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## **Factors Influencing the Lime and Magnesia Requirements of Soils: A method for the determination of the immediate lime requirements**

University of Tennessee Agricultural Experiment Station

W. H. MacIntire

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OF THE  
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JANUARY, 1916

FACTORS INFLUENCING THE LIME AND MAG-  
NESIA REQUIREMENTS OF SOILS

A METHOD FOR THE DETERMINATION OF THE IMMEDIATE  
LIME REQUIREMENTS

By  
W. H. MacINTIRE

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# The Agricultural Experiment Station

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## LETTER OF TRANSMITTAL

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Department of Chemistry and Agronomy  
Agricultural Experiment Station  
University of Tennessee  
Knoxville

August 2, 1915.

*Prof. H. A. Morgan, Director.*

DEAR SIR:

A considerable part of the data and many of the statements and conclusions given in this manuscript have been published in Bulletin 107 of this Station. However, in order to present the subject of the factors influencing the lime and magnesia requirements of soils as clearly and in as nearly complete a form as possible, from the point of view entertained, such a restatement appears to me to be necessary and to add materially to the value of the additional data obtained. I therefore recommend that this manuscript be published by the Station as a research bulletin.

Very respectfully,

C. A. MOOERS,  
*Chemist and Agronomist.*



# FACTORS INFLUENCING THE LIME AND MAGNESIA REQUIREMENTS OF SOILS

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## A METHOD FOR THE DETERMINATION OF THE IMMEDIATE LIME REQUIREMENTS

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By  
W. H. MACINTIRE

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The work reported in this bulletin was begun in the spring of 1912, and was undertaken as an "Adams Fund" project. The investigation was based upon a study of the factors influencing the decomposition of  $\text{CaCO}_3$  in the determination of the lime requirement of soils. The Veitch method<sup>1</sup> was taken as the original basis of the study. Some results bearing upon certain phases of the work have been reported elsewhere by the writer and his associates.<sup>2</sup> When the present work was undertaken there had been proposed only two quantitative methods, other than the method of Veitch, in which lime requirements were determined by the direct application of lime to soils. Tacke<sup>3</sup> agitated a mixture of soil and  $\text{CaCO}_3$ , and from the estimation of liberated  $\text{CO}_2$  calculated the amount of  $\text{CaCO}_3$  decomposed. Süchting<sup>4</sup> concluded that the continued evolution of  $\text{CO}_2$  during the long period of contact of the Tacke method results in part from the action of carbonate of lime upon neutral organic matter. Süchting modified Tacke's method by agitating the soil and an excess of  $\text{CaCO}_3$  for two hours, drawing off and discarding the liberated  $\text{CO}_2$ . The residual  $\text{CaCO}_3$  is then determined by treatment with 20 per cent  $\text{HCl}$  and aspiration with agitation for 1 hour. Hydrogen is used as a current of gas to remove the  $\text{CO}_2$ . Süchting thus contends that the action of the sparingly soluble  $\text{CaCO}_3$  upon organic matter is greater than that exerted by strong acid during extended periods of contact at normal temperatures. This is not at all in accord with the experience of the writer, who believes that the fallacy of the contention is at once apparent. It will be shown that the continued evolution of  $\text{CO}_2$ , which results from an extension of the period of contact of soil and carbonate, is the result of a continued reaction be-

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1. Jour. Am. Chem. Soc., 1902, Vol. 24, p. 1120.

2. Tenn. Station Bul. 107.

3. Chem. Ztg., 1897, Vol. 21, p. 174.

4. Zts. Agnew Chem., 21, (1908), No. 4. p. 151.

tween  $\text{CaCO}_3$  and acid silicates, as well as a possible result of action of  $\text{CaCO}_3$  upon soil organic matter. As will be shown later, neither of these last two named procedures effects maximum decomposition of a carbonate in the case of an acid-clay subsoil, in which instance consideration of the question of organic matter is eliminated.

Of the three methods, that of Veitch has been most generally accepted in this country. It was thought possible that an investigation of the principles involved in the Veitch method might lead to a modification which would expedite the manipulation of the determination, while retaining its salient features and accuracy. It was also intended to conduct supplementary basket experiments in order to determine any correlation between laboratory results and plant response. Since the completion of much of the work herein reported, a method has been described by Hutchinson and MacLennan<sup>1</sup>. This method consists of the agitation of the soil for 3 hours with  $\text{CaCO}_3$  in solution of carbonated water and then filtering. The difference in the alkalinity of the original solution and that of the filtrate is taken as a measure of soil acidity. Without wishing in any way to detract from the priority of claim to publication of the innovation of using a solution of  $\text{CaCO}_3$ , which priority rightfully belongs to Hutchinson and MacLennan, the writer would state that the method given at the end of this article had been perfected prior to his knowledge of the work of Hutchinson and MacLennan, whose method appeared a few weeks in advance of the November (1914) meeting of the Association of Official Agricultural Chemists, to which body the Tennessee Station method was proposed. The paper giving the essentials of the latter method was published in the abstracts of the proceedings of the Association<sup>2</sup>. The Association's Referee for soils is now studying these two methods, which direct that  $\text{CaCO}_3$  be used in solution. The work of Hutchinson and MacLennan was brought to the attention of the writer at the meeting above mentioned. A copy of the article was then secured and the method tested and compared with the one proposed by the writer. The results of the comparison are given later in this report.

The various procedures suggesting the use of different soluble salts of the several alkalis were not included in the study. Several of these proposed absorption methods have embodied very neat manipulation and rapid handling under laboratory conditions—features which appeal to the laboratory worker. Extensive bibliographies of these various quantitative and qualitative procedures have been presented in several recent publications,<sup>3</sup> and will not therefore be included in this bulletin. Such methods are predicated upon the assumption of chemical equivalence between the amounts of bases extracted by soil from readily soluble neutral salts and the amount fixed by the soil from the relatively insoluble carbonate. The methods have no basis upon which they may be legitimately compared to actual

1. Chem. News, England, 110 (1914), No. 2854.

2. American Fertilizer, Nov. 28, 1914.

3. Frear, Wm., Dept. of Agr. Com. of Pa., Harrisburg, Bul. 261, pp. 103-106. See also, Conner, S. D., Jour. Ind. and Eng. Chem., vol. 8, No. 1, p. 35.

conditions existing in field soils. The results of such methods must, however, be interpreted from terms of the salt used into terms of burnt or carbonated lime, in order to be in harmony with practice. Sodium and potassium nitrate tend to produce alkalinity when applied to field soils, but any liberated acid does not leach away uncombined, as in the laboratory procedure; yet the liberation of the acid radical under laboratory conditions has been used as a measure of acidity, or lime requirement.

Previously published work of the writer and his associates has shown that there was a constant and vast difference between the reaction of the closely allied carbonates of calcium and magnesium upon three distinct types of soil, which were studied in pot and cylinder experiments under normal conditions. Now, if there exist this vast difference between the reaction of acid-reacting soil constituents upon  $\text{CaCO}_3$  and that upon  $\text{MgCO}_3$ , it would seem to indicate as fallacious the assumption of equal or proportional activities between the carbonate of calcium and the other neutral salts of the same element. The same would apply in the case of the various suggested salts of the other bases. We know that we cannot assume that there would be an equivalent dissociation of the salts of carbonic, oxalic, acetic, nitric, sulphuric and other acids, nor that the bases of these several salts would be absorbed in equal or equivalent amounts by the same acid salts<sup>1</sup>.

The writer was of the opinion, when beginning these studies, that the correct procedure to be followed in the determination of the lime requirement of a soil involved contact between the soil and calcium carbonate, the material generally used in practice. He continues in this belief and is entirely in accord with Harris<sup>2</sup>, who states, "The only sure way to determine the lime requirement of an acid soil is to use the same material in the test as is used in the field, for correcting the acidity."

The different treatments given in this bulletin were therefore based upon the reactions effected by bringing both the "C. P." and the natural carbonates of calcium and magnesium into contact with soils and soil constituents, under various conditions, normal and forced. By so doing it was hoped to determine definitely some facts concerning the results of the treatment of soils with calcium and magnesium carbonates, the forms more generally used in practice.

## MEASURE OF TREATMENTS

In laboratory work upon the Veitch method, supplemented by extensive pot work, Gardner and Brown<sup>3</sup> studied the soils of the 36 treatments and checks of the General Fertilizer Experiment plots at the Pennsylvania Station. Burnt lime and ground limestone were applied in amounts indicated by the Veitch method. Clover was sown and twice

1. See Parker, E. G., Jour. Agr. Research, 1913, vol. 1, No. 3; Harris, J. E., Mich. Agr. Exp. Sta., Bul. 19; Conner, S. D., Jour. Ind. and Eng. Chem., vol 8, No. 1, p. 35.

2. Science, Oct. 2, 1914, p. 493.

3. Pa. Station, Report, 1910-11, pp. 25-76.

TABLE I—*Reactions of soils to litmus and Veitch tests after treatments of CaCO<sub>3</sub> and MgCO<sub>3</sub>, based upon the Veitch-method indications*

Treatment	Sandy loam								Silty loam								Loam							
	CaCO <sub>3</sub>				MgCO <sub>3</sub>				CaCO <sub>3</sub>				MgCO <sub>3</sub>				CaCO <sub>3</sub>				MgCO <sub>3</sub>			
Amount* .....	V.†	V.+	V.+	V.+	V	V.+	V.+	V.+	V.	V.+	V.+	V.+	V.	V.+	V.+	V.+	V.	V.+	V.+	V.+	V.	V.+	V.+	V.+
		⅓	1785	16070		⅓	1785	16070		⅓	1785	16070		⅓	1785	16070		⅓	1785	16070		⅓	1785	16070
Reaction to litmus .....	Acid	Acid	Neut	Alk.	Acid	Acid	Neut.	Alk.	Acid	Acid	Acid	Alk.	Acid	Acid	Acid	Alk.	Acid	Neut.	Neut.	Alk.	Acid	Neut.	Neut.	Alk.
Reaction to Veitch method...	Acid	Acid	Acid	Alk.	Acid	Acid	Acid	Alk.	Acid	Acid	Acid	Alk.	Acid	Acid	Acid	Alk.	Acid	Acid	Alk.	Alk.	Acid	Acid	Alk.	Alk.

\*Pounds per acre 3,500,000 pounds of soil.

