700 | 2200 |
| 4 | Kalkaska Sand | 1000 | 1.80 | 1800 | 1000 |
| 14 | Hillsdale Sandy Loam | 6000 | 4.52 | 4520 | 3000 |
| 31AS | Arenac Sand | 6000 | 5.75 | 5750 | 3100 |
| 98AS | Berrien Sand | 1500 | 1.74 | 1740 | 1500 |
| 42AS | Coloma Sand | 1000 | 1.10 | 1100 | 900 |
| 10 | Warsaw Loam | 9500 | 7.27 | 7270 | 5400 |
| 10AS | Miami Clay | 3000 | 6.10 | 6100 | 2600 |
| 16 | Waukesha Sandy Loam | 10000 | 8.80 | 8800 | 7000 |
| 97AS | Isabella Clay | 4000 | 4.89 | 4890 | 3000 |
| 75ASS | Napanee Clay | 5500 | 5.00 | 5000 | 3000 |
| 21AS | Miami Clay Loam | 4000 | 4.20 | 4200 | 3000 |
| 100AS | Kent Clay | 2000 | 3.60 | 3600 | 2000 |
| 7AS | Fox Loam | 4200 | 4.95 | 4950 | 3800 |

* Average of duplicate samples

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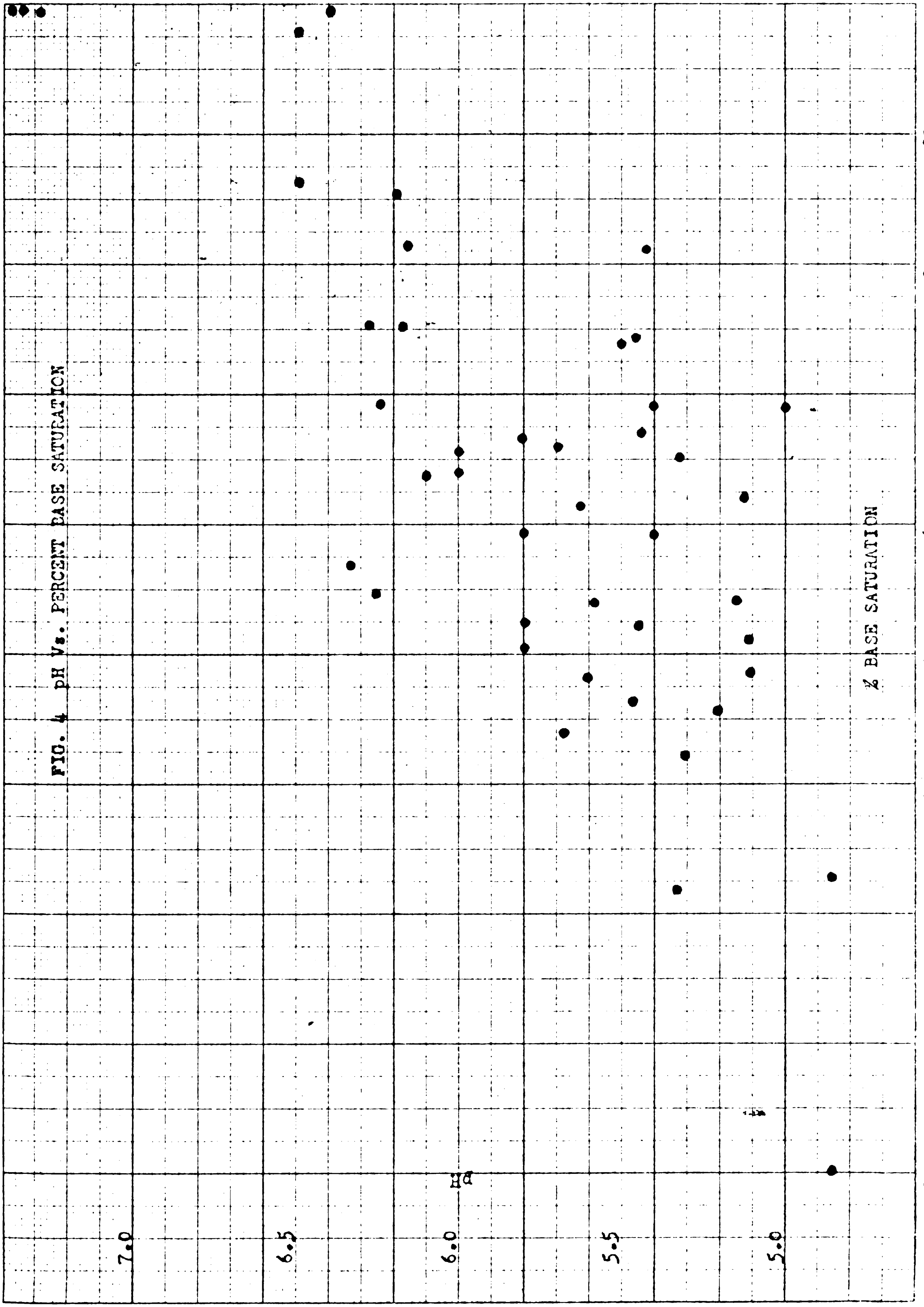


