

# THE EFFECT OF GYPSUM ON SOIL REACTION

L. W. ERDMAN<sup>1</sup>

*Iowa Agricultural Experiment Station*

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## INTRODUCTION

Gypsum has been used as a fertilizer for many years, and has often proven to be valuable especially when applied to small grains and clovers. The early investigators claimed that gypsum increased crop yields for a time, but its continued use failed to maintain those increases, and as it contained no nitrogen, phosphorus, or potassium, it was regarded as a soil stimulant. Several more recent investigations have indicated that the value of gypsum is probably due to its sulfur content, and to the indirect action it may have on other soil constituents. Recently many soils have been found to be deficient in sulfur, one of the essential plant-food elements, and sulfur requirements of certain crops are apparently much greater than formerly supposed. Since gypsum supplies this necessary element in an available form it may play an important rôle in soil fertility in those regions where sulfur is needed.

It is generally conceded that gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , cannot replace lime as a means of correcting soil acidity, but there seems to be some difference of opinion as to whether or not when applied to soils it tends to make them acid. Gypsum is a neutral salt and its dissociation in pure water produces hydrogen and hydroxyl ions of equal concentration. It is quite natural to expect it to act in a similar way when dissolved in the soil solution. However, through crop production or bacterial activities there may be a utilization of either the sulfate or the calcium ion, leaving one or the other free to react with the soil constituents in such a way as either to increase or decrease the acidity of the soil. There is also the possibility of a chemical reaction, the calcium combining with the insoluble soil acids, leaving the readily soluble sulfate ion which theoretically may cause a certain amount of acidity. The object of this work was to determine as far as possible by laboratory experiments the effect of gypsum on soil reaction.

## HISTORICAL

In reviewing the literature on the effect of gypsum on soil reaction, the investigations reported may well be considered from two viewpoints: first,

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experiments dealing with gypsum itself; and, second, experiments showing the effect of acid phosphate on acidity. Acid phosphate contains about 60 per cent gypsum and consequently any effect of this fertilizer on acidity may indirectly be interpreted as due at least partly to the presence of gypsum.

In 1910 Gardner and Brown (9), using the Veitch method, tested the lime requirement of the general fertilizer plots of the Pennsylvania station. Plots 13 and 33 received gypsum at the rate of 320 pounds per acre every two years. After 30 years the average of all the check plots had a lime requirement of 172 pounds of CaO per acre, as compared with 146 pounds for the gypsum plots. Frear (8) concluded from these results that where land plaster was used the land was no more acid than where no fertilizer at all was applied.

Ames and Schollenberger (1) used the Hopkins potassium nitrate and the vacuum method and found that gypsum applied with manure decreased the acidity of the soil.

Lipman (19) stated that gypsum possesses no alkalinity and therefore will not be of any assistance nor act as a corrective to a sourness or acidity in soils.

Skinner and Beattie (26) used a number of square-rod plots to test the effects of fertilizers and soil amendments on soil acidity.  $\text{CaSO}_4$  was used at the rate of 500 pounds per acre each year and after 5 years the plots were tested for lime requirement by the Veitch method. They concluded that the soil in each plot to which  $\text{CaSO}_4$  had been added was more acid than the untreated plot growing the same crop. The average lime requirement for the  $\text{CaSO}_4$  plots in excess of the check plots was 343 pounds of  $\text{CaCO}_3$  per acre.

Singh (25), using pot cultures, tested the soil (after cropping) by the modified Tacke method and found that the acidity was increased by the application of gypsum, the larger amount giving the greatest increase.

Connor (7) tested gypsum as a means of correcting soil acidity on two types of very acid soils. The rate of application was 2 tons of gypsum per million pounds of soil. The gypsum treatment showed an actual decrease in acidity when compared with the check pots, the average decrease for the two soils being 580 pounds of  $\text{CaCO}_3$  per million pounds of soil by the Hopkins potassium nitrate method, and 937 pounds by the Jones calcium acetate method.

Veitch (29) tested the lime requirement of the soil from a number of the plots in the 5-year rotation experiments at Wooster, Ohio, and found that acid phosphate had slightly reduced the acidity of the soil.

Brooks (4) concluded from his work that the use of an acid phosphate (dissolved bone black), at least had not increased the necessity for lime and, on the contrary, it seemed that the bone black had reduced the acidity.

Conner (6), testing the experimental plots at Purdue, observed that soils treated with acid phosphate for 20 years showed less acidity than soils that had received no treatment.

Ames and Schollenberger (1) claim that acid phosphate did not have any important influence on the depletion of the soil's supply of bases.