† "V." signifies indication by the Veitch method.

harvested. Eight months after treatment a second series of analyses were made by the Veitch method. An average of these last analyses gave 29 per cent and 28 per cent of the original lime requirements for treatments of burnt lime and limestone, respectively. Accordingly, in making applications of  $\text{CaCO}_3$  in pot work upon soil of three distinct types, with the intention of learning the relation of the Veitch-method results to the absolute, the writer planned to apply the amount of the Veitch indication and also the Veitch requirement plus one-third. Applications of both 1785 pounds and 16070 pounds of  $\text{CaCO}_3$  per acre 3,500,000 pounds of soil in excess of the Veitch method were also made. These amounts represent 1000 pounds and 9000 pounds, respectively, of  $\text{CaO}$  in excess of the Veitch-method indications. Kalbaum's "C. P." precipitated carbonate was used and the treatments were thoroughly mixed throughout the soil. In order to eliminate consideration of root growth and utilization of lime as plant food, portions of the soil were kept fallow for the subsequent analytical work. Other portions were sown to wheat. The heavy amount was included, both to determine the effect of the excess upon plant growth and to insure an appreciable amount of residual carbonates, the determinations of which would afford a means of establishing, quantitatively, the amount of  $\text{CaCO}_3$  decomposed above that indicated by the Veitch method. As a parallel study, the various treatments based upon the Veitch-method indications were checked by applications of chemically equivalent amounts of Kahlbaum's "C. P."  $\text{MgCO}_3$ . Three soils, a loam, a sandy loam, and a silty loam, were selected for study. The Veitch-method requirements of these three soils per 3,500,000 pounds of soil were 6807 pounds, 2350 pounds, and 1894 pounds of  $\text{CaCO}_3$  for the loam, the sandy loam, and the silty loam, respectively, on moisture-free basis. Whenever used in terms of pounds per acre, and when making comparisons between residual carbonates, as well as when stating extent of the dissipation of  $\text{CO}_2$ , the magnesium carbonate amounts stated are in terms of  $\text{CaCO}_3$  equivalence. Three paraffined wire baskets of approximately 25-pounds capacity each were used for each treatment of each soil. The soils in the baskets were sown to wheat October, 1912, and the wheat was harvested in February, 1913. The yields resulting from the various treatments have been reported elsewhere.<sup>1</sup> After cropping, the roots were removed and the soils of the check pots, and the pots containing the Veitch plus one-third, and the Veitch plus 1785-pound treatment, were bottled. Each soil was then carefully tested as to its reaction by both Veitch and litmus-paper tests. The results are given in Table I.

The results of Table I confirm those of Gardner and Brown<sup>2</sup>. It is plainly evident from the Veitch tests made over a year after treatment that there is a *continued decomposition* of calcium and magnesium carbonates in the unleached fallow soils. As will be shown later, the soils receiving the heavy  $\text{MgCO}_3$  treatments were devoid of residual carbonates at the end of the one-year period, but the excess of silicates afforded alka-

<sup>1</sup> Tenn. Station Bul. 107.

<sup>2</sup> Pa. Station, Report, 1910-11, pp. 25-76.

TABLE II—*Decomposition of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  in excess of Veitch-method indications—determined by difference between original and residual carbonates*

Soil type	Treatment	Veitch indication of $\text{CaCO}_3$ per acre 3,500,000 lbs. of soil	$\text{CaCO}_3$ equivalent added per acre 3,500,000 lbs. of soil	Increase of $\text{CaCO}_3$ equivalent, per acre 3,500,000 lbs. found 1 year afterward	$\text{CaCO}_3$ decomposed in excess of Veitch-indication	
					Per 3,500,000 lbs. of soil	Per cent of original Veitch indication
		Lbs.	Lbs.	Lbs.	Lbs.	
Loam .....	$\text{CaCO}_3$	6807	22877	11288	4782	70.25
Silty loam .....	$\text{CaCO}_3$	2350	18420	6143	9927	422.42
Sandy loam .....	$\text{CaCO}_3$	1894	17964	9961	6109	322.54
*Loam .....	$\text{MgCO}_3$	6807	22877	*0	16070	236.06
Silty loam .....	$\text{MgCO}_3$	2350	18420	*0	16070	683.82
Sandy loam .....	$\text{MgCO}_3$	1894	17964	*0	16070	949.52

\* Plus or minus error of .008 per cent allowed between original and residual  $\text{CaCO}_3$  determinations.



linity reactions in both Veitch and litmus-paper tests. The amounts of carbonate decomposed by the continued contact of fallow soil and excess of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  are considerably above the original Veitch indications. In the heavy  $\text{CaCO}_3$  treatments of 16070 pounds in excess of the Veitch requirements, it was anticipated that the residual carbonate would afford a means of measuring the relation between the Veitch requirements and the amounts actually decomposed by the different types of soil. Accordingly, the heavy treatments of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  were analyzed for  $\text{CO}_2$ , by the Tennessee Station method<sup>1</sup>, exactly one year after treatment. The results are given, on the moisture-free basis, in Table II.

It will be noted that a considerable portion of the excess of  $\text{CaCO}_3$  above the Veitch indication and treatment was decomposed. The  $\text{CO}_2$  of  $\text{MgCO}_3$ , however, was completely dissipated. This decomposition of  $\text{MgCO}_3$  was substantiated by analyses of the air-dried composites of fallow soils from eight field cylinders which had received treatments of  $\text{MgCO}_3$  equivalent to 28,180 pounds  $\text{CaCO}_3$  per acre 2,000,000 pounds of soil. The loam soil of the baskets was used in this case, and two treatments of  $\text{CaCO}_3$  in chemical equivalence were analyzed as checks. The cylinder treatments had been made only eight weeks prior to analysis, and no leaching had taken place during the period of exposure. Determinations made by boiling the original soil showed a  $\text{CO}_2$  occurrence of .0740 per cent, while .0666 per cent was found as an average of four determinations made by boiling the soils which had received the heavy  $\text{MgCO}_3$  treatments. The  $\text{CaCO}_3$  treatments resulted in a gain over the original of 19170 pounds of  $\text{CaCO}_3$  per acre 2,000,000 pounds of soil.

From these data and succeeding results, it is readily seen that the excessive  $\text{MgCO}_3$  decomposition noted in Table II was not the limit of the immediate ability of the loam soil to decompose precipitated  $\text{MgCO}_3$ .

Had the different treatments been subjected to leaching, the disappearance of carbonates subsequent to  $\text{MgCO}_3$  treatments might have been explained by the assumption of a replacement of magnesium for readily leached sodium and potassium. As stated, however, the original soils were in baskets, and were not subjected to leaching during the one-year period of contact, nor did leaching take place during the eight weeks' exposure of the cylinder soils.

The results secured upon determination of residual carbonates demonstrate the existence of a long continued reaction between soils and carbonates. Furthermore, they emphasize the necessity of defining more specifically the term "lime requirement." To the writer, the data seem to necessitate differentiation between temporary, or immediate, lime requirement and the continued propensity of a soil to decompose  $\text{CaCO}_3$ , when soil continues in contact with excess of carbonates. This question also arises. Should the lime requirement of a soil be considered as its maximum coefficient of  $\text{CaCO}_3$  decomposition, under laboratory conditions in given time, or should it be considered as the amount of lime essential to maxi-

<sup>1</sup> Tenn. Station, Bul. 100; Jour. Ind. and Eng. Chem., March, 1915.



imum crop response for a definite period after treatment, according to relationship to some definite laboratory results obtained under controlled conditions? The feasible procedure would be to determine a method which would effect the maximum decomposition of  $\text{CaCO}_3$  by its contact with the acid-reacting soil constituents under well controlled laboratory conditions, and then, if possible, to establish a relationship between this maximum decomposition and practice.

The disappearance of  $\text{MgCO}_3$  presented an additional unanticipated problem, that of determining the reason for this previously unreported tendency. Accordingly, the studies were continued with a view to acquiring data upon both lime and magnesia requirements and the existence of any definite relationship between the activities of the two carbonates which might be attributed to solubility, molecular equivalence, or other factors.

### LABORATORY STUDIES

Two of the three soils studied in the pot work were exceedingly low in organic matter, and it was therefore difficult to account for the loss of carbonates by assuming reactions to have taken place between the bases and organic constituents. Consequently a laboratory study was begun to determine the activities of the three soils of Table I and various mineral soil constituents upon the two earthy carbonates. The scheme followed was to bring the soils and carbonates into contact under different moisture conditions, with means of determining accurately the  $\text{CO}_2$  evolved from the treated soils. The moisture conditions maintained were air-dry, estimated optimum, and a large excess of water. This, of course, necessitated the elimination of any biological influences. In order to avoid the use of heat for purposes of sterilization, one of the alkaline soils was impregnated with .5 gram benzoic acid, as neutral sodium benzoate, treated with 2 grams of  $\text{MgCO}_3$  and placed in Erlenmeyer flasks. These preliminary tests as to the influence of different moisture conditions showed that the estimated optimum condition gave the greatest activities, as measured by  $\text{CO}_2$  evolutions; but it appeared that there was an interference from the organic salt used to produce sterility.

In order to test this point, the untreated loam soil and some of that which had decomposed the excessive  $\text{MgCO}_3$  treatment, both being carbonate-free, and the same soil with an accumulation of  $\text{CaCO}_3$  from its previous heavy treatment, were used to determine the influence of the three conditions of the same soil upon sodium benzoate. The amounts of  $\text{CO}_2$  evolved are shown in Table III.

The sterility of the soils treated with the preservative seemed to be beyond question.

It therefore appeared that the catalytic oxidative power of the soil effected oxidation of the sodium benzoate. Hence, its use was discontinued and sterilization was accomplished by steam and maintained through the use of cotton filters and washing solutions.

TABLE III—*Evolution of CO<sub>2</sub> from acid and alkaline soils when in contact with sodium benzoate*

Type	Soil used		Treatment		CO <sub>2</sub> evolved during 147 days' contact
	Amount	Reaction	Previously given	This experiment	
	Gms.				Gms.
Loam .....	200	Acid	None	Sodium benzoate	.5001
Loam .....	200	Alkaline	CaCO <sub>3</sub> —22877 lbs. per acre	Sodium benzoate	.3407
Loam .....	200	Alkaline	MgCO <sub>3</sub> —22877 lbs. per acre	Sodium benzoate	.5014

## DECOMPOSITION OF EARTH CARBONATES BY STERILE ALKALINE SOILS

Two hundred grams of each of the air-dried soils of Table I were next used for contact carbonate treatments. These soils had previously decomposed 22877, 18420, and 17964 pounds of  $\text{MgCO}_3$  per acre, respectively, for loam, silty loam, and sandy loam. It would seem reasonable to assume that this heavy treatment and long-continued contact of carbonates and soil would have satisfied the requirements of physical absorption and that further decomposition should be attributed to chemical activities. The charges were subjected to moist contact treatment in Erlenmeyer flasks with (a)  $2\frac{1}{2}$  grams precipitated  $\text{MgCO}_3$ , (b) 3 grams of 100-mesh dolomite, and (c) a mixture of  $2\frac{1}{2}$  grams  $\text{MgCO}_3$  and 2 grams  $\text{CaCO}_3$ . The  $\text{CO}_2$  of the atmosphere of the sterile flasks was then drawn off and the closed flasks were permitted to remain under laboratory conditions. The rubber connections between the glass tubing and stopcocks were wired, after being immersed in hot paraffin, in order to insure long use without deterioration. At various intervals, the  $\text{CO}_2$  of the atmosphere was drawn off and absorbed in soda-lime tubes. The figures of Table IV represent the  $\text{CO}_2$  evolved.

These data show a continued evolution of  $\text{CO}_2$  from these strongly alkaline sterile soils which had already effected a very excessive carbonate decomposition. The fact that for a long time these soils had been strongly alkaline and that they were also sterile would preclude the consideration of free organic acids as the cause of the decomposition of the carbonates. However, in view of the inherent oxidative power of soil as shown by Sullivan and Reid<sup>1</sup>, Shreiner and Sullivan<sup>2</sup>, and others, the entire  $\text{CO}_2$  evolutions could not be attributed to the liberation of the  $\text{CO}_2$  radical from the carbonates. Since the contact is to be continued for a longer period, the treated soils in the flasks were not available for determination of residual carbonates.