FIG. 4 pH Vs. PERCENT BASE SATURATION

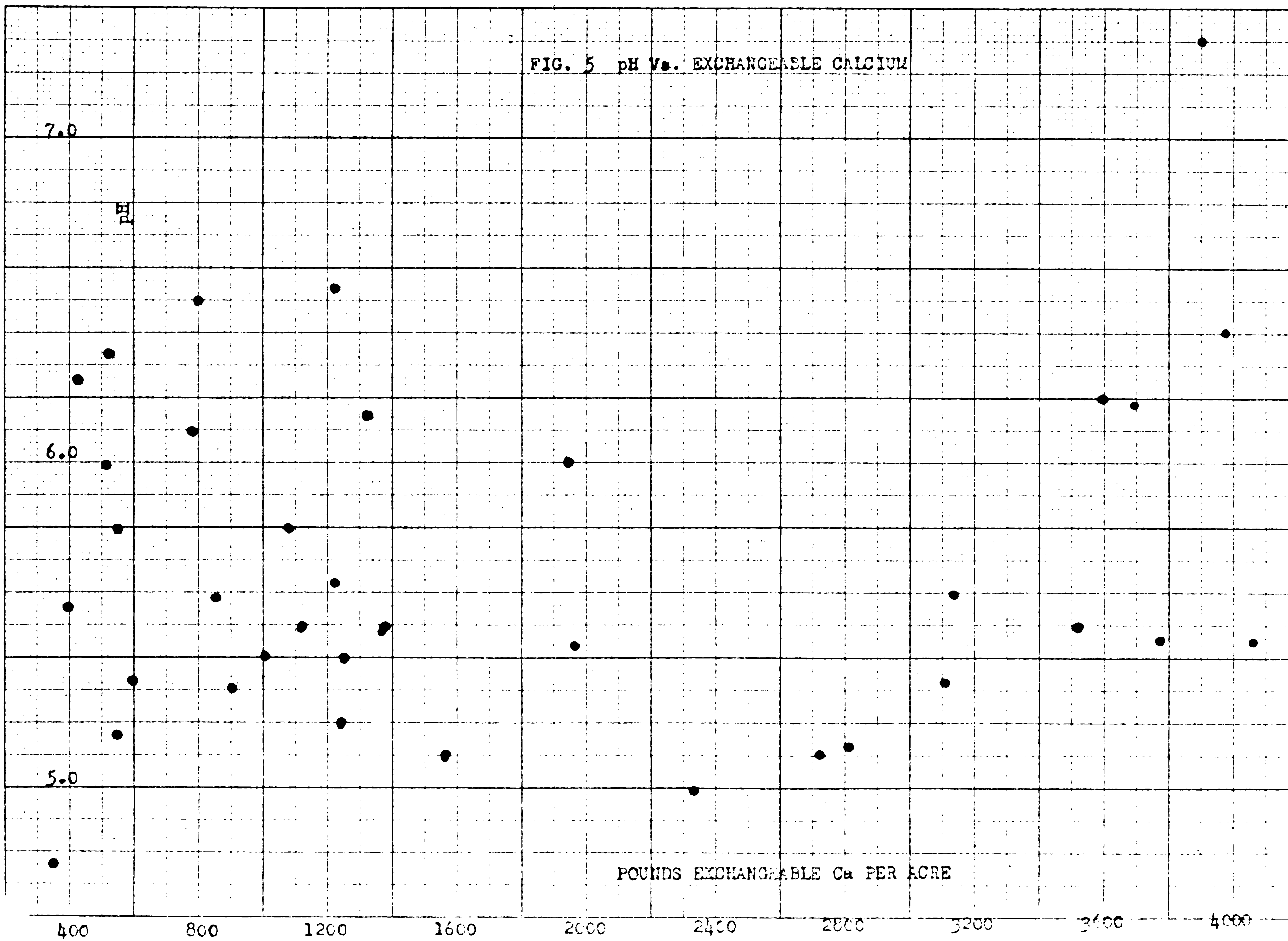
FIG. 5 pH Vs. EXCHANGEABLE CALCIUM
7.0
pH
6.0
5.0
POUNDS EXCHANGEABLE Ca PER ACRE
400
800
1200
1600
2000
2400
2800
3200
3600
4000

given pH value, such as 5.5 in Fig. 4, the percent base saturation may range from as low as 45% to as high as 75% for a number of different soils.

Fig. 5 data of pH and exchangeable calcium were plotted to see if a definite relation exists between these two soil properties. From the scatter diagram it is doubtful whether there is a relation. By examining only the left hand portion of Fig. 5, the pH is noted. to increase with decreasing calcium. This is just the opposite of what one might expect. However, by close examination it is seen that the soils with higher pH values and lower exchangeable calcium contents have relatively low cation exchange capacities and therefore do not require a large amount of calcium for complete saturation. Although this observation is not borne out too well in Fig. 5, it is emphasized because later figures show a similar relationship to a much greater degree.

By comparing pH with Woodruff lime requirement values in Fig. 6, a definite relationship is noted; as pH decreases lime requirment increases. Although this correlation is greater than that between pH and percent base saturation, the fact remains that the points on the diagram are still widely scattered.