Bear and Salter (2) tested the residual effects of fertilizers and concluded that the use of manure or fertilizers (with the exception of  $K_2SO_4$ ) had a tendency to decrease the acidity of the soil.

More recently Plummer (22) studied soil reaction by means of the hydrogen electrode. The plots to which acid phosphate had been added did not show any greater hydrogen ion concentration than the ones used as controls. These plots had received rather heavy annual applications of this fertilizer for the past 15 years, the total amount being over 3,000 pounds per acre.

Some of the above-mentioned investigations show a difference of opinion regarding the effects of gypsum on soil acidity. However, in every case where it is claimed that gypsum produced acidity the results obtained by the particular lime-requirement method employed are so small as to be well within the limit of experimental error, since it is doubtful whether any lime-requirement method in use at the present time is accurate to 400 pounds of calcium carbonate per acre. All the work reported relating to the effect of acid phosphate on acidity shows conclusively that this fertilizer tends to decrease rather than increase soil acidity.

#### EXPERIMENTAL

Two laboratory experiments were planned to determine:

- (a) The effect of gypsum on an acid soil, a neutral soil, and a basic soil;
- (b) The effect of gypsum on a soil with different degrees of acidity.

#### *Experiment I*

The three soils used in the first experiment were obtained from different locations in the Wisconsin drift soil area and all would be classed as Carrington loam.

The acid soil had a lime requirement of 2260 pounds of  $CaCO_3$  per acre as determined by the modified Tacke method (27).

The neutral soil gave a negative test for acidity by the modified Tacke method and the Truog qualitative test.

The basic soil was obtained from a typical Iowa alkali spot and was very high in calcium bicarbonate.

The soils were air-dried and 2500 gm. of each soil was placed in 6 1-gallon pots. Treatments were made as follows:

- Pot 1. Check
- Pot 2. 100 pounds gypsum per acre
- Pot 3. 200 pounds gypsum per acre
- Pot 4. 500 pounds gypsum per acre
- Pot 5. 1000 pounds gypsum per acre
- Pot 6. 2000 pounds gypsum per acre

The gypsum was mixed with the entire contents of the pots and distilled water added to bring all the soils to their optimum moisture content. The pots were then weighed and covered loosely with a wooden block to prevent

rapid evaporation. The pots were kept in the laboratory at ordinary room temperature. A record was kept of the amounts of soil removed by sampling and every 2 weeks during the experiment the pots were reweighed and the moisture content maintained by additions of distilled water to weight. This experiment was begun March 3, 1920, and discontinued January 10, 1921.

The soil used in the second experiment was the same neutral soil as used in experiment I.

A preliminary test was made to compare the effect of gypsum on the hydrogen-ion concentration of a soil, made acid by treatment with  $H_2SO_4$  and  $HCl$ . For this test 1000 gm. of neutral soil was used with each treatment and the hydrogen-ion concentration of a suspension from each treated soil determined. Another test was made to compare the effect of gypsum on the hydrogen-ion concentration of pure water made acid by treatments with  $H_2SO_4$  and  $HCl$ , and for this test 200 cc. of double distilled water was used with each treatment. The acid treatments were calculated to give the same hydrogen-ion concentration. The tests may be best understood by the treatments as shown in table 1 which also gives the results.

TABLE 1

*Hydrogen-ion concentration of a soil suspension and of pure water made acid by treatments with sulfuric and hydrochloric acids*

NUMBER	TREATMENT	SOIL SUSPENSION	WATER
		pH	pH
1	Check.....	7.13	7.60
2	$H_2SO_4$ , 1 gm.....	6.39	1.28
3	$HCl$ , 1.93 gm.....	6.39	1.18
4	$H_2SO_4$ , 1 gm.; 2 gm. gypsum.....	6.28	1.21
5	$HCl$ , 1.93 gm.; 2 gm. gypsum.....	6.25	1.15
6	$H_2SO_4$ , 1 gm.; 4 gm. gypsum.....	6.23	1.18
7	$HCl$ , 1.93 gm.; 4 gm. gypsum.....	6.35	1.15

It will be noticed from table 1 that upon the addition of 2 gm. of gypsum to the soil treated with  $H_2SO_4$  and  $HCl$ , the hydrogen-ion concentration remained the same for each acid. With the 4-gm. gypsum treatment there was an increase in acidity for the  $H_2SO_4$  amounting to 0.12 pH over the  $HCl$  treatment. In the case of the water solution the pH values were practically the same for 2-gm. and 4-gm. gypsum treatments, and also each acid showed the same pH value. The results of these tests clearly showed that sulfuric and hydrochloric acid acted in the same manner as far as the reaction in the soil and water was determined by the hydrogen electrode.