The next step was the elimination of organic matter from consideration as a possible source of the  $\text{CO}_2$  liberated by contact treatment of soils and carbonates. A parallel series under conditions identical with those of the foregoing table contained a red clay secured six feet underground, and kaolin secured from a mineral supply house. Both materials showed absence of any soluble acids in distilled-water digestion. The decompositions resulting from these organic-matter-free substances are given in Table V.

These results agree with the observations of Morse and Curry<sup>3</sup> as to the ability of clay to decompose carbonates. The decompositions of both  $\text{CaCO}_3$  and  $\text{MgCO}_3$  effected by kaolin are not, however, in harmony with the observations of Dumont, quoted by Harris<sup>4</sup>. Dumont found that kaolin effected no decomposition of potassium carbonate. It appears to be

1. Jour. Ind. and Eng. Chem., Vol. 3, No. 1.

2. Bureau of Soils, Bul. 73.

3. N. H. Station, Report, 1907-1908, p. 271.

4. Mich. Station, Tech. Bul. 19, p. 14; Compt. Rend. l' Acad. d. Science, 1906, p. 34.

TABLE IV—*Decomposition of earthy carbonates by sterile alkaline soils, measured by determination of evolved gas*

Soil, 200 grams	Reaction to litmus and Veitch	Treatment	CO <sub>2</sub> evolved after	
			205 days CaCO <sub>3</sub> equivalent	545 days CaCO <sub>3</sub> equivalent
			Gms.	Gms.
Loam .....	Strongly alkaline	MgCO <sub>3</sub> <sup>a</sup>	1.0384	1.2082
Loam .....	Strongly alkaline	MgCO <sub>3</sub> and CaCO <sub>3</sub> <sup>b</sup>	.9932	1.1473
Loam .....	Strongly alkaline	Dolomite <sup>c</sup>	.4861	.6087
Silty loam .....	Strongly alkaline	MgCO <sub>3</sub> <sup>a</sup>	.8559	1.1646
Silty loam .....	Strongly alkaline	MgCO <sub>3</sub> and CaCO <sub>3</sub> <sup>b</sup>	.7604	1.0093
Silty loam .....	Strongly alkaline	Dolomite <sup>c</sup>	.5536	.6151
Sandy loam .....	Strongly alkaline	MgCO <sub>3</sub> <sup>a</sup>	.5309	.8128
Sandy loam .....	Strongly alkaline	MgCO <sub>3</sub> and CaCO <sub>3</sub> <sup>b</sup>	.4224	.6743
Sandy loam .....	Strongly alkaline	Dolomite <sup>c</sup>	.3941	Lost

a, 2½ gms.; b, 2½ gms. and 2 gms.; c, 3 gms.

TABLE V—*Decomposition of earthy carbonates by sterile organic-matter-free hydrated silicates*

Substance, 200 grams	Reaction of distilled water extract	Treatment	CO <sub>2</sub> evolved after	
			205 days CaCO <sub>3</sub> equivalent	545 days CaCO <sub>3</sub> equivalent
			Gms.	Gms.
Red clay .....	Very slightly alkaline	MgCO <sub>3</sub> <sup>a</sup>	1.1297	1.2538
Red clay .....	Very slightly alkaline	MgCO <sub>3</sub> and CaCO <sub>3</sub> <sup>b</sup>	.9229	1.2476
Red clay .....	Very slightly alkaline	Dolomite <sup>c</sup>	.8013	.9194
Kaolin .....	Very slightly alkaline	MgCO <sub>3</sub> <sup>a</sup>	.4107	.5537
Kaolin .....	Very slightly alkaline	MgCO <sub>3</sub> and CaCO <sub>3</sub> <sup>b</sup>	.3450	.5034
Kaolin .....	Very slightly alkaline	Dolomite <sup>c</sup>	.3552	.5185

a, 2½ gms.; b, 2½ gms. and 2 gms.; c, 3 gms.

worthy of note that although not reacting with alkali carbonates until leached by acid, kaolin will react with the alkali earth bases during long periods in moist contact. This direct chemical reaction between the acid silicates and earthy carbonates took place under conditions which, originally, at least, bring the carbonate and silicate together in water solution devoid of  $\text{CO}_2$  gas.

### THE ACTIVITY OF $\text{SiO}_2$ AS AN ACID

The work was carried one step further by the introduction of pure  $\text{SiO}_2$ , under the same conditions of moist, sterile contact which existed in the two preceding studies. In this parallel,  $\frac{1}{2}$  mm sand, and the same ground to pass 100-mesh, was used, together with pulverized quartz. The amounts of  $\text{CO}_2$  evolved as a result of the treatment are shown in Table VI.

TABLE VI—*Decomposition of earthy carbonates by moistened sterile sand and pulverized quartz*

Substance, 200 grams	Treatment*	$\text{CO}_2$ evolved after	
		205 days, $\text{CaCO}_3$ equivalent	545 days, $\text{CaCO}_3$ equivalent
		Gms.	Gms.
Sand, $\frac{1}{2}$ mm mesh .....	Precipitated $\text{MgCO}_3$ .....	.0902	.1382
Sand, $\frac{1}{2}$ mm mesh .....	Precipitated $\text{MgCO}_3$ and $\text{CaCO}_3$ .....	.1275	.2291
Sand, $\frac{1}{2}$ mm mesh .....	Dolomite .....	.1141	.1497
Fine sand, 100 mesh .....	Precipitated $\text{MgCO}_3$ .....	.2272	.3277
Fine sand, 100 mesh .....	Precipitated $\text{MgCO}_3$ and $\text{CaCO}_3$ .....	.2072	.3803
Fine sand, 100 mesh .....	Dolomite .....	.0952	.1765
Ground quartz .....	Precipitated $\text{MgCO}_3$ .....	.5155	.8157
Ground quartz .....	Precipitated $\text{MgCO}_3$ and $\text{CaCO}_3$ .....	.2357	.3256
Ground quartz .....	Dolomite .....	.2238	.3697

\*Amounts same as in Tables IV and V.

As would be expected, the influence of fineness of the silica on its solubility is indicated by the greater decomposition of the carbonates by the silt. The writer was induced to test for this possible quantitative reaction because of the well-known formation of magnesium silicate where evaporations of  $\text{MgCl}_2$  and  $\text{SiO}_2$  are heated too high, in the process of dehydrating silica. The decomposition of carbonates at room temperature was checked by boiling  $\text{CaCO}_3$  and  $\text{MgCO}_3$  separately with both pulverized quartz and finely ground rutile. The decompositions effected by 30 minutes' boiling are given in terms of grams of  $\text{CaCO}_3$  (Table VII).

The decomposition of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  by pulverized quartz was also accomplished in the procedure of evaporation given later in this bulletin, and, in less degree, in the use of the method of Tacke.

These data are confirmatory of the belief of Morey<sup>1</sup>, who wrote, "Indeed, there is ground for the belief that silicic acid is considerably strong-

<sup>1</sup> Jour. Am. Chem. Soc., 36, No. 2, p. 216.



er than has been supposed." From the results of the two preceding tables, it is easy to conceive of an appreciable decomposition of earthy carbonates through the action of the relatively large amount of exceedingly finely divided hydrated silica which must be present as a result of the long-continued dissolving and precipitating of  $\text{SiO}_2$  in soils. It is possible that, in many cases, the undesirable physical conditions of soil are due largely to the occurrence of excessive amounts of colloidal silica.

Hall and Morison<sup>1</sup>, however, found a decided benefit was observed over a long-time period when an alkaline silicate (sodium) was applied to soil. The silica seemed to perform a well-defined function. Their work was planned so as to check the effect of the sodium of the treatments. (The sodium silicate would most probably hydrolyze, yielding  $\text{NaOH}$  and colloidal silica). Where lime is added in amounts sufficient both to meet lime requirements and to insure an excess of carbonate, which would be the more subject to action of carbonated water, any calcium silicate resulting from treatment would probably remain largely as such. However, in presence of carbonated water the lime-silica reaction is readily reversed.<sup>2</sup>

TABLE VII—*Decomposition of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  by boiling with  $\text{SiO}_2$  and  $\text{TiO}_2$*

Substance, 20 grams	Treatment,* 2 grams	$\text{CO}_2$ evolved, terms of $\text{CaCO}_3$
		Gms
Ground quartz .....	Precipitated $\text{CaCO}_3$	.0230
Ground quartz .....	Precipitated $\text{MgCO}_3$	.0966
Ground rutile .....	Precipitated $\text{CaCO}_3$	.0165
Ground rutile .....	Precipitated $\text{MgCO}_3$	.0520

\*Freed of hydrates by  $\text{CO}_2$  treatments.

## THE INFLUENCE OF CARBONIC ACID UPON ALKALI EARTH SILICATES

As bearing further upon this point, the reversal of the lime silica and magnesia-silica reactions was studied. From 6 to 8 hours' simultaneous extractions were made daily of 10-gram charges of serpentine and wollastonite, and these compared with extractions of native carbonates. Limestone, about 92 per cent, dolomite of approximately the same chemical equivalence, and 93 per cent magnesite were used. All substances passed through the 100-mesh sieve. The wollastonite and magnesite, however, appeared to be somewhat finer than the other substances. The substances were kept agitated by the current of  $\text{CO}_2$ , as far as possible, and the extracts were filtered and titrated. The residue from each extraction

1. Proc. Royal Soc., Ser. B, 77 (1906).

2. Since writing the above, the author has seen thriving crops of wheat growing in nutrient cultures of 1% silica gel—unpublished thesis, D. S. Jennings, Cornell University, 1915. See also, A. Gregoire, Bul. Soc. Chem. Belg., 25, 1911, No. 2, pp. 85-103.



TABLE VIII—*Reversal of lime-silica and magnesia-silica reactions by hydrolysis of native silicates in carbonated water—terms of  $\text{CaCO}_3$ , grams, room temperatures, atmospheric pressure*

Hours of passage of $\text{CO}_2$ through mixture	Limestone, 100-mesh, 10 grams	Wollastonite, 100-mesh, 10 grams	Dolomite, 100-mesh, 10 grams	Serpentine, 100-mesh, 10 grams	Magnesite, 100-mesh, 10 grams
1st day, 6 hours.....	.8500	1.0250	.4750	.1250	.5050
2nd day, 7 hours.....	.7500	.8850	.3100	.0725	.4500
3rd day, 6½ hours.....	.7500	.6800	.2950	.0475	.4350
4th day, 8 hours.....	.7555	.6000	.3000	.0275	.2700
5th day, 7 hours.....	.7450	.6100	.2800	.1400	.2800
6th day, 6 hours.....	.6800	.3450	.2100	.0500	.1850
Total days 6, total hours 40½...	4.5300	4.1450	1.8700	.4625	2.1250
Correction for $\text{CaCO}_3$ impurities..	.....	.6740	.....	.1870	.....
$\text{CaCO}_3$ derived by hydrolysis....	.....	3.4710	.....	.2755	.....

was returned to its flask for extraction upon the following day. Carbonate determinations upon the native samples of wollastonite and serpentine gave 6.74 and 1.87 per cent of  $\text{CaCO}_3$ , respectively. Corrections for these amounts are made in the table, the corrected amounts showing alkalinity necessarily derived from hydrolysis of the silicates.

As observed in the previous tables, the reaction between magnesium carbonates and silica and siliceous compounds is more extensive than that between these substances and calcium carbonate. The reversal of the magnesia-silica reaction through hydrolysis, in the presence of  $\text{CO}_2$  in solution, is correspondingly more difficult than that of the lime-silica compounds.