Since there is a closer correlation between Woodruff lime requirement and pH than is exhibited between pH and percent base saturation, it is only logical that there should be a rather loose relationship between Woodruff lime requirement and percent base saturation. These data are shown in Fig. 7. There is a moderate decrease in percent base saturation with an increased lime requirement

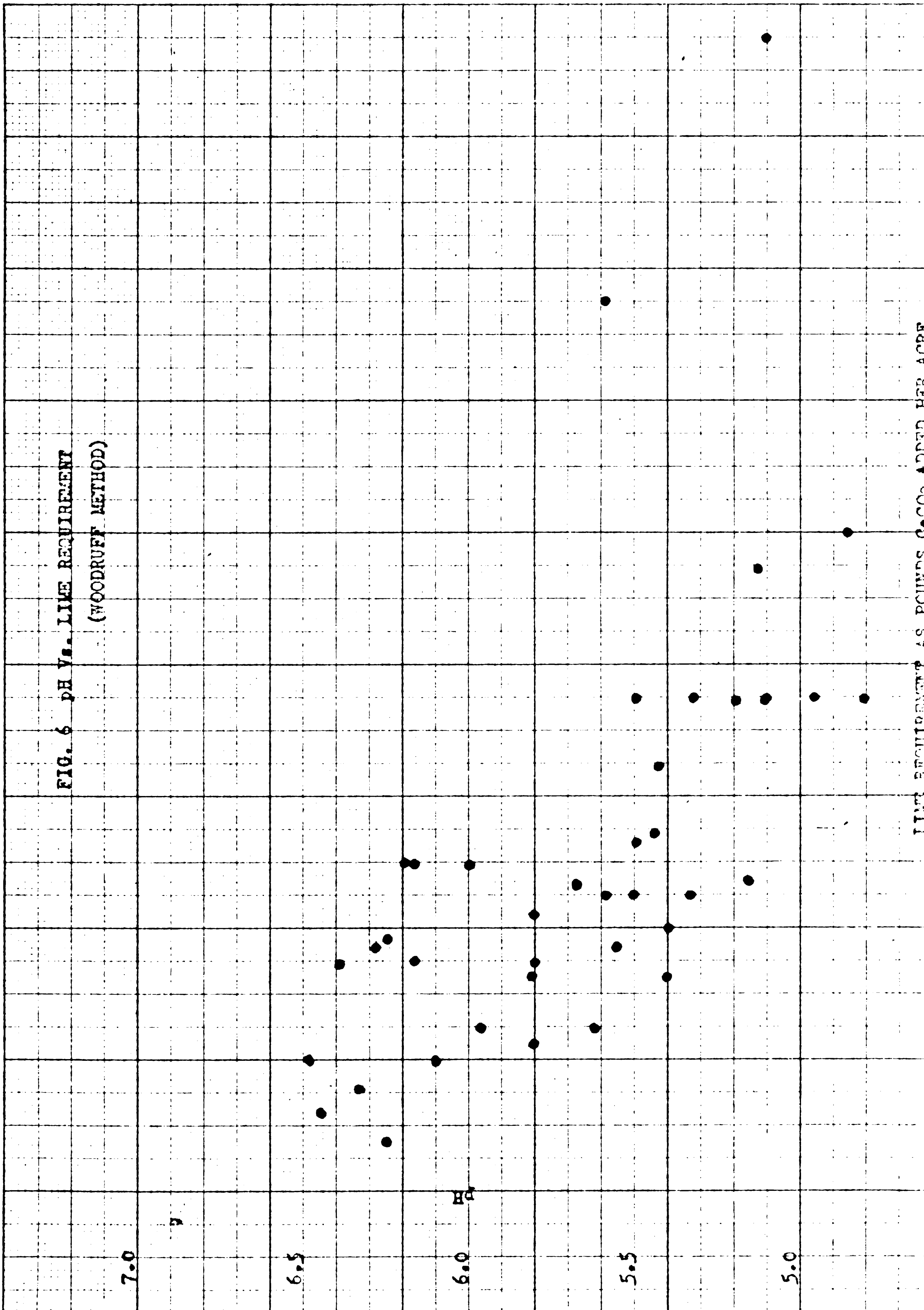


FIG. 6 pH Vs. LIME REQUIREMENT
(WOODRUFF METHOD)