Accordingly, for the second experiment hydrochloric acid was used to make the soil of varying degrees of acidity, in order to eliminate the sulfate ion which would be produced from the sulfuric acid.

For this experiment 16 1-gallon glazed pots were filled with 4200 gm. of the air-dried neutral soil and treatments made as follows:

Pots 1 and 2. Check

Pots 3 and 4. 500 pounds gypsum per acre

Pots 5 and 6. 4000 pounds  $\text{CaCO}_3$  per acre

Pots 7 and 8. 4000 pounds  $\text{CaCO}_3$  per acre plus 500 pounds gypsum

Pots 9 and 10. HCl equivalent to 2-ton lime requirement

Pots 11 and 12. HCl equivalent to 2-ton lime requirement plus 500 pounds gypsum

Pots 13 and 14. HCl equivalent to 4-ton lime requirement

Pots 15 and 16. HCl equivalent to 4-ton lime requirement plus 500 pounds gypsum

The gypsum and  $\text{CaCO}_3$  were mixed with the 4200 gm. of soil, and the hydrochloric acid was added to the distilled water required to bring the soil to the optimum moisture content. The pots were weighed and covered in the same manner as those in experiment 1. This experiment was begun July 30, 1920, and discontinued December 29, 1920.

### Methods

**Lime requirement.** The method used for determining the lime requirement in these experiments was a modification of the one designed by Tacke (28). The original method consisted of treating the soil with an excess of calcium carbonate and water, bubbling hydrogen through the mixture and collecting the carbon dioxide expelled with an alkaline absorbent contained in a Pettenkofer absorption tube. The lime requirement was calculated from the carbon dioxide thus obtained.

Several modifications of this method have been used by investigators in this country. Wheeler, Hartwell, and Sargent (30) boiled the mixed soil and  $\text{CaCO}_3$  solution in water and determined the carbon dioxide evolved.

Ames and Schollenberger (1) used a method similar to the one just described, the essential difference being the temperature employed. The boiling was conducted *in vacuo* and the temperature need not exceed  $50^\circ \text{C}$ . This step was taken to reduce the decomposition of the organic matter by heat to a minimum.

Knight (18) mixed a weighed quantity of soil with precipitated calcium carbonate, added about 25 cc. of a neutral salt solution, boiled for a definite period and determined the carbon dioxide evolved by the Parr method.

The modification used in this work was the one described and used by Stephenson (27). A machine was used which held 8 300-cc. Kjeldahl flasks and 8 sodium-hydroxide towers. Twenty grams of soil, 2 gm. of calcium carbonate and 50 cc. of  $\text{CO}_2$ -free water were placed in the flasks and the carbon dioxide evolved during the shaking was absorbed in a solution containing 50 cc. 0.2 *N* NaOH and 100 cc. of  $\text{CO}_2$ -free water. A stream of  $\text{CO}_2$ -free air was constantly drawn through the system and continuous shaking employed for 5 hours. Determinations were made in duplicate, and blanks, without the calcium carbonate solution, were run for each determination. Results were obtained by double titration with phenolphthalein and methyl orange. Thus using a 20 gm. sample of soil and titrating against 0.04*N* acid, each cubic centimeter of

the titration represents a lime requirement of 400 pounds of calcium carbonate per two million pounds of soil. In the results the blank is always subtracted.

*Acidity.* In these experiments the acidity, or hydrogen-ion concentration, of the soil was measured by the hydrogen electrode. The possibilities of this method of studying soil reactions have been realized only during comparatively recent years. Gillespie (10) used the electrometric and colorimetric methods and determined the hydrogen-ion concentrations of a number of soils of different types. Sharp and Hoagland (24) studied the hydrogen-ion concentration in various soil suspensions and in soil extracts, and noted the effect of certain factors on the hydrogen-ion concentration. Hoagland and Sharp (15) found that the hydrogen-ion concentration of soil suspensions of acid soils was not markedly affected by increasing the CO<sub>2</sub> content up to 10 per cent.

Gillespie and Hurst (12, 13) studied the hydrogen-ion concentration of two soil types, the Caribou loam and Washburn loam, and showed a correlation between hydrogen-ion concentration and the occurrence of the potato scab. Martin (21) studied the relation of the potato-scab organism to soil acidity as measured by the hydrogen-ion concentration, and also for determining the relation of hydrogen-ion concentration of extracts from soils to which varying amounts of sulfur had been added.