### INFLUENCE OF HYDRATION OF SILICA UPON ITS REACTIONS WITH EARTHY CARBONATES

The first step in the study of the influence of hydration of silicates upon their activities was an attempt to eliminate organic matter from a strongly calcareous soil without resorting to heat of combustion sufficiently high to effect complete dehydration of the silicates.<sup>1</sup> The loam soil

TABLE IX—*Action of calcareous soil upon earthy carbonates, after oxygen combustion to remove organic matter*

Soil, 200 grams	Treatment	$\text{CO}_2$ drawn off, terms of $\text{CaCO}_3$ , grams, after	
		133 days	473 days
Alkaline loam.	Precipitated $\text{MgCO}_3$ , $2\frac{1}{2}$ gms.	.2868	.4805
Alkaline loam.	Precipitated $\text{CaCO}_3$ , 2 gms.	.0797	.1310

used had been in contact with a large excess of  $\text{CaCO}_3$  for over a year. Gentle relay heatings of 200 grams of the soil were accomplished in platinum dishes in the open by the use of a current of oxygen. It is, of course, not certain that partial or complete dehydration did not result, though a comparison of the results of Tables IX and X would indicate that complete dehydration was not effected. Possibly a better method of elimination of organic matter is that used by Harris<sup>2</sup>, who boiled soil with concentrated  $\text{H}_2\text{SO}_4$  and then freed the soil of acid by washing and filtering. After the oxygen-combustion treatment, the soil was mixed moist with calcium and magnesium carbonates separately and placed in closed Erlenmeyers, as previously described. The  $\text{CO}_2$  found in the atmosphere of the flask later is given in Table IX.

1. It should probably be emphasized that because of treatments given which would be expected to eliminate colloids, both organic and inorganic, it naturally follows that the continued activities are to be attributed to chemical reactions rather than to physical absorption.
2. Mich. Station, Tech. Bul. 19.

The data of Table IX demonstrate that the occurrence of an excess of calcium carbonate from previous treatment is not an absolute deterrent in the continued silica-lime and silica-magnesia reactions. That is, the decomposition of earthy carbonates continues long after the satisfying of the initial, or temporary, lime-requirement indication of the Veitch laboratory procedure. The presence of  $\text{CaCO}_3$  seemed to have but little, if any, depressing effect upon the phenomenon of decomposition of  $\text{MgCO}_3$ . The effect of previously applied excessive treatments of  $\text{MgCO}_3$  was also tried after dehydration of the soil by ignition. Another portion of the loam soil which had previously decomposed 22877 pounds per acre 3,500,000 of soil was subjected to white heat in the muffle furnace for 16 hours. The residues from 200-gram charges of the initially treated soil were then moistened and mixed with separate charges of "C. P."  $\text{CaCO}_3$  and  $\text{MgCO}_3$  in closed Erlenmeyer flasks. The activities between the ignited residues and the two carbonates are shown in Table X.

It should be emphasized that before ignition this last soil was free of carbonates, though strongly alkaline from excessive amounts of magnesium silicate formed from previous  $\text{MgCO}_3$  treatments. In spite of this treatment the decomposition of  $\text{MgCO}_3$  is still far in excess of that of  $\text{CaCO}_3$ . The 16-hour ignition would certainly have accomplished dehydration, and it is difficult to account for the  $\text{CO}_2$  evolution except by assuming appreciable rehydration of the dehydrated silica. This excessive decomposition of  $\text{MgCO}_3$  was then effected under a short-time period of evaporation of ignited calcareous silty loam and  $\text{MgCO}_3$ , which in this case was added in solution of carbonated water. Four 10-gram charges of the calcareous silty loam of Table I were ignited for 16 hours in a muffle furnace. After ignition two charges were analyzed for residual  $\text{CO}_2$ , together with 150 cc of boiled  $\text{MgCO}_3$  solution as blanks. The other two charges were evaporated on the water bath with the same volume of  $\text{MgCO}_3$ , and residual  $\text{CO}_2$  was then determined. The blank showed a  $\text{CaCO}_3$  value of 1.8863 gram, while the evaporated charges gave but 1.6075 gram, a loss of .2788 gram. That the same result cannot be obtained in any marked degree from  $\text{CaCO}_3$  will later be shown.

## RECOVERY OF WATER BY DEHYDRATED SILICA

The ability of pure  $\text{SiO}_2$  to become hydrated again after ignition was then studied by comparison of the action of 200 grams of opal,  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ , upon earthy carbonates with its activity subsequent to ignition in a muffle furnace for a period of 16 hours. A parallel of  $\text{TiO}_2$  was also included, the only difference being an 8-hour ignition period for  $\text{TiO}_2$  instead of one of 16 hours. The occurrence of rutile in soils has been shown to be almost universal<sup>1</sup>. Especially is it to be found in clays. For this reason it was included in the study.

From the data of Table XI it would appear that the recovery of hydration by  $\text{TiO}_2$ , upon contact with moisture after heating, is much less

1. Am. Jour. of Sc., Dec. 1891; Chem. News, 65, 65.

TABLE X—*Action of ignited residues of magnesian soils upon calcium and magnesium carbonates under moist contact*

Soil, 200 grams	Previous treatment	Present treatment	CO <sub>2</sub> evolved after	
			133 days CaCO <sub>3</sub> equivalent	473 days CaCO <sub>3</sub> equivalent
Strongly alkaline carbonate-free loam .....	22877 lbs. per acre MgCO <sub>3</sub>	CaCO <sub>3</sub> 2 gms.	Gms. .1545	Gms. .2232
Strongly alkaline carbonate-free loam .....	22877 lbs. per acre MgCO <sub>3</sub>	MgCO <sub>3</sub> 2½ gms.	.2259	.3560

TABLE XI—*Decomposition of CaCO<sub>3</sub> and MgCO<sub>3</sub> by opal and rutile, before and after ignition of minerals*

Substance	Treatment	CO <sub>2</sub> evolved, terms of CaCO <sub>3</sub> grams after 133 days' contact		CO <sub>2</sub> evolved after 473 days' contact	
		Before ignition CaCO <sub>3</sub> equivalent	After ignition CaCO <sub>3</sub> equivalent	Before ignition CaCO <sub>3</sub> equivalent	After ignition CaCO <sub>3</sub> equivalent
Opal, 200 grams.....	Precipitated MgCO <sub>3</sub> 2½ gms.	Gms. .0425	Gms. .0271	Gms. .....	Gms. .1580
Opal, 200 grams .....	Precipitated CaCO <sub>3</sub> 2 gms.	.0523	.0264	.2371	.0470
Rutile, 300 grams .....	Precipitated MgCO <sub>3</sub> 2½ gms.	.1803	.0186 <sup>a</sup>	.2708	.0602 <sup>b</sup>
Rutile, 300 grams .....	Precipitated CaCO <sub>3</sub> 2 gms.	.0479	.0125 <sup>a</sup>	.1221	.0787 <sup>b</sup>

a. Total period of contact, 91 days.

b. Total period of contact, 431 days.

extensive than that effected by  $\text{SiO}_2$ . However, by reference to Table VI it will be seen that the decomposition of the carbonates by ground quartz is much greater than that effected by opal. Decomposition of carbonates produced by evaporation of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  with equal quantities of quartz and opal seemed practically identical, when the decomposition was measured by determinations of residual carbonates.

### CARBONATE DECOMPOSITIONS UNDER LABORATORY CONDITIONS SUFFICIENTLY FEASIBLE FOR ADOPTION AS A METHOD

The data offered demonstrate conclusively that after the elimination of biological influences and the removal of organic and inorganic colloidal matter, we secure a continued decomposition of earthy carbonates by alkaline soils under moist contact conditions at normal temperatures. This decomposition is shown to be very appreciable in the absence of any hydrated silicates. The problem then resolved itself into an investigation to determine a procedure which would permit the maximum activities between soils and soil component materials under laboratory conditions during a period of time consistent with analytical work. This seemed to necessitate the use of an excess of earthy carbonate reagents in solution. The quantitative procedure relied upon to determine the presence of a sufficient amount of lime salts in humid soils is the determination of carbonate present, by the estimation of carbonate  $\text{CO}_2$ . Excess of carbonates in soils is usually coincident with appreciable quantities of silicates of lime. Gaither<sup>1</sup> has shown that the presence of carbonates is always characterized by absence of soil acidity. Hence, when there is obtained an indication of soil acidity and also an indication of  $\text{CaCO}_3$  in the same soil, it necessarily follows that one of the two procedures is erroneous. The old procedure for determining carbonates by boiling soil invariably gives indications of carbonates, though the soil may be devoid of them and possess a high lime requirement. It has been shown, however, that absence of carbonates does not necessarily mean that lime-loving plants may not flourish. An abundance of lime as silicates will function as does the lime of carbonate in promoting good crops of clover<sup>2</sup>. However, the presence of carbonates of lime, in more than mere traces attributable to laboratory error, is usually taken as evidence that the lime-combining power of the acid radicals contained in soil has been satisfied. It would thus seem that the condition most nearly in accord with actual practice would be to determine the residual calcium carbonate from a definite application of it to the soil, after the soil has fully performed its immediate function of decomposing the carbonate.

1. Jour. Ind. and Eng. Chem., Vol. 6, No. 12.  
2. Jour. Ind. and Eng. Chem., Vol. 5, No. 2.



The method of adding lime in solution naturally appealed first as the most feasible and adaptable when large numbers of determinations are to be made. The use of an aliquot is decidedly more rapid and less subject to error than the use of individually weighed charges. Another reason which prompted the use of aliquots is the uncertain composition of the precipitated "C. P." carbonates. The occurrence of basic hydrates is almost a positive source of error in differential  $\text{CO}_2$  work, and it is necessary to carbonate the "C. P." products before differences between their original and residual  $\text{CO}_2$  contents may be taken as the true measure of lime reaction. In previous work, unpublished, while at the Pennsylvania Station, the writer had endeavored to modify the Veitch procedure by adding a definite excessive amount of lime water, and evaporating to dryness, after which this evaporated soil and lime mixture was kept in suspension in water through which  $\text{CO}_2$  passed for various periods, with the object of carbonating the excess of lime and holding it in solution for titration, after filtration through disc filters.

Two objections arose in the procedure. Apparently the excess of  $\text{CaO}$  acted upon organic matter during the evaporation, and different periods of carbonated-water extraction yielded varying alkalinities up to amounts considerably in excess of the lime actually applied. This, of course, meant that although the soil acid substances combined with the lime, the products of the reaction, together with original lime silicates and other salts were again converted to carbonates through hydrolysis, effected by the carbonated water. It still seemed feasible, however, to bring dissolved lime into contact with the soil under conditions which would not effect hydrolysis of the silicates. The idea of adding the solutions of lime and magnesia to the soils follows the thought that no matter in what form we may apply these two bases to soil in practice, their continued chemical dissemination throughout the surface mass occurs as solutions of the carbonates in carbonated water. It is true, however, that maximum reaction between the earthy carbonates and the acid silicates cannot transpire under optimum conditions of moisture, approaching saturation, when the moisture is impregnated with  $\text{CO}_2$ . That this is true is evidenced by the fact that normal leachings of strong acid, rock-derived humid soils and subsoils are universally alkaline. However, such leachings might become acidified in some instances when passing through extensive deposits of such substances as ferrous and other sulphides. The reversal of the hydrolysis effected by carbonated water may be expected to transpire when there occur temperature increases and moisture decreases, or when the carbonate is in dilute solution with moisture less rich in  $\text{CO}_2$ . As bearing on the point of an excess of  $\text{CO}_2$  preventing the maximum reaction between  $\text{CaCO}_3$  in solution and acid soils, the following was done: Definite aliquots of partly saturated  $\text{CaCO}_3$  solution were added to eight 10-gram charges of different soils, the lime requirement by the Veitch method being known of several of the samples. After standing for 1 hour with several gentle stirrings, the soils were filtered through Buchner funnels and washed with slightly carbonated water by gentle suction. The solutions were then titrated and found to be almost

identical in alkalinities to those of the original, in case of the acid soils, and slightly more alkaline for two alkaline soils. It appeared essential, therefore, to rid the solution of the excess of  $\text{CO}_2$  gas in order to bring about the desired reactions. This would, of course, result in the precipitation of  $\text{CaCO}_3$ , which would preclude the direct titration feature.