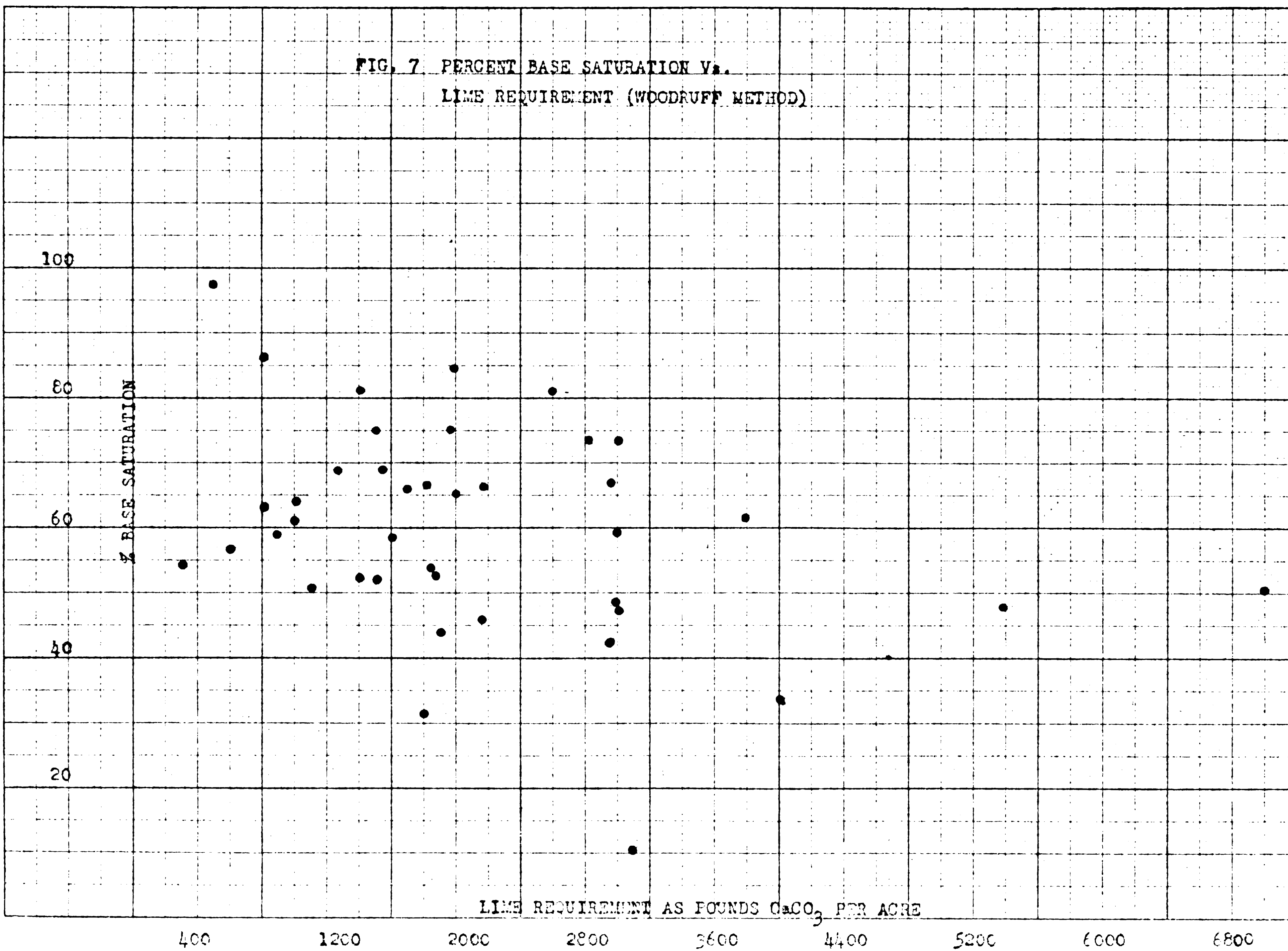
FIG. 7 PERCENT BASE SATURATION Vs.
LIME REQUIREMENT (WOODRUFF METHOD)
% BASE SATURATION
100
80
60
40
20
LIME REQUIREMENT AS POUNDS CaCO3 PER ACRE
400
1200
2000
2800
3600
4400
5200
6000
6800