Plummer (22) used the hydrogen electrode method in comparing hydrogen-ion concentrations of a number of untreated soil samples and also of a few samples of soil treated with different fertilizers. Kappen and Zapfe (17) measured the hydrogen-ion concentration of peat soils and of peat and humus-forming plants.

Gillespie (11) proposed a colorimetric method for the determination of hydrogen-ion concentrations without buffer mixtures. His indicators were chosen from the series of Clark and Lubs (5). Wherry (31, 32) described a set of six indicators suitable for the study of soil reactions in the field, and gave detailed instructions for making the test.

Several investigators have compared the hydrogen-ion concentration of soil extracts with certain lime-requirement methods. Knight (18) found that the vacuum method approached nearer to the lime requirement as shown by the hydrogen electrode than any of the five methods studied. The Veitch method showed results considerable lower.

Blair and Prince (3) observed a close correlation between the hydrogen-ion concentration of the soil extract and the lime requirement by the Veitch method. Soils having a pH value of 6.7 or over were alkaline by the Veitch method. Joffe (16) found that soils having a pH value 6.6 to 6.8 before evaporation indicated that the end point of the lime requirement by the Veitch method had been reached.

The apparatus used in determining the hydrogen-ion concentration in this work was similar to that described by Sharp and Hoagland (24) which is a modification of Hildebrand's (14) apparatus. A normal calomel cell and an

accurate Weston voltmeter were used in the present work. Results could be obtained with this apparatus accurate to within 0.05 pH. Fifteen grams of soil and 30 cc. of double distilled water were used in the manipulation of the test, duplicate determinations being made for each sample. The voltmeter readings were transformed into pH values from the tables prepared for this purpose by Schmidt and Hoagland (23).

*Residual Carbonates.* Residual carbonates were determined by the method of MacIntire and Willis (20). The same apparatus was used as that described for determining the lime requirement. Twenty grams of air-dry soil, and 50 cc. of 1 to 15 phosphoric acid solution, prepared by diluting 85 per cent  $H_3PO_4$  with  $CO_2$ -free water, were placed in the flasks. The flasks were constantly shaken for 30 minutes. A current of  $CO_2$ -free air was drawn through the system at a very slow rate for the first 10 minutes. The second 10 minutes the rate was slightly increased and during the last 10 minutes the air was drawn through fairly rapidly. The carbon dioxide evolved was absorbed in a sodium hydroxide solution, and results were obtained by double titration with phenolphthalein and methyl orange.

#### *Discussion of results*

Twenty-gram samples of the wet soils were taken from the pots of the first experiment at different times and tested for their lime requirement by the Tacke method as described. Correction was made for moisture in the samples and the results were figured in pounds of  $CaCO_3$  per 2,000,000 pounds of soil. It may be well to call attention at this point to the accuracy of this method as it was used in this work. Duplicate determinations usually checked to within 200 pounds of  $CaCO_3$  per acre, but occasionally differences were obtained as much as 400 pounds of  $CaCO_3$ . Consequently it would be safe to say the method is accurate only to 400 pounds of  $CaCO_3$  per acre.

The results for the three soils, acid, neutral, and basic, are grouped under table 2. It will be seen from the data presented for the acid soil, that the first determinations made on March 18, showed wider variations between the check pot and the gypsum treatments than at any other date. The 200-pound gypsum treatment showed a decrease of 321 pounds of  $CaCO_3$  in lime requirement when compared with the check. The 2000-pound gypsum treatment showed an increased lime requirement over the check amounting to 554 pounds of  $CaCO_3$ . This amount would indicate a slight acidity caused by the gypsum, but the average of the four determinations for the 2000-pound treatment is only a little over half this amount. While the lime requirements of the variously treated pots do not agree very closely at each sampling, there is a rather close agreement for the average. The gypsum treatments up to and including 1000 pounds per acre show practically the same lime requirement as the check pot. There is an increase of 243 pounds of  $CaCO_3$  in lime requirement for the 2000-pound gypsum treatment over the check pot, which would indicate a slight increase in acidity if the method was accurate to 100

pounds of  $\text{CaCO}_3$  per acre, but when the accuracy is really about 400 pounds no increase in acidity can be concluded.