There appears to be a question as to the existence of an acid carbonate of lime at the pressures which would be exerted in soils and upper subsoils. Cameron and Robinson<sup>1</sup> and Leather and Sen<sup>2</sup> offered data which tend to show that the compound  $\text{CaH}_2(\text{CO}_3)_2$  does not exist at atmospheric pressure below  $4\frac{1}{2}$ , while McCoy and Smith<sup>3</sup> and Keiser and McMaster<sup>4</sup> offer contrary data.<sup>5</sup> The existence of the acid salt appears to be exceedingly doubtful. For the sake of brevity, however, whenever the term "bicarbonate" is used in this paper, it is intended to convey the meaning of a definite amount of  $\text{CaCO}_3$  in solution of large excess of  $\text{CO}_2$ .

### REACTION OF SOIL AND $\text{CaCO}_3$ THROWN OUT OF CARBONATED WATER SOLUTION BY AGITATION AND SUCTION

The activity of  $\text{CaCO}_3$  toward soil after its precipitation from carbonated water at room temperature was then tried. The plan was to measure the  $\text{CaCO}_3$  content of a boiled aliquot and then to determine the residual  $\text{CaCO}_3$  after contact of carbonate with soil for different periods. Duplicate aliquots of 150 cc  $\text{CaH}_2(\text{CO}_3)_2$  were added to 10 grams of soil in 300-cc Erlenmeyer flasks. Suction of 4 inches was applied during a 30-minute period to throw the  $\text{CaCO}_3$  from solution and displace the excess of  $\text{CO}_2$ . In one set, agitation and aspiration was then continued for 1 hour, and in another set for an overnight period. A third set was immediately evaporated to dryness. The residual  $\text{CaCO}_3$  from these three treatments was then determined by the Tennessee Station method<sup>6</sup>. The results are recorded in Table XII.

The two procedures at room temperature proved ununiform and unsatisfactory. It appeared doubtful whether the atmospheric  $\text{CO}_2$  could be completely liberated from the bicarbonate solution before the additions of acid to decompose the residual carbonate, under the conditions of volume and agitation. The necessary volume of  $\text{CaH}_2(\text{CO}_3)_2$  to insure sufficient excess of  $\text{CaCO}_3$  was too great to permit of the most efficient agitation. The results from the evaporation showed that the decompositions of carbonates at room temperature were certainly not the maxima. That the greater reaction resulting from evaporation could not be attributed to the effect of heat upon organic matter is shown by the difference in the case of the clay subsoil.

1. Jour. Phys. Chem., 1908, XII, 561.

2. Memoirs Dept. Agr., India, Chem. Series, Vol. 1, No. 7.

3. Jour. Am. Chem. Soc., April, 1911.

4. Jour. Am. Chem. Soc., 1908, 1714.

5. See also, Johnston, Jour. Am. Chem. Soc., vol. XXXVII, No. 9, Sept., 1915. and Stieglitz, Carnegie Inst. Publ., No. 107, 1909.

6. Jour. Ind. and Eng. Chem., March, 1915.



TABLE XII—Comparison of decomposition of  $\text{CaCO}_3$ , when added in solution and thrown out by suction, with its action when thrown out of solution by evaporation—terms of  $N/20$  acid of titration

Soil No. 10-gm. charge	Type	Reaction	Blank—soil + $\text{CaCO}_3$	Residual $\text{CO}_2$ , determined by liberation with $\text{H}_3\text{PO}_4$		
				After 1 hour's contact	Overnight contact	Immediate evaporation
			cc	cc	cc	cc
3459	Silty loam.....	Acid .....	31.2	29.35	34.45	22.95
3464	Clay .....	Acid .....	31.2	23.8	29.1	17.7
3460	Silty loam .....	Alkaline .....	31.2	45.9	50.8	33.9
3461	Sandy loam .....	Acid .....	31.2	50.8	37.3	23.5
				37.5	37.9	24.5

# EFFECT OF PERIOD OF CONTACT OF SOIL AND $\text{CaH}_2(\text{CO}_3)_2$ SOLUTION BEFORE EVAPORATION

The effect of immediate evaporation, as compared to that after 3 hours' agitation with suction to remove the excess  $\text{CO}_2$ , was then determined. One hundred cc aliquot of  $\text{CaCO}_3$  solution was used alone and also supplemented by .2 gram of "C. P." precipitated  $\text{CaCO}_3$ . Results are given in N/20 acid titration for  $\text{CO}_2$ , by the Amos procedure for the absorption of  $\text{CO}_2$ . The results of Table XIII do not show any increased  $\text{CaCO}_3$  decomposition when the longer contact period is used prior to evaporation.

TABLE XIII—Comparison between decomposition of  $\text{CaCO}_3$  upon immediate evaporation and evaporation after 3 hours' agitation

	Sandy loam		Silt loam	
	100 cc alone	100 cc plus .2 gm $\text{CaCO}_3$	100 cc alone	100 cc plus .2 gm. $\text{CaCO}_3$
Residual $\text{CO}_2$ from immediate evaporation—cc N/20 acid..	13.8	14.6	49.3	52.8
Evaporation after 3 hours' agitation—cc N/20 acid .....	14.3	15.4	50.4	52.0

The next comparison made was between determinations of the decomposition effected by evaporation and boiling for periods of 5 and 30 minutes without subsequent evaporation. These determinations are given in Table XIV.

In the case of the clay, sandy loam and silty loam, the evaporation appeared to give somewhat greater decomposition than 5 minutes' boiling; but the reverse occurred in the case of the swamp soil. This might be

TABLE XIV—Comparisons between immediate evaporation of soil with 100cc  $\text{CaH}_2(\text{CO}_3)_2$  and boiling 5 minutes and 30 minutes

Soil		Reaction	Residual $\text{CaCO}_3$ , by determination of $\text{CO}_2$ , terms of N/20 acid		
Lab. No.	Type		After evaporation	After boiling 5 minutes	After boiling 30 minutes
			cc	cc	cc
3459	Silty loam ...	Acid .....	20.9	23.5	14.9
3461	Sandy loam ..	Acid .....	23.5	25.3	21.1
3466	Swamp .....	Acid .....	6.6	4.4	1.7
3464	Clay .....	Acid .....	16.1	19.6	14.9
Average			16.8	18.2	13.2

readily attributed to the intervening factor of action of heat and carbonate upon organic matter. Ground quartz also effected a greater decomposition of carbonates when evaporated with them than when subjected to the shorter period of boiling. The continued boiling would undoubtedly involve the extensive decomposition of soil organic matter, thereby making the procedure undesirable. The effects of different periods of evaporation were then studied. Two soils were evaporated with carbonate solution in porcelain evaporating dishes, which require from  $1\frac{1}{2}$  to 2 hours for evaporation, and also in 150-cc Jena beakers. After 9 hours' evaporation the residue of soil and  $\text{CaCO}_3$  had been reduced to a very thin paste in the beakers. It remained thus overnight before determination of residue  $\text{CaCO}_3$ . The estimations of residual carbonates are given in Table XV.

TABLE XV—*Effect of variation in period of evaporation*

	Loam, N/20 acid	Silt loam, N/20 acid
	cc	cc
$1\frac{1}{2}$ hour .....	14.3	19.95
9 hours plus overnight..	11.7	16.9

It thus appears that a great difference in time of contact in the laboratory affects to some degree the extent of the reaction between the carbonate and soils. Very little error can be expected, however, in the slight variation of time involved in laboratory procedure when porcelain evaporating ware is uniformly used. This was shown by the evaporation of a soil with 100 cc of  $\text{CaCO}_3$  solution and the repetition of the treatment and two additional 100 cc aliquots. The residual  $\text{CO}_2$  in the single evaporation gave a  $\text{CO}_2$  titration of 15.9 cc N/20 acid, while the triple evaporation gave 56.3 cc, the blank on two aliquots being represented by 38 cc. The residual  $\text{CO}_2$  after evaporation of a clay subsoil with 150 cc  $\text{CaH}_2(\text{CO}_3)_2$  was then compared to that found after the addition of 150 cc of distilled water to the evaporated clay and a subsequent evaporation. The residual  $\text{CO}_2$  determinations were practically identical. From this point, a definite-sized container, a 150-cc porcelain evaporating dish, was used. Time of contact at room temperature was also found to exert an influence when the Tacke method was used. Twenty grams of clay, 4 gram  $\text{CaCO}_3$  and 60 cc of  $\text{CO}_2$ -free water were agitated for 3 hours, with 4 inches of vacuum. This treatment gave a lime requirement of .44 per cent, while a second 3 hours gave an additional requirement of .09 per cent. Evaporation of the same clay and determination of residual  $\text{CO}_2$  gave .53 per cent. That the further contact of soil and  $\text{CaCO}_3$  for a period of 3 hours after the determination at room temperature is made by the Tacke method results in a further evolution of  $\text{CO}_2$  is also shown in Tables XXIII and XXIV.

A comparison was next made between partial and complete evaporation of the  $\text{CaCO}_3$  aliquot in contact with soil, with the results shown in Table XVI. Residual  $\text{CO}_2$  is given in terms of N/20 acid titration.

TABLE XVI—Comparison of evaporation of soil and 100 cc  $\text{CaH}_2(\text{CO}_3)_2$  to dryness, and evaporation to approximately 50 cc

Treatment	Residual $\text{CaCO}_3$ , by determination of $\text{CO}_2$ , terms of N/20 acid				
	Silty loam	Sandy loam	Clay	Swamp	Average
	cc	cc	cc	cc	cc
Evaporation to dryness.....	20.0	21.8	18.3	11.65	17.9
Evaporation to one-half original volume .....	21.1	21.3	16.75	10.6	17.4

The results of Table XVI indicate that it is unnecessary to evaporate to complete dryness, in order to obtain the maximum of reaction between soil and carbonate, and that a thin paste is permissible. This facilitates the removal of the evaporated soil to flasks by washing with  $\text{CO}_2$ -free distilled water, in the determination of residual carbonates. Simultaneous evaporations were next made, with and without stirring. Stirring was done about the time of the precipitation of the carbonate from solution by the increasing heat, and again at about 75-cc and 50-cc volumes.