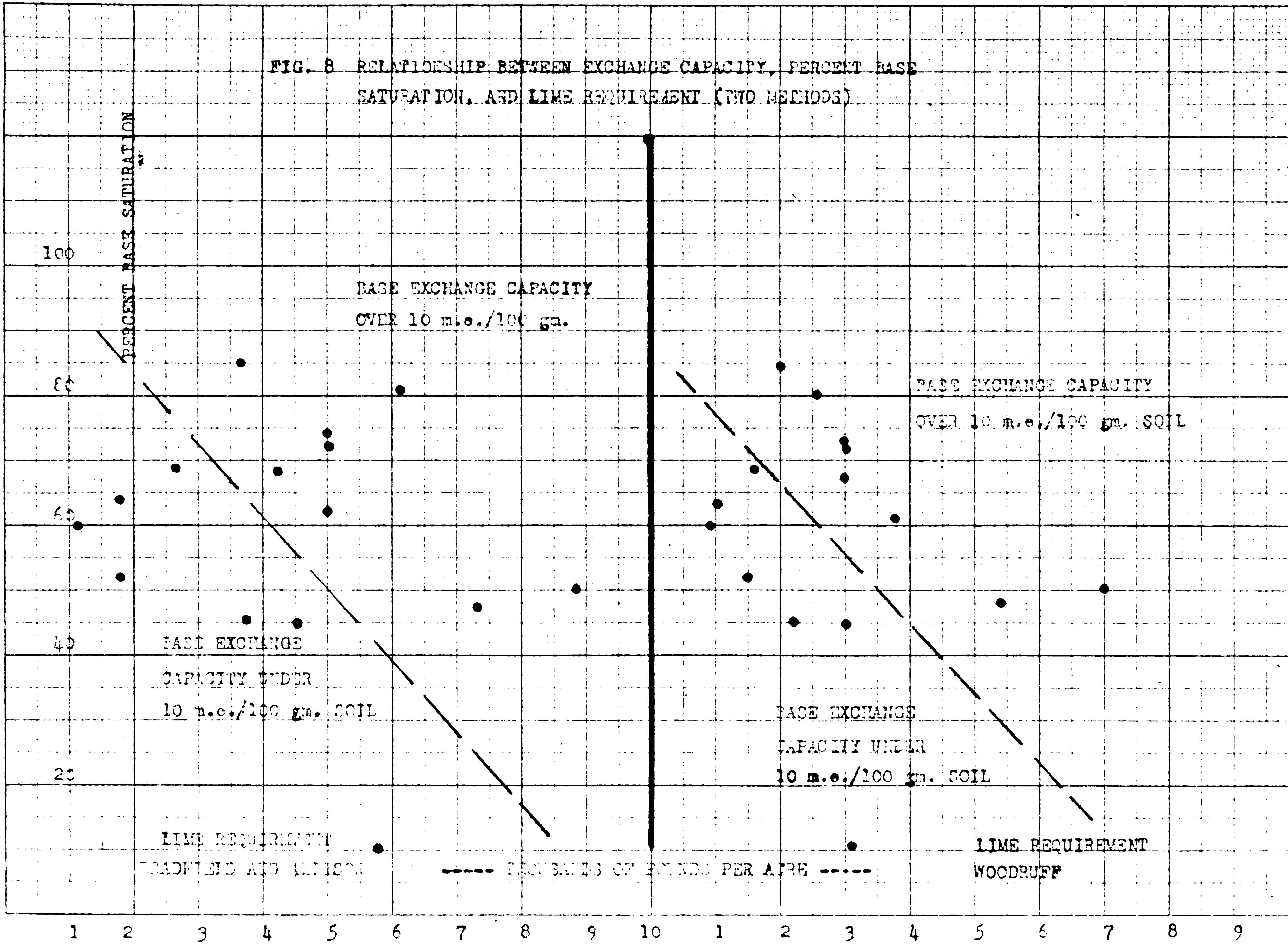


FIG. 8 RELATIONSHIP BETWEEN EXCHANGE CAPACITY, PERCENT BASE SATURATION, AND LIME REQUIREMENT (TWO METHODS)

as shown by the Woodruff method. However, the diagram shows a large scattering of points.

Fig. 8 has been included to explain why a definte correlation between percent base saturation and lime requirement should not be expected. In this graph two different methods of lime requirement, Bradfield and Allison, and Woodruff, are plotted against percent base saturation. Both lime requirement methods in Fig. 8 show the lime requirement values to be higher for the soil with a greater exchange capacity, even though the percent base saturation values are nearly equal. A similar relationship was previously shown in Fig. 3 between pH and lime requirement.

Exchangeable calcium and lime requirement values are plotted in Fig. 9. In this diagram exchangeable calcium is definitely shown to increase with an increasing requirement for lime by the soils. Once again, as in Fig. 5., this relationship might not be expected. A reasonable explanation is that soils which have higher lime requirements (and higher calcium contents) have larger exchange capacities. Even though the calcium content is relatively high, it requires considerably more lime to saturate the exchange complex of a soil with a high saturation capacity than it does with a low capacity. From these observations it would seem plausable to conclude that determination of exchangeable calcium is a poor indicator for lime requirement of soils.

The important effect of cation exchange capacity on lime requirement is illustrated in Fig. 10. A relatively constant increase

TABLE 6

MECHANICAL ANALYSES OF 15 SELECTED SOILS USING THEY HYDROMETER METHOD

| Soil No. | Soil Type | Corrected* 40 sec. reading | % Sand 2.00-0.05 m.m. | Corrected* 2 hr. reading | % Silt 0.05-0.002 m.m. | % Clay below 0.002 m.m. |
|---|---|---|---|---|---|---|
| 9 | Bellfontaine Sandy Loam | 14.36 | 71.28 | 5.36 | 18.00 | 10.72 |
| 13 | Plainfield Sandy Loam | 11.86 | 76.38 | 5.86 | 4.62 | 19.00 |
| 4** | Kalkaska Sand | 6.68 | 93.32 | 3.82 | 2.86 | 3.82 |
| 14 | Hillsdale Sandy Loam | 17.36 | 65.28 | 5.86 | 33.00 | 11.72 |
| 31AS** | Arenac Sand | 10.18 | 89.82 | 4.32 | 5.86 | 4.32 |
| 98AS | Berrien Sand | 4.86 | 90.28 | 3.36 | 3.00 | 6.72 |
| 42AS** | Coloma Sand | 8.68 | 91.32 | 4.32 | 4.36 | 4.32 |
| 10 | Warsaw Loam | 25.18 | 49.64 | 6.82 | 36.72 | 13.64 |
| 10AS | Miami Clay | 34.68 | 30.64 | 23.82 | 21.72 | 47.64 |
| 16 | Waukesha Sandy Loam | 17.68 | 64.64 | 8.32 | 18.72 | 16.64 |
| 97AS | Isabella Clay | 34.86 | 30.28 | 24.86 | 20.00 | 49.72 |
| 75AS | Napanee Clay | 31.36 | 37.28 | 24.86 | 13.00 | 49.72 |
| 21AS | Miamia Clay Loam | 29.18 | 41.64 | 19.32 | 19.72 | 38.64 |
| 100AS | Kent Clay | 33.18 | 33.64 | 21.82 | 23.72 | 42.64 |
| 7AS | Fox Loam | 33.36 | 33.28 | 14.32 | 38.08 | 28.64 |

* Corrected for temperature variation.
** 100 gm. sample used. For all others a 50 gm. sample was used.