Before treatment the neutral soil showed no lime requirement by the Tacke test. After treatment the check soil showed a lime requirement of 250 pounds. The pots receiving 100 and 200 pounds of gypsum showed a smaller lime

TABLE 2

*Lime requirement by the Tacke method of three soils treated with different amounts of gypsum*  
Acid soil

POT NUMBER	TREATMENT PER ACRE	DATE SAMPLED				AVERAGE
		March 18	June 18	November 17	January 10	
		lbs.	lbs.	lbs.	lbs.	lbs.
1	Check.....	2278	3183	3271	3270	3000
2	Gypsum 100 lbs.....	2570	3271	3037	3066	2986
3	Gypsum 200 lbs.....	1957	3154	3592	3416	3029
4	Gypsum 500 lbs.....	2480	3271	3592	3153	3124
5	Gypsum 1000 lbs....	2366	3329	3388	3550	3158
6	Gypsum 2000 lbs....	2832	3329	3329	3601	3243

## Neutral soil

POT NUMBER	TREATMENT PER ACRE	DATE SAMPLED			AVERAGE
		March 17	June 16	November 15	
		lbs.	lbs.	lbs.	lbs.
1	Check.....	390	90	270	250
2	Gypsum 100 lbs.....	330	150	60	180
3	Gypsum 200 lbs.....	Alkali	60	Alkali	20
4	Gypsum 500 lbs.....	120	420	600	380
5	Gypsum 1000 lbs.....	540	180	330	350
6	Gypsum 2000 lbs.....	330	390	480	400

## Basic soil

POT NUMBER	TREATMENT PER ACRE	DATE SAMPLED		
		March 19	June 24	November 24
1	Check,.....	Trace	Alkali	Alkali
2	Gypsum 100 lbs.....	Trace	Trace	Alkali
3	Gypsum 200 lbs.....	Alkali	Alkali	Alkali
4	Gypsum 500 lbs.....	Alkali	Alkali	Trace
5	Gypsum 1000 lbs.....	Alkali	Alkali	Trace
6	Gypsum 2000 lbs.....	Alkali	Alkali	Alkali

requirement than the check pot, but the pots receiving 500, 1000, and 2000 pounds of gypsum showed increases in lime requirement over the check, amounting to 130, 100, and 150 pounds of calcium carbonate, respectively. These amounts, however, are too small to permit the conclusion that gypsum has any effect on acidity, since differences as much as 400 pounds of  $\text{CaCO}_3$  could be within the limit of experimental error.



It would not be expected to get a lime requirement by the Tacke method on the untreated basic soil, but determinations were made along with the acid and neutral soil to see if the gypsum would cause sufficient acidity to show a lime requirement on this soil. In nearly every case an alkaline reaction was obtained but several tests show a trace of a lime requirement. It would appear from the results by the Tacke method shown in table 1 that gypsum had no effect on soil reaction, regardless of whether the soil was acid, neutral, or basic.

To determine the effect of gypsum on the soil reaction, samples were taken from the pots in experiment 1 in 3 days, 10 days, 30 days, 5 months and 10 months after treatment for the determination of the hydrogen-ion concentration by the hydrogen electrode. The results for the three soils are summarized in table 3. The results are expressed in terms of pH values to simplify comparison. Each figure in the table represents the average of two determinations checking within 8 millivolts.

From a study of table 3 it will be noted that there is a striking uniformity in the results reported for the different samplings, and therefore in discussing these data only the average of the five determinations will be considered.

The first four treatments of the acid soil, including the check, showed an average pH value of 5.5 indicating no production of acidity due to applications of gypsum to 500 pounds per acre. The 1000-pound gypsum treatments showed an increase in acidity of 0.21 pH over the check, and the 2000-pound treatment showed an increase of 0.28 pH. Since the apparatus used for these determinations was accurate to 0.05 pH, these differences noted are large enough to conclude that gypsum does produce very slight acidity in an acid soil when applied at the rate of 1000 or 2000 pounds per acre. Comparing the 1000-pound gypsum treatment with the 2000 pounds we note the amount of acidity produced was not in proportion to the amount of gypsum applied.

The average of the first four treatments of the neutral soil showed almost identical pH values. The last two treatments, 1000 and 2000 pounds of gypsum, showed slight increases in acidity over the check of 0.14 pH and 0.27 pH, respectively. In the case of the neutral soil the amount of acidity caused by the 1000-pound treatment with gypsum was smaller by 0.07 pH than the same treatment of the acid soil. The same amount of acidity was produced by the 2000-pound gypsum treatment in both the acid and neutral soils. The acidity of the 2000-pound treatment of the neutral soil is just twice that of the 1000-pound treatment, showing that the increase in acidity was directly proportional to the amount of gypsum added. This was not true with the acid soil.

The average pH values were the same for the first four treatments for the basis soil. The 1000-pound gypsum treatment showed an increase in acidity of only 0.09 pH, and the 2000-pound treatment showed an increase of only 0.12 pH as compared with the check. Thus the pH values for the 1000 and the 2000-pound treatments were approximately the same, since the 0.03

pH difference is within the limit of experimental error. There being a difference of only 0.09 pH between the check and the 1000-pound treatment, it is safe to conclude that the heavier applications of 1000 and 2000 pounds of gypsum are less apt to cause acidity in a basic soil than they are in an acid soil or a neutral soil.