TABLE XVII—Comparison between stirring mixtures of soils and  $\text{CaH}_2(\text{CO}_3)_2$  solution during evaporation and evaporation without stirring

Treatment	Residual $\text{CO}_2$ , terms of N/20 acid			
	Silty loam	Sandy loam	Clay	Average
	cc	cc	cc	cc
Stirring 3 times.....	19.2	21.0	15.1	18.4
No stirring .....	20.9	21.8	15.9	19.5

The results of Table XVII, though not greatly at variance, are consistently lower in the estimation of residual carbonates when stirring was done. In succeeding work the definite procedure as to size of evaporating dish, and the three stirrings during evaporation, was followed consistently.

### ADDITIONAL POINTS CONSIDERED

The next point considered was the possible action of the excess of  $\text{CO}_2$  in the carbonated water of the  $\text{CaCO}_3$  solution upon the silicates of an acid soil during the brief contact of soil with solution before expulsion of excess of  $\text{CO}_2$  by evaporation. For soils low in lime and other silicates, this point was touched upon by the comparison between immediate evapora-

tion and evaporation after 3 hours' shaking (Table XIII). In order to make conditions more severe, the following was done: Ten-gram charges of calcium silicate and calcium-magnesium silicate were evaporated with the  $\text{CaCO}_3$  aliquots. The determinations of residual carbonates gave no indication of any increase of carbonates as a result of hydrolysis during the brief period of contact of silicates and bicarbonate solution before expulsion of the excess  $\text{CO}_2$  gas by heat of evaporation.

The relative activities of the  $\text{CaCO}_3$  of aliquot solutions when soil was added prior to and after precipitation of  $\text{CaCO}_3$  from bicarbonate solution were also studied. Aliquots of calcium and magnesium bicarbonate were placed on the water bath and soil added after the expulsion of  $\text{CO}_2$  had caused precipitation of the carbonates. The evaporations were then continued and residual carbonates determined. Simultaneous evaporations of the bicarbonate solution were made after the addition of soil charges at room temperature. No difference could be detected in residual carbonates as a result of the difference in the time of introducing soil into the bicarbonate aliquots, which emphasized the previous observations that the reaction between carbonates and the acid-reacting soil constituents takes place to maximum extent under conditions which effect solution of the carbonates in water comparatively free of  $\text{CO}_2$ . That is, the presence of excess of  $\text{CO}_2$  will tend to hold the  $\text{CaCO}_3$  in solution and hinder the maximum reaction of carbonate with acid salts of the soil, or else a secondary hydrolytic reaction will recover  $\text{CaCO}_3$  after its previous decomposition and conversion to silicates.

Repetitions of evaporations with additional charges added with each evaporation gave an apparent continued, but not extensive, decomposition of  $\text{CaCO}_3$ , but marked continuation in the decomposition of  $\text{MgCO}_3$ . However, as previously stated, the same holds true with  $\text{CO}_2$ -free water treatments in the cold, in Tacke's method.

The effects of various excessive amounts of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  were next studied. One-half-gram charges and 2-gram charges of the earth carbonates were evaporated with 10-gram charges of alkaline and acid soils, and residual  $\text{CO}_2$  determinations made. The results showed slight, if any, tendency toward increase of carbonate of lime decomposition as a result of the use of the heavy charge. Charges as heavy as 2 grams are exceedingly difficult to determine with accuracy volumetrically, because of the influence of the vast amount of  $\text{CO}_2$  upon the sensitiveness of the indicator. The use of excessive amounts of  $\text{MgCO}_3$ , however, appeared to increase appreciably the  $\text{MgCO}_3$  decomposition. The repetition of the evaporation of soil and  $\text{MgCO}_3$  also resulted in continued decomposition of  $\text{MgCO}_3$  to a greater extent than was true of  $\text{CaCO}_3$ .

The addition of a sufficient amount of  $\text{CaCO}_3$  to insure a constant supply of carbonates in solution fulfilled the requirements essential to maximum decomposition under reasonable conditions.

## EFFECT OF SOURCE OF CARBONATES ON REACTION WITH SOIL AND ON SOLUBILITY UNDER DIFFERENT CONDITIONS

The accuracy of the determination of residual carbonates, especially by the volumetric method, is enhanced by the use of the smaller excesses of  $\text{CaCO}_3$ . The carbonate giving the greatest solubility from a definite weight would therefore be the most desirable. The "C. P." precipitated carbonate is more nearly comparable in fineness with the carbonate thrown out of  $\text{CaH}_2(\text{CO}_3)_2$  than with the finely ground mineral carbonates. The relative  $\text{CO}_2$ -free water solubilities of 100-mesh limestone, dolomite, and magnesite of approximately 92 per cent  $\text{CaCO}_3$  values were accordingly compared with "C. P."  $\text{CO}_2$ -treated precipitated carbonates. Two-gram charges of each carbonate, in duplicate, were digested with 200 cc of distilled water in 250-cc flasks, for 45 minutes, at  $94^\circ \text{C}$ ., three agitations being given the solutions. They were then immediately filtered through triple fluted gravity filters, and duplicates of 100 cc titrated with N/20 acid, phenolphthalein being used as the first indicator. Methyl orange was then added, and the titration continued. As comparisons, the same procedure was followed with  $\text{CO}_2$ -free distilled water at  $20^\circ \text{C}$ . and .02056 normal  $\text{H}_2\text{CO}_3$  at the same temperature.

The results of titration are given in Table XVIII. As would be expected, the more finely divided carbonates gave the greater total solubility under each of the three conditions. The  $\text{CaCO}_3$  precipitated from the bicarbonate is exceedingly fine, and its use by means of aliquots of  $\text{CaCO}_3$  would therefore give maximum requirements with minimum charges. This point was further tested by evaporation of the different carbonates of calcium and magnesium with two soils and with serpentine, which, considered as the acid salt of orthosilicic acid, would be expected to decompose carbonates. The greatest decompositions were effected by the precipitated carbonates of both calcium and magnesium.

## RELATIONSHIP BETWEEN $\text{CaCO}_3$ AND $\text{MgCO}_3$ REQUIREMENTS OF SOILS

Data obtained in contact treatment over long periods at room temperature showed that the satisfying of a soil's requirement for lime did not preclude its further reaction with and decomposition of large amounts of magnesium carbonate. It also appeared that though both substances are capable of neutralizing the acidity of silicic acid, as well as that of acid silicates, during long periods of moist contact at ordinary temperatures, there appears to be no definite relationship between the amount of  $\text{CO}_2$  given off from the two carbonates. Investigation was then made of the relation between the activities of the two carbonates under the conditions of the procedure proposed as a laboratory method for lime requirement.

A clay subsoil was treated with 100 cc of  $\text{MgCO}_3$  and  $\text{CaCO}_3$  solutions separately, and residual  $\text{CaCO}_3$  equivalents determined after evaporation.



TABLE XVIII—*Solubilities of mineral and "C. P." carbonates in CO<sub>2</sub>-free distilled water and in carbonated water under different digestion conditions, terms of N/20 acid*

2 gms. of substance	CO <sub>2</sub> -free distilled water, 45 minutes at 94° C.			CO <sub>2</sub> -free distilled water, 45 minutes at 20° C.			45 minutes N/.02056 H <sub>2</sub> CO <sub>3</sub>		
	Phenol-phthalein	Methyl orange	Total	Phenol-phthalein	Methyl orange	Total	Phenol-phthalein	Methyl orange	Total
	cc	cc	cc	cc	cc	cc	cc	cc	cc
Precipitated CaCO <sub>3</sub> ..	1.10	.85	1.95	.05	.80	.85	0	29.6	29.6
Precipitated MgCO <sub>3</sub> ..	.5	3.20	3.70	1.85	2.40	4.25	0	70.0	70.0
Limestone, 100-mesh..	.1	.95	1.05	.025	.725	.75	0	24.45	24.45
Dolomite, 100-mesh..	.15	1.10	1.25	.25	.75	1.00	0	11.2	11.2
Magnesite, 100-mesh..	.15	1.35	1.50	.175	.75	.925	0	11.45	11.45



The  $\text{CaCO}_3$  decomposition was represented by .0720 gram from a treatment of .1011 gram, and the  $\text{MgCO}_3$  by .1960 gram, 10-gram charges of clay being used in each instance.

This decomposition of  $\text{MgCO}_3$  was in accord with the results obtained by simple long-continued contact treatments in the laboratory at room temperature. Treatments of four acid soils were then made by the Hutchinson-MacLennan process,  $\text{MgCO}_3$  solution, as well as one of  $\text{CaCO}_3$ , being used. The results are given in Table XIX.

TABLE XIX—*Reaction between soils and  $\text{CaH}_2(\text{CO}_3)_2$  and soils and  $\text{MgH}_2(\text{CO}_3)_2$ , terms of  $\text{CaCO}_3$  extracted from the solution as in Hutchinson-MacLennan procedure*

Soils	Loam	Silty loam	Sandy loam	Sandy loam	Average
Gms. $\text{CaCO}_3$ extracted .....	.0078	.0073	.0173	.0071	.0099
Gms. $\text{MgCO}_3$ extracted .....	.0375	.0275	.0575	.0325	.0388

From the data of Table XIX it would appear that in every instance where soil is afforded opportunity to effect decomposition of the two carbonates, the magnesium salt is far more extensively decomposed.

That the presence of an excess of  $\text{CaCO}_3$ , applied a long time previously, does not prevent the further decomposition of  $\text{MgCO}_3$  under laboratory conditions was determined by the evaporation of two strongly calcareous soils with  $\text{MgCO}_3$ , which treatment resulted in the decomposition of appreciable amounts of  $\text{MgCO}_3$ . This observation was again made with a weaker solution of  $\text{MgCO}_3$ . The magnesium carbonate solution was diluted ten times to make it approximate more nearly the 90 per cent saturated  $\text{CaCO}_3$  solution. Twenty-gram charges of the calcareous loam and silty loam of Table I were then added to 150 cc of boiled  $\text{CaCO}_3$  and run as a blank, while another 150-cc portion of  $\text{CaCO}_3$  was evaporated with the soil. The blank was then compared to the evaporated residue for residual carbonates. The same treatment was duplicated, with  $\text{MgCO}_3$ . The relative activities of the two carbonates upon the calcareous soils are given in Table XX.

TABLE XX—*Comparison between evaporations of calcareous soils with  $\text{CaH}_2(\text{CO}_3)_2$  and diluted  $\text{MgH}_2(\text{CO}_3)_2$ , terms of  $\text{N}/20$  acid in  $\text{CO}_2$  determinations*

	$\text{CaCO}_3$		$\text{MgCO}_3$	
	Loam	Silty loam	Loam	Silty loam
	cc	cc	cc	cc
Blank .....	46.6	39.3	54.4	58.5
After evaporation ..	44.9	38.6	44.7	34.3
Difference .....	1.7	.7	9.7	24.2

The close agreements between blanks and treatments in the  $\text{CaCO}_3$  treatments, and the wide difference between the  $\text{MgCO}_3$  blank and treatment, could not be attributed to the difference in the solubilities of the two carbonates shown in Table XVIII. They undoubtedly prove that  $\text{CaCO}_3$  and  $\text{MgCO}_3$  have different relationships from those which would be indicated definitely by solubilities, fineness, or molecular weight, in the extent of their requirements by soils.

In view of this disparity between relations of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  as influenced by their solubilities, but more particularly by the extensive affinity of  $\text{MgO}$  for  $\text{SiO}_2$  and its compounds, it would appear fallacious in the extreme to endeavor to interpret a soil's requirement for one carbonate by the chemical equivalence of any one carbonate to that of any other. The fact is thus emphasized that the correct procedure to follow in determination of  $\text{CaCO}_3$  requirement would involve the use of that same carbonate.