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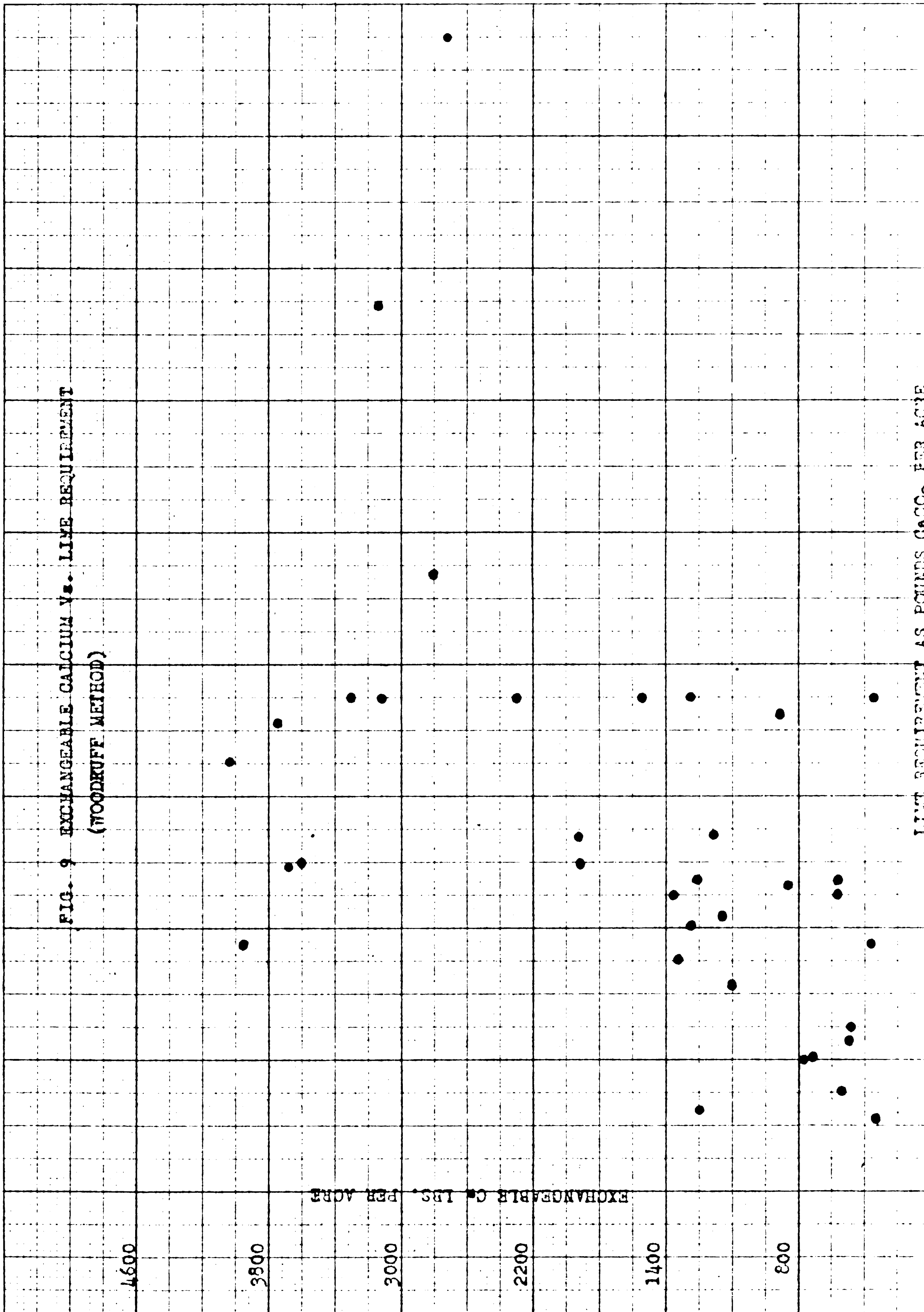



FIG. 9 EXCHANGEABLE CALCIUM Vs. LIME REQUIREMENT (WOODRUFF METHOD)

FIG. 10 BASE EXCHANGE CAPACITY Vs. LIME REQUIREMENT (WOODRUFF METHOD)