TABLE 3  
*Hydrogen-ion concentration of three soils treated with different amounts of gypsum*  
Acid soil

POT NUMBER	TREATMENT PER ACRE	DATE SAMPLED					AVERAGE
		March 6	March 13	March 26	August 6	January 5	
		pH	pH	pH	pH	pH	pH
1	Check.....	5.69	5.68	5.57	5.35	5.47	5.55
2	Gypsum 100 lbs.....	5.78	5.64	5.52	5.29	5.30	5.50
3	Gypsum 200 lbs.....	5.56	5.66	5.51	5.35	5.30	5.47
4	Gypsum 500 lbs.....	5.52	5.63	5.52	5.35	5.44	5.49
5	Gypsum 1000 lbs.....	5.35	5.52	5.46	5.20	5.19	5.34
6	Gypsum 2000 lbs.....	5.29	5.35	5.32	5.19	5.19	5.27

Neutral soil

POT NUMBER	TREATMENT PER ACRE	DATE SAMPLED					AVERAGE
		March 6	March 12	March 25	August 5	January 6	
		pH	pH	pH	pH	pH	pH
1	Check.....	7.06	7.05	6.96	7.05	7.15	7.05
2	Gypsum 100 lbs.....	7.03	7.03	6.98	7.05	7.06	7.03
3	Gypsum 200 lbs.....	7.03	6.99	6.91	7.03	6.98	6.99
4	Gypsum 500 lbs.....	6.96	7.01	6.91	6.99	7.05	6.98
5	Gypsum 1000 lbs.....	6.88	6.88	6.89	6.94	6.99	6.91
6	Gypsum 2000 lbs.....	6.71	6.72	6.71	6.88	6.88	6.78

Basic soil

POT NUMBER	TREATMENT PER ACRE	DATE SAMPLED					AVERAGE
		March 7	March 15	March 27	August 7	January 7	
		pH	pH	pH	pH	pH	pH
1	Check.....	7.89	8.03	8.01	8.04	8.04	8.00
2	Gypsum 100 lbs.....	7.87	7.92	8.01	8.04	8.18	8.00
3	Gypsum 200 lbs.....	7.89	7.92	8.01	8.03	8.04	7.98
4	Gypsum 500 lbs.....	7.89	7.98	7.89	7.99	8.06	7.96
5	Gypsum 1000 lbs.....	7.76	7.82	7.89	8.01	8.06	7.91
6	Gypsum 2000 lbs.....	7.76	7.86	7.76	7.89	8.04	7.88

It is interesting to note in the case of the acid soil that the hydrogen-ion concentration for the check soil remained almost constant for the first month after the experiment was started. Five months later there was a slight increase in acidity amounting to a little over 0.2 pH. Also, with the pots treated with gypsum there was the same tendency for a constant hydrogen-ion con-

centration for the first month after treatment, and 5 months later a development of acidity. These data would indicate that the soil organisms were active during the continuance of the experiment and were able to aid in any possible chemical reaction with the gypsum and other soil constituents.

To summarize the results of table 3, it may be concluded that gypsum applied in amounts up to and including 500 pounds per acre does not increase or decrease the hydrogen-ion concentration of an acid soil, a neutral soil, or a basic soil high in calcium bicarbonate. When gypsum is applied in amounts as high as 1000 and 2000 pounds per acre there is a slight increase in hydrogen-ion concentration of an acid soil and a neutral soil, but the increase is very slight in the basic soil. These treatments, however, are much larger applications than are used under actual field conditions.

### *Experiment II*

Experiment II was planned to determine the effect of gypsum on the reaction of a neutral soil treated with calcium carbonate and hydrochloric acid to give different degrees of acidity.

The soils in this experiment were sampled at three different times and tested for their lime requirement. The results of these tests, expressed in pounds of  $\text{CaCO}_3$  per acre, appear in table 4. Determinations were made in duplicate for each treatment and each figure in the table represents the average of four determinations.

Considering first the data presented in table 4 for the neutral soil with and without gypsum, it will be noted that each test showed an increased lime requirement for the gypsum treatment over the untreated soil. The average lime requirement for the gypsum treatment in excess of the untreated soil, however, was only 230 pounds of  $\text{CaCO}_3$  per acre, which is too small an amount to consider important, because the range of the experimental error for the method was 400 pounds of  $\text{CaCO}_3$  per acre.