A study was then undertaken to determine whether the magnesium carbonate decomposition eliminates a soil's ability to decompose calcium carbonate. The three  $\text{MgCO}_3$ -treated soils of Table I were next evaporated with  $\text{CaCO}_3$  solution. Ten-gram charges of soil and 150-cc aliquots of the solution were used. Determinations of residual carbonates after evaporation showed that the alkaline magnesian soils possessed very limited, if any, ability to decompose  $\text{CaCO}_3$  after they had already accomplished a heavy dissipation of  $\text{CO}_2$  from previously applied  $\text{MgCO}_3$ .

Thus we find that  $\text{MgCO}_3$  will satisfy a soil's requirement for lime, but that the satisfying of a soil's requirement for lime, by long-continued contact with  $\text{CaCO}_3$  does not inhibit the excessive decomposition of added  $\text{MgCO}_3$  under laboratory treatment. Not only is this true of normal calcareous soils, but it is also true of soils which have been ignited with an excess of  $\text{CaCO}_3$ .

### **EFFECT OF THE PRESENCE OF ALKALI CARBONATES UPON THE DECOMPOSITION OF MAGNESIUM CARBONATES BY SOIL**

The influence of the presence of sodium and potassium carbonates upon the decomposition of  $\text{MgCO}_3$  was then studied. Twenty-gram charges of the calcareous loam and the silty loam of Table I were evaporated with 50-cc aliquots of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  separately, the aliquots representing .5 gram of the alkali carbonates. One hundred and fifty cc aliquots of  $\text{MgCO}_3$  solution were added and evaporated, while the blank was evaporated again with the same volume of distilled water. Determinations of residual carbonates were then made upon the treated soils and compared with the blank plus 150 cc of the boiled magnesium carbonate solution. The alkali carbonates of course attacked the organic matter of the soil, but this was accounted for by the blanks. The decomposition of magnesium carbonate shown in Table XXI resulted, then, after calcium carbonate had been in contact with the soils for one year, and after evaporation with both sodium and potassium carbonates.

TABLE XXI—Decomposition of  $MgCO_3$  from  $MgH_2(CO_3)_2$  by calcareous soils, after preliminary evaporation with  $Na_2CO_3$  and  $K_2CO_3$

Loam	CaCO <sub>3</sub> value	Silty loam	CaCO <sub>3</sub> value
	Gms		Gms.
Blank soil evaporated with $Na_2CO_3$ solution and 150 cc of boiled $MgH_2(CO_3)_2$ solution added .....	1.6850	Blank soil evaporated with $Na_2CO_3$ solution and 150 cc of boiled $MgH_2(CO_3)_2$ solution added .....	1.6500
Soil evaporated with $Na_2CO_3$ and 150 cc $MgH_2(CO_3)_2$ solution .....	1.2625	Soil evaporated with $Na_2CO_3$ and 150 cc $MgH_2(CO_3)_2$ solution. ....	1.2375
Decomposed by evaporation .....	.4225	Decomposed by evaporation .....	.4125
Blank soil evaporated with $K_2CO_3$ solution and 150 cc of boiled $MgH_2(CO_3)_2$ solution added .....	1.6825	Blank soil evaporated with $K_2CO_3$ solution and 150 cc of boiled $MgH_2(CO_3)_2$ solution .....	1.6725
Soil evaporated with $K_2CO_3$ and 150 cc of $MgH_2(CO_3)_2$ solution .....	1.2225	Soil evaporated with $K_2CO_3$ and 150 cc of $MgH_2(CO_3)_2$ solution .....	1.2350
Decomposed by evaporation .....	.4600	Decomposed by evaporation .....	.4375
Soil, plus boiled $MgH_2(CO_3)_2$ solution without alkali carbonates .....	1.3540	Soil, plus boiled $MgH_2(CO_3)_2$ solution without alkali carbonates .....	1.3510
Soil after evaporation with $MgH_2(CO_3)_2$ solution .....	.9096	Soil after evaporation with $MgH_2(CO_3)_2$ solution .....	.9650
Decomposed by evaporation .....	.4444	Decomposed by evaporation .....	.3860

It would thus appear that the addition of precipitated  $\text{MgCO}_3$  or burnt magnesia to *alkali* soils would result in the decomposition of  $\text{MgCO}_3$ .

It further appears that the combined presence of calcium, sodium and potassium carbonates is not necessarily inhibitory of the decomposition of the precipitated carbonate of magnesium.

### EFFECT OF ALKALI TREATMENT UPON THE ABILITY OF RUTILE TO DECOMPOSE $\text{MgCO}_3$

Satisfying of the alkali requirement of titanium oxide does not prevent the continued reaction between  $\text{TiO}_2$  and  $\text{MgCO}_3$ . Rutile was treated with strong  $\text{NaOH}$  for 10 days and then freed of the alkali, after which treatment it was subjected to contact with  $\text{MgCO}_3$  at room temperature. One hundred grams of rutile was moistened and mixed with 1 gram of precipitated  $\text{MgCO}_3$ . After 330 days' contact of rutile and carbonate the  $\text{CO}_2$  gas was drawn off and was found to represent an equivalent of .1484 gram of  $\text{CaCO}_3$ .

### COMPARISON OF PROPOSED METHOD WITH THE PROCEDURE OF HUTCHINSON AND MacLENNAN

The method proposed in this bulletin was then compared with the method of Hutchinson and MacLennan. Two strengths of  $\text{CaH}_2(\text{CO}_3)_2$  were used. One hundred cc of .1011-gram  $\text{CaCO}_3$  equivalent was used and also the same volume after dilution by the addition of 50 cc of carbonated water. The differences between the amounts of  $\text{CaCO}_3$  used by the soils when the carbonate was offered in solution of  $\text{CO}_2$ , and in water free of  $\text{CO}_2$  by evaporation, are shown in Table XXII.

Inspection of Table XXII shows that a greater decomposition is effected in every case where the evaporation is made, above that effected by agitation with the bicarbonate solution.

### RELATION OF THE INDICATIONS OF THE TWO METHODS TO THOSE OBTAINED BY THE VEITCH METHOD

The soils of Table XXII were then treated with the respective  $\text{CaCO}_3$  indications of the two methods and carried out from that point as Veitch-method determinations. In addition to the indicated amounts of  $\text{CaCO}_3$  solution, two drops of saturated lime water were added to each treatment in order to insure a slight excess and to allow for a plus or minus analytical error. After evaporation with the amounts of  $\text{CaCO}_3$  indicated by the respective methods the soils were run as blank Veitch determinations. In each instance the Hutchinson-MacLennan-method indication plus lime water failed to show alkalinity by the Veitch test. On the other hand, every soil treated with the indication of the proposed method plus two drops of lime water gave an alkaline Veitch test.

These tests demonstrate that the Hutchinson-MacLennan method falls short of satisfying the Veitch requirement, while the proposed method

TABLE XXII—Comparison of proposed method with the Hutchinson-MacLennan method, and the latter when modified by the addition of 50 cc of carbonated water

Soil		Reaction	Hutchinson-MacLennan method				Hutchinson-MacLennan method modified				Proposed method			
Lab. No.	Type		CaCO <sub>3</sub> added in solution	CaCO <sub>3</sub> found in filtrate	CaCO <sub>3</sub> utilized	CaCO <sub>3</sub> requirement lbs. per acre 2,000,000	CaCO <sub>3</sub> added in solution	CaCO <sub>3</sub> found in filtrate	CaCO <sub>3</sub> utilized	CaCO <sub>3</sub> requirement lb. per acre 2,000,000	CaCO <sub>3</sub> added in solution	Residual CaCO <sub>3</sub>	CaCO <sub>3</sub> utilized	CaCO <sub>3</sub> requirement lbs. per acre 2,000,000
			Gms.	Gms.	Gms.	Lbs.	Gms.	Gms.	Gms.	Lbs.	Gms.	Gms.	Gms.	Lbs.
3455	Clay loam....	Acid...	.1011	.0933	.0078	1560	.1011	.0921	.0090	1800	.1011	.0750	.0261	5220
3458	Silty loam ...	Acid...	.1011	.0938	.0073	1460	.1011	.0938	.0073	1460	.1011	.0730	.0281	5620
3459	Silty loam ...	Acid...	.1011	.0828	.0183	3660	.1011	.0893	.0118	2360	.1011	.0553	.0458	9160
3466	Swamp .....	Acid...	.1011	.0490	.0521	10220	.1011	.0583	.0428	8560	.1011	.0240	.0771	15420
3462	Loam .....	Acid...	.1011	.0838	.0173	3460	.1011	.0888	.0123	2460	.1011	.0690	.0321	6420
3464	Clay .....	Acid...	.1011	.0660	.0351	7020	.1011	.0693	.0318	6360	.1011	.0291	.0720	14400
3463	Sandy loam ..	Acid...	.1011	.0940	.0071	1420	.1011	.0985	.0026	520	.1011	.0935	.0076	1520
3461	Sandy loam ..	Acid...	.1011	.0922	.0089	1780	.1011	.0958	.0053	1060	.1011	.0820	.0191	3820
3465	Loam .....	Acid...	.1011	.0745	.0266	5320	.1011	.0798	.0213	4260	.1011	.0480	.0531	10620
	Average		.1011	.0810	.0201	3989	.1011	.0851	.0160	3204	.1011	.0610	.0401	8002



meets the Veitch requirement in every instance. As to the relation of the results to those of the Veitch indication, further work is offered in Table XXIII.

Not only does the Hutchinson-MacLennan method fail to produce the decompositions equivalent to those effected by the Veitch or the proposed method, but the carbonated water solvent depresses the reaction and gives less carbonate decomposition than is effected by agitation with  $\text{CaCO}_3$  in  $\text{CO}_2$ -free water for the same period at room temperature, as per the Tacke procedure. That this is true is shown by the data of Table XXIII.

Gardner and Brown<sup>1</sup>, after applying the exact amounts indicated by the Veitch method, and then growing two crops of clover, found 28 per cent of the original Veitch as the residual lime requirement eight months after treatment. Hutchinson and MacLennan<sup>2</sup> found .05 per cent requirement by their method upon a soil which had one year previously received

TABLE XXIII—*Comparison of the proposed method with the methods of Veitch, Tacke, and Hutchinson and MacLennan*

Soil	$\text{CaCO}_3$ per 2,000,000 lbs. of soil			
	Proposed	Veitch	Tacke	Hutchinson-MacLennan
	Lbs.	Lbs.	Lbs.	Lbs.
Clay subsoil .....	14400	7420	8850 <sup>a</sup>	7020
Swamp silt .....	15420	11428	19900 <sup>b</sup>	10220
River-bottom silt-clay loam .....	10620	7536	9850 <sup>c</sup>	5320
Average .....	13480	8794	12866	7520

Three hours additional: a, 1750; b, 4850; c, 3800.

.36 per cent  $\text{CaCO}_3$ , although its original lime requirement, according to their method, was but .26 per cent; and in another instance, .02 per cent requirement after an application of .54 per cent to a soil showing an original need of but .43 per cent by their method. In other words, after adding an average excess of 33 per cent above their method's indications, and permitting contact for one year without cropping, they found that both soils were still acid to their method, which when run at the end of the year showed that their original lime-requirement indications had been but 56 per cent of the final indications.