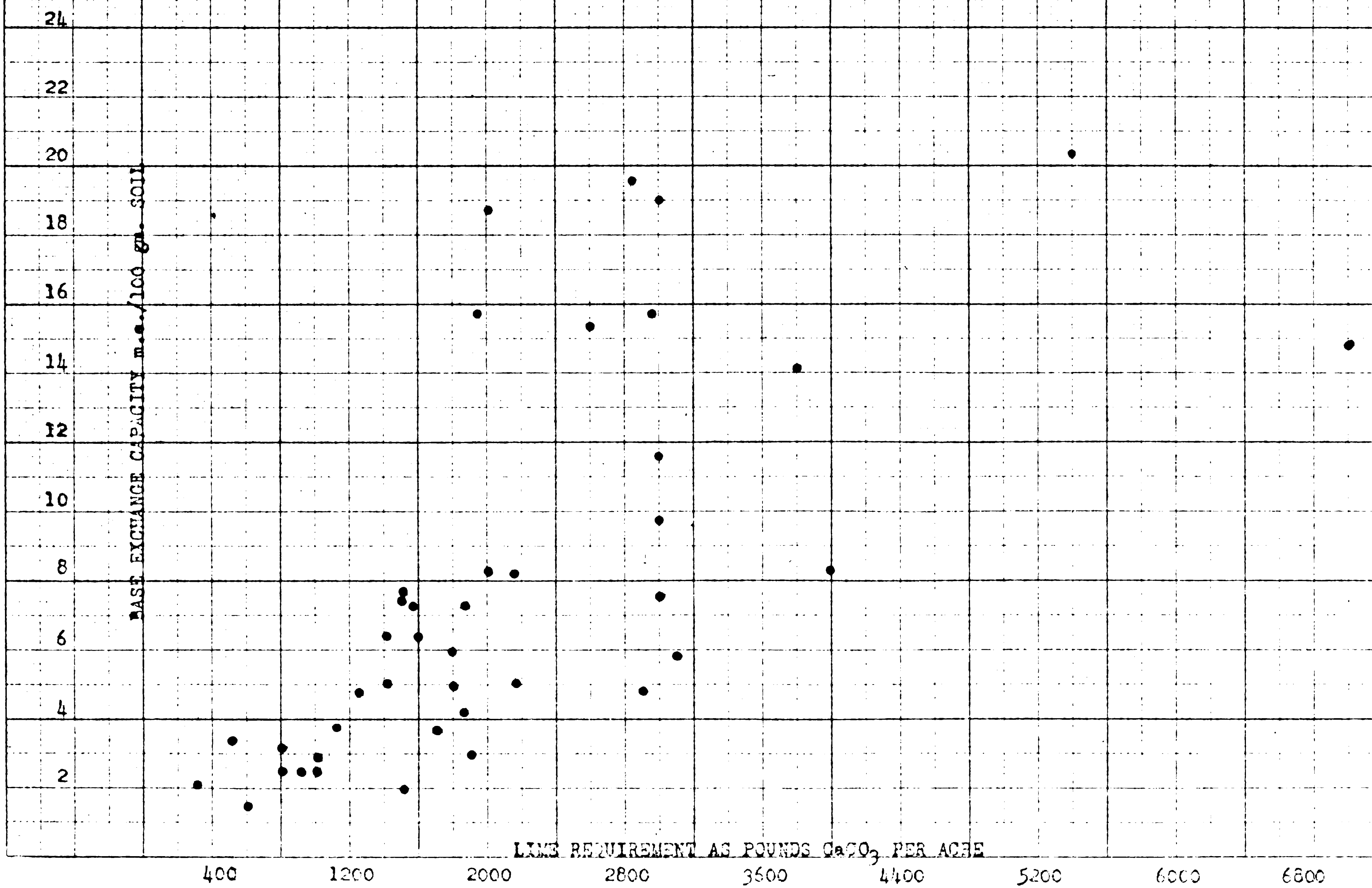
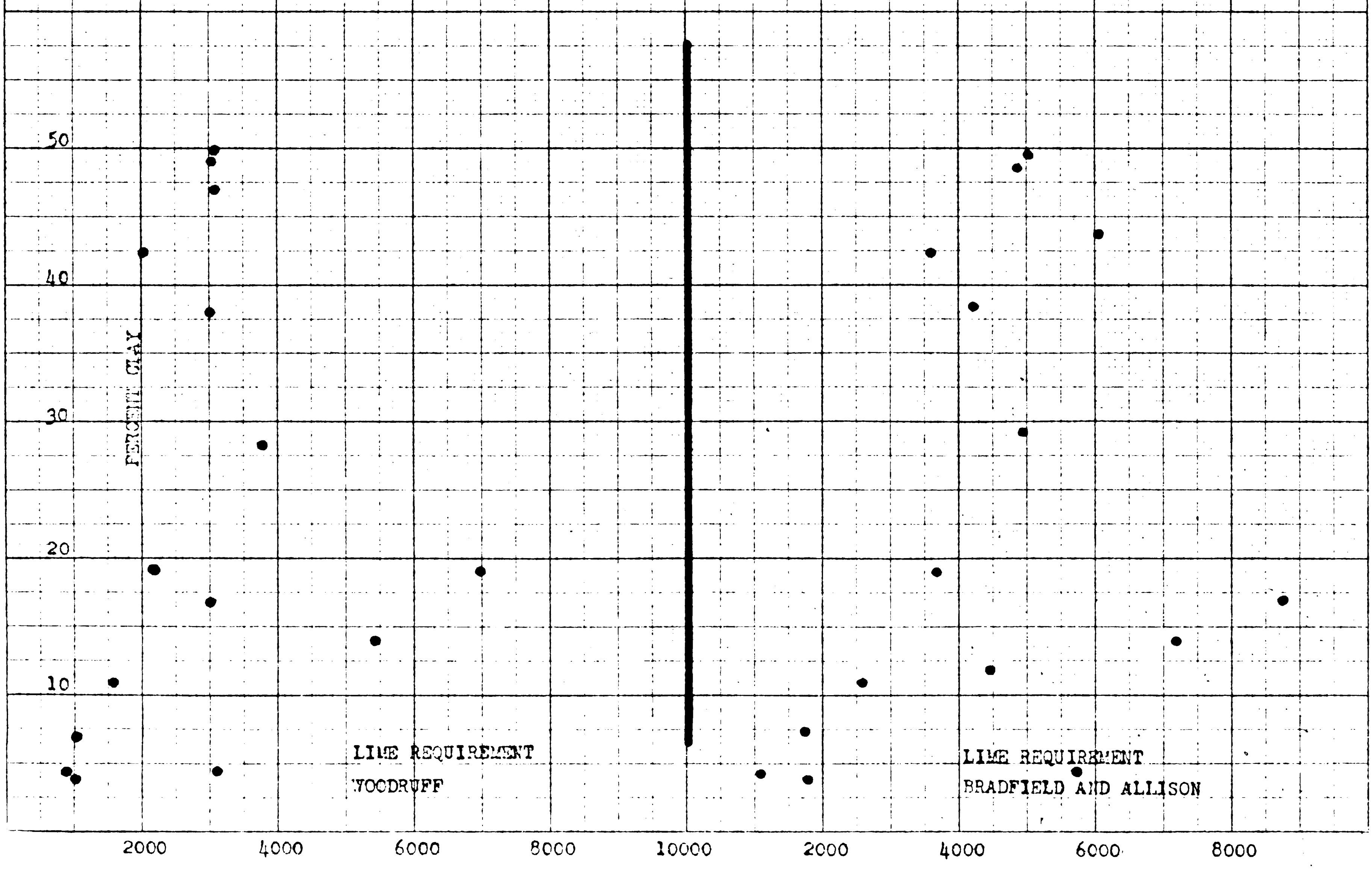