The soil treated with calcium carbonate showed a trace of lime requirement with and without the gypsum. This statement is in accord with the conclusion drawn from the effect of gypsum on the basic soil used in experiment I.

The soil treated with hydrochloric acid to make a 2-ton lime requirement also showed an increased lime requirement for the gypsum treatment in excess of the untreated soil. In the case of the test made on August 14, the gypsum treatment showed a lime requirement of 765 pounds of  $\text{CaCO}_3$  in excess of the untreated soil, but the average lime requirement for the three tests in excess of the untreated soil was 370 pounds of  $\text{CaCO}_3$ , which also is within the 400 pound limit.

The soil treated with hydrochloric acid to make a 4-ton lime requirement showed an average lime requirement of 280 pounds of  $\text{CaCO}_3$  for the gypsum treatment in excess of the soil without gypsum. This amount likewise is not sufficient to justify the claim that any production of acidity was due to the presence of gypsum.

The residual limestone was determined in the soils of experiment II to note whether the production of acidity caused by the gypsum would decrease the amount of carbonates present in the soil. The average results of the three determinations are included in table 4. Comparing the results of the lime-requirement tests with those of the residual limestone, we see in each case, except one, that where there is an increase in lime-requirement, apparently due to the gypsum, there is a gain in residual limestone. But these differences, as in the case of the average lime-requirement tests, are very small and well within the limit of experimental error. They do show, however, that the apparent acidity caused by the gypsum does not decrease the supply of soil carbonates, and this fact would indicate that gypsum does not increase the acidity.

TABLE 4

*Lime requirement by the Tacke method and residual limestone of a neutral soil treated to vary in different degrees of acidity*

POT NUM- BER	TREATMENT PER ACRE	LIME REQUIREMENTS			AVERAGE	
		August 4	August 14	Decem- ber 1	Lime require- ment	Resid- ual car- bonates
1- 2	Check, (neutral soil).....	375	315	15	235	1496
3- 4	Gypsum, 500 lbs.....	810	450	135	465	1633
5- 6	CaCO <sub>3</sub> , 4000 lbs.....	Trace	Trace	Trace		4829
7- 8	CaCO <sub>3</sub> , 4000 lbs., plus gypsum, 500 lbs.....	Trace	Trace	Trace		4886
9-10	HCl equivalent to 2 tons lime requirement. . .	1965	1500	915	1460	1533
11-12	HCl equivalent to 2 tons lime requirement plus gypsum, 500 lbs.....	2220	2265	1005	1830	1833
13-14	HCl equivalent to 4 tons lime requirement. . .	3990	5085	2100	3725	1346
15-16	HCl equivalent to 4 tons lime requirement plus gypsum, 500 lbs.....	4170	6120	1725	4005	1276

It seems strange to have a lime requirement of varying amounts up to 4000 pounds of CaCO<sub>3</sub> per acre and still have residual limestone present. This condition may possibly be explained by the nature of the methods involved and the particular soil which was used in this experiment. This neutral soil undoubtedly contained small particles of limestone, the outer surfaces of which were hard and weathered, which caused them to be more or less resistant to the reaction that takes place in the lime-requirement determination. On the other hand, the constant agitation of the soil with the phosphoric acid, as used in the determination of carbonates, would permit the complete decomposition of all limestone particles and hence show residual carbonates present.

It will be seen also from table 4, that residual carbonates were found even in the soils treated with hydrochloric acid to make a 2-ton and 4-ton lime requirement. The amount of carbonates present in the soil with the 2-ton lime requirement was practically the same as reported for the untreated soil. But

the amount of carbonates present in the soil with the 4-ton lime requirement is smaller by 200 pounds of  $\text{CaCO}_3$  per acre than the soil with the 2-ton lime requirement. This would indicate that the weak dilution of acid used for the 2-ton lime requirement treatment was not strong enough to decompose the limestone particles of the soil, and that the 4-ton requirement treatment was sufficient to decompose them only slightly.

Samples were drawn at three different times from the soils in experiment II and determinations made for hydrogen-ion concentrations. The results, expressed in terms of pH values, are given in Table V. Duplicate determinations were made of the soil in each pot, thus each figure in the table represents the average of four determinations.