FIG. 11 THE PERCENT CLAY IN THE SOIL AS COMPARED TO LIME REQUIREMENT BY TWO METHODS



in lime requirement as calculated by the method of Woodruff is accompanied by an increase in base exchange capacity.

All relationships thus far would seem to indicate that cation exchange capacity is one of the predominating factors in determining lime requirement for soils. If this is true, then some relationship between percent clay and lime requirement should be expected. In table 6 is presented the mechanical analyses for 15 selected soils obtained using the Bouyoucos hydrometer method. The percentage of clay for each of these soils has been plotted against lime requirement as calculated by Woodruff's method and the method of Bradfield and Allison in Fig. 11. The relationship in both cases is only fair, since in all cases lime requirement does not increase with percent clay. Indications are then, that percent clay should be used in conjunction with other soil properties such as organic matter content in order to be of value as a lime requirement indicator.

## DISCUSSION

From the foregoing experimental work, the factors influencing lime requirement determinations are seen to be numerous. To choose any one of these (such as exchangeable hydrogen) as a basis for lime requirement is very likely to involve some approximations. This becomes evident when results of the three methods, used in this study for obtaining lime requirement values in soils, are compared. Since they are not in close agreement, it is evident that there are factors either in the soil or in the methods themselves which are not being evaluated correctly or in the same manner. It is possible, then, that one source for variance in results when determining lime requirement by various methods is the extraction of exchangeable hydrogen. Bradfield and Allison's buffer solution, at a pH of 7.4, might be expected to extract more of the total exchangeable hydrogen than would the ammonium acetate or Woodruff's buffer at a pH of 7.0.

Woodruff (28) has stated that for soils of low base exchange capacity his method for evaluating lime requirment may be as much as 43% below the actual requirement of the soil. By using the carbonate lime requirement method as a standard,this investigation did not reveal Woodruff's method to give results below that of the carbonate method with any more consistency on light textured soils than on soils of heavy texture.

There were no indications that the Woodruff method was subject to any more error than the other methods compared with it. This along with the fact that it is the simplest and most rapid method of

any used in this investigation should serve to emphasize its value as a chemical test for lime requirement.

The relationship between pH and percentage base saturation, which has been considered previously in this work, has been given attention by Mehlich (13,14). He has stated that the pH - base saturation relationship varies for different soils because of differences in the predominating exchange complex in the soils. His results have shown that the pH - percentage base saturation is too imperfect for the soils studied to permit its use as a single factor for lime requirement values. However, the relationship is fairly constant on all soils with the same exchange complex or soils of a specific soil type. The results of this investigation tend to corroborate his work.

## SUMMARY

The objective of this investigation was to study some of the relationships between pH, exchangeable calcium, percent base saturation, and lime requirement in some Michigan soils. The soils used were gathered from a number of different counties in the lower penninsula of Michigan.

The above mentioned chemical soil properties were determined for all soils used and the relationships were shown by plotting them in a series of graphs.

Three methods were used for the determination of lime requirement and the results compared.

Mechanical analyses of selected soils were completed to show the effect of clay on the lime requirement of soils.

As a result of these studies the following statements can be made:

1. pH alone does not give an accurate liming value for soils of widely varying textures and exchange capacities.

2. The quantitative determination of exchangeable hydrogen is probably the best known method for determining lime requirement, since it correlated more closely with the lime requirement when compared to the other soil chemical properties studied.

3. The methods for determining lime requirement compared as follows: The Bradfield and Allison method gave consistently higher results than did the Woodruff method.

4. The pH - percentage base saturation relationship is too

imperfect to permit its use as a single factor in lime requirement determinations.

5. Lime requirement as calculated by the Woodruff method exhibits a close relationship to the soil pH.

6. There exists only a very limited correlation between lime requirement, as calculated by the Woodruff method, and percent base saturation of the soil. In general, soils of higher exchange capacity require greater quantities of lime for neutralization than do soils of low exchange capacity at the same initial percentage base saturation.

7. The determination of exchangeable calcium in soils is a poor test for lime requirement, since exchangeable calcium, in general, increases with increasing lime requirement.

8. There is a close relationship between total base exchange capacity and lime requirement in soils when considering soils of similar pH.

9. The Woodruff buffer method for determining lime requirement was the simplest and most rapid method used to determine lime requirement in this study. The results obtained by the Woodruff method compared with the carbonate method as well as did the method of Bradfield and Allison.

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