A study of table 5 shows that the 500-pound treatment with gypsum for the neutral soil had the same average hydrogen-ion concentration as the

TABLE 5  
*Hydrogen-ion concentration of a neutral soil treated to varying degrees of acidity*

POT NUMBER	TREATMENT PER ACRE	DATE SAMPLED			AVERAGE  pH
		August 2	August 16	Decem- ber 13	
		pH	pH	pH	
1- 2	Check (neutral soil).....	7.05	7.54	7.02	7.20
3- 4	Gypsum, 500 lbs.....	7.05	7.45	7.05	7.18
5- 6	$\text{CaCO}_3$ , 4000 lbs.....	7.38	7.89	7.54	7.60
7- 8	$\text{CaCO}_3$ , 4000 lbs.; plus gypsum, 500 lbs.....	7.39	7.81	7.47	7.58
9-10	HCl equivalent to 2 tons lime requirement.....	5.50	4.47	6.27	5.41
11-12	HCl equivalent to 2 tons lime requirement plus gypsum, 500 lbs.....	5.63	4.85	6.22	5.56
13-14	HCl equivalent to 4 tons lime requirement.....	4.87	3.85	5.70	4.80
15-16	HCl equivalent to 4 tons lime requirement plus gypsum, 500 lbs.....	4.67	4.13	5.80	4.86

same soil without gypsum. This condition was also true with the soil treated with 4000 pounds of  $\text{CaCO}_3$  per acre.

Considering next the soil treated with hydrochloric acid to make a 2-ton lime requirement, we see that the determinations at each sampling for the soil with and without gypsum do not agree very closely. The average pH value of the three determinations for the soil without gypsum was 5.41, while the soil with gypsum showed an average pH value of 5.56. This showed a decrease in acidity amounting to 0.15 pH value for the gypsum treatment as compared with the soil without gypsum. However, this variation is not in agreement with the other soils under consideration, and because of the large differences obtained with different samplings, it cannot be concluded that gypsum decreased the acidity in this soil.

The soil treated with hydrochloric acid to make a 4-ton lime requirement also showed wide variations in pH values at different samplings. The first determination showed that the gypsum treatment increased the acidity

amounting to 0.2 pH as compared with the soil without gypsum. The next determination showed the reverse to be true. In this case gypsum decreased the acidity amounting to 0.28 pH. In the third determination the gypsum again showed a small decrease in acidity compared with the soil without gypsum. The average pH values of the three determinations were practically the same for the soil with and without gypsum.

It may be concluded from the results shown in table 5 that gypsum applied at the rate of 500 pounds per acre does not have any effect on the hydrogen-ion concentration of a neutral soil treated so as to vary in degrees of acidity.

While the results here reported are from laboratory experiments it is probable that they would apply in their essential points to field conditions. The writer has under way actual field experiments on several soil types in Iowa, and a study is being made to determine the effect of gypsum on soil reaction in the field. These results will be reported later.

#### COMPARISON OF RESULTS BY THE TACKE LIME REQUIREMENT METHOD WITH HYDROGEN-ION DETERMINATIONS

From the data presented in these experiments an opportunity is taken at this point to make a comparison of the results by the Tacke method with the hydrogen-ion determinations. By referring to tables 2 and 3 it will be noted in the case of the neutral soil that the average lime requirement for the first four treatments, including the check, was 207 pounds of  $\text{CaCO}_3$  per acre, and the average hydrogen-ion concentrations of the same treatments with the same soil was 7.0 pH. The neutral point for the hydrogen-ion determinations in this work was 7.0 pH, while the neutral point for the Tacke method was from 0 to 400 pounds of  $\text{CaCO}_3$  per acre. Thus a close correlation exists between the neutral points of the respective methods. No attempt was made to determine the lime requirement in this work by the hydrogen electrode, and consequently any further comparisons of the methods would be inconclusive and misleading because of different soil types and soil conditions.

#### CONCLUSIONS

1. Gypsum added in amounts from 100 to 2000 pounds per acre to an acid soil, a neutral soil, and a basic soil, did not increase or correct the acidity of the soil as shown by the Tacke lime-requirement method.
2. Gypsum applied at the rate of 100, 200, and 500 pounds per acre did not raise or lower the hydrogen-ion concentration of the soil as measured by the hydrogen electrode.
3. Excessive amounts of 1000 and 2000 pounds of gypsum per acre showed increases in acidity by the hydrogen electrode amounting to 0.21 pH and 0.28 pH, respectively, for the acid soil studied; 0.14 pH and 0.27 pH, respectively, for the neutral soil studied; and 0.09 pH and 0.12 pH, respectively, for the basic soil.

4. Gypsum applied at the rate of 500 pounds per acre to a neutral soil made to vary in degrees of acidity by additions of HCl and CaCO<sub>3</sub> had no effect on the hydrogen-ion concentration of the soil, and did not show sufficient lime requirement by the Tacke method to permit of the conclusion that gypsum had any effect on acidity.

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