Tests as to the attaining of maximum decomposition of  $\text{CaCO}_3$  by the Hutchinson-MacLennan method were then made by the use of three different charges of a silty soil and an acid clay subsoil. The soils were filtered by gentle suction through Buchner funnels, and a 5/6 aliquot of each was titrated. The residues were then washed twice with rapid

1. Pa. Station, Report, 1910-11, pp. 25-76.

2. Chem. News, 110, No. 2854, 1914.



TABLE XXIV—*Effect of variations in soil charges in the Hutchinson-MacLennan method and continued reaction of the method's soil residues upon further additions of CaCO<sub>3</sub> solution—constant volumes of CaCO<sub>3</sub> solution used throughout*

Charge	CaCO <sub>3</sub> removed from solution by soil in the Hutchinson-MacLennan method						CaCO <sub>3</sub> decomposed by subsequent contact of residues with CaCO <sub>3</sub> in CO <sub>2</sub> -free water					
	5 gm.		10 gm.		20 gm.		5 gm.		10 gm.		20 gm.	
	Gms.	Per ct.	Gms.	Per ct.	Gms.	Per ct.	Gms.	Per ct.	Gms.	Per ct.	Gms.	Per ct.
Silty loam . .	.0093	.186	.0063	.063	.0145	.073	.0125	.250	.0220	.220	.0310	.155
Clay subsoil	.0244	.488	.0345	.345	.0615	.308	.0185	.370	.0220	.220	.0340	.170

passages of carbonated water, then with distilled water, after which they were agitated for 3 hours with  $\text{CO}_2$ -free distilled water and .4 gram of precipitated carbonate. The agitations with both carbonated water solution and  $\text{CO}_2$ -free water solution were uniformly and efficiently made by mechanical shaking. The results are given in Table XXIV.

These data show that not only does the Hutchinson-MacLennan procedure fail to effect maximum decomposition of carbonates, but the reaction is not in proportion to the charge of soil used.

In proposing the method described at the conclusion of this bulletin, the writer believes that the conditions of the procedure effect a complete satisfying of the *temporary lime requirement* of soils. That the determinations by the Veitch method, after previous Veitch-indication treatments had been applied, showed an extensive additional lime requirement in the work of Gardner and Brown<sup>1</sup> and in that reported in this bulletin would be justification for the higher results by the proposed method. Opportunity has not yet been afforded for the testing of lime requirements after treatments with the indications of this method, as was done in the case of the Veitch studies. The laboratory studies would leave no doubt, however, that the same observations would follow the use of this method's indications as to additional amounts necessary to meet a soil's *continuous lime requirement*.

The proposed method is intended to supply a simple procedure which will permit the satisfying of the maximum immediate lime requirement of acid silicates and silicic acid, the principal causes of lime requirement to be found in rock-derived soils. The method of determining lime requirement is believed to be an improvement upon the Veitch method, in that it does not involve so tedious manipulation and in that it eliminates the heating of soil organic matter with the more active hydrate of lime.

The repetition of the evaporation in the procedure gives practically no action between soil and calcium carbonate, while continuation of the Tacke procedure gives a large proportion of the original indication of the method. Such being the case, the residual carbonate determined in the Söchting method would necessarily be greater than the amount which the soil would decompose if it had further opportunity for contact at normal temperature, which would mean lower results than the maxima.

## RELATION BETWEEN LABORATORY AND FIELD LIME REQUIREMENTS

The writer believes that the relationship between the laboratory determinations and actual crop needs is a phase of the subject to be tested by extensive field work, under various conditions of climate, soil-type, and fertility. After determining the maximum decomposition of  $\text{CaCO}_3$  under laboratory conditions, that is, the maximum temporary lime requirement, we could then determine for various types the factors which would prove most desirable in practice. And under practical conditions, where loss by

1. Pa. Station, Report, 1910-11, pp. 25-76.

leaching is a factor, the results should be based upon plant response for more than one season. For though the application of indications of two methods giving appreciable differences might give comparable results in the crop increase of the first season, the response during the second and succeeding seasons might be considerably greater from the larger treatment.

The continuous lime requirement observed in laboratory and pot studies appears to bear but little if any relation to the practice of liming, except as to the influence of the lime-silica reaction upon the conservation of lime in the soil. However, the continued decomposition of carbonates when present in excess under laboratory conditions and in basket work is entirely in harmony with observations in practice. That this is true is shown by analyses of the burnt lime and limestone plots of the Pennsylvania Station General Fertilizer Experiments, where about 35 per cent of the lime accumulated from treatment is now to be found as silicates.<sup>1</sup>

## THE OCCURRENCE OF SOIL ACIDITY IN FIELD AND LABORATORY EXPERIMENTS

The studies here reported, and other observations in kindred experiments, have led the writer to adhere to certain pronounced views as to the existence of, and reasons for, soil acidity. The writer has had no experience in the investigation of peat soils, and the discussion following is therefore based upon soils of mineral origin.

By the term "soil acidity" it is intended to refer to a soil's ability to decompose calcium carbonate. First, it must be emphasized *that in uncarbonated  $H_2O$  solution,  $SiO_2$  proves to be a stronger acid radical than  $CO_2$  of earthy carbonates. The reversal of conditions is effected when there is present an excess of  $CO_2$  gas.* This would be expected as sequence of mass action. It is probably true, as indicated by data given, that both of these conditions actually exist at different times under field conditions. At times, a soil solution near the surface may be heavily charged with  $CO_2$  gas, while at other times it may be almost free therefrom.

Silica precipitated from soil solutions is considerably finer and more soluble than finely ground quartz, which has been shown, in this bulletin, to react appreciably with alkali-earth carbonates, and we would expect it to give more extensive decomposition of  $CaCO_3$  than is effected by silt, even as ground quartz is more active upon the carbonate than is fine sand, which in turn is more active than coarse sand. The methods which direct the use of calcium carbonate in laboratory treatments of soils are influenced by this lime-silica reaction. But those methods which bring salts of the stronger acids into contact with silicic acid do not involve the replacement of the strong acid radicals of the neutral salts by that of silicic acid; that is, calcium carbonate is decomposed by silicic acid,  $H_2SiO_3$ , but the solutions of nitrates are not affected by contact with finely ground moist  $SiO_2$ .

It is true that there is vast difference between soils in the field and the same soils in the air-dry laboratory condition. In laboratory studies

1. Pa. Station, Report, 1911-1912, p. 640.

of soil acidity, however, consideration of this difference in many cases appears to be minimized or entirely disregarded. Leaching studies of field soils, however, emphasize this difference. A soil may be acid to litmus in both field and laboratory, but its natural solution, as judged by its leachings, may be distinctly alkaline. Its solution in  $\text{CO}_2$ -free water in the laboratory will usually be neutral, but if the laboratory solution be made with carbonated water it will generally be alkaline. Though the extract be alkaline in reaction, the alkalinity may be attributed more particularly to acid salts, so regarded when calcium and magnesium carbonates in solution are considered as bicarbonates, rather than as carbonates in solution. The extract will of course in some cases contain some carbonates of sodium and potassium. The normal alkali-earth silicates of calcium are the most readily hydrolyzed, and  $\text{CaCO}_3$  predominates in the alkaline leachings of an acid soil well supplied with calcium silicate. Thus we have an acid, a weak organic acid,  $\text{H}_2\text{CO}_3$ , removing an alkaline-reacting extract and leaving a soil with a greater tendency to absorb lime. As bearing on this point, the writer extracted a charge of an acid sandy clay soil with carbonated water. The extract was of course distinctly alkaline, but lime requirements made upon the soil by the proposed method, before and after extraction, showed that the soil's lime requirement had increased after extraction almost sufficiently to account for the alkalinity of the filtered carbonated water extract. Likewise, when we apply ammonium sulphate to soil, the resultant liberated acid radical extracts bases from the normal silicates, and increases the occurrence of acid silicates, which means increase in lime requirement. Possibly the use of acid phosphate results in the utilization of the bases of soil silicates and a consequent increase in lime requirement. This conclusion was drawn by Gardner and Brown<sup>1</sup> with reference to the dissolved-bone-treated plots of the Pennsylvania Station.<sup>2</sup>

It has been held that soil acidity is due to the existence in the soil of free organic and mineral acids. "Humic acid" is the collective, though indefinite, term ordinarily used for the supposed organic acids. That we do have free mineral acid—silicic acid—in soil, is true. It has been shown in this bulletin that this acid effects appreciable and long-continued decomposition of  $\text{CaCO}_3$ , and excessive decomposition of  $\text{MgCO}_3$ , and that its acid salts—clays—are even more active than the relatively insoluble acid itself.<sup>3</sup> But the assumption that organic acids other than  $\text{H}_2\text{CO}_3$  exist in soils more than a brief transitory period is unproved. Free organic and mineral acids would be subjected either to contact with a soil solution of  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ , and other silicate-derived carbonates, or they would come into contact with calcium and magnesium, and possibly other silicates, upon which citric, oxalic, and such weak organic acids react. As showing that nitric and organic acids do become neutralized as they are formed from nitrification and fermentation in soils, the following

1. Pa. Station, Report, 1910-11, pp. 25-76.

2. See also Conner, Jour. Ind. and Eng. Chem., Jan., 1916.

3. The purely physical absorptive properties of soil colloids are admittedly extensive, but after the elimination of these substances we have observed a continued decomposition of  $\text{CaCO}_3$ , making it necessary to attribute to chemical activities at least a part of the reaction noted.

was done: Five-cc and ten-cc aliquots of both  $\text{HNO}_3$  and  $\text{C}_2\text{H}_2\text{O}_4$ , N/20, were placed separately in 250 cc of freshly distilled water, containing 10 grams of *acid clay* subsoil, and a current of  $\text{CO}_2$  was passed through the mixtures for 4 hours. The mixtures were then immediately filtered separately and each extract was found to be distinctly alkaline, requiring as much as 5 cc N/20 acid to neutralize. Checks run simultaneously with  $\text{CO}_2$ -free distilled water gave very slightly alkaline or neutral solutions for both organic and mineral acid treatments. Ten-gram charges of the same acid soil, in duplicate, were then shaken gently overnight with 12½ cc of N/2  $\text{HNO}_3$ , diluted to 125 cc, filtered, washed, and extract titrated. Nearly 8 cc of the N/2 acid had been used by the acid soil. Such an amount would represent the nitrification to  $\text{HNO}_3$ , or over 11000 pounds of N per 2,000,000 pounds of soil, and the conversion of the acid to neutral salts. The same treatment with oxalic acid utilized 9.6 cc of N/2 acid, while 10.5 cc of the trivalent citric acid was neutralized. It is thus plain that even without the soluble bicarbonates, which are present when there is an abundance of  $\text{CO}_2$ , the readily attacked silicates would prevent the continued occurrence of any free organic or mineral acids, excepting carbonic and silicic. Thus, in a soil we may have not only neutral salts of mineral acids, more particularly  $\text{HNO}_3$ , but also organic acid and neutral salts, especially of calcium.

That organic acids are products of green manuring and normal soil fermentation is undoubtedly true, but, were the generated acids not quickly neutralized by the alkaline soil solution derived from calcium and magnesium and other silicates, we would have characteristic acidity in those soils which have received frequent and heavy applications of barnyard manure. But, instead of increasing the soil acidity, the use of manure tends to maintain near-alkaline conditions to an extent which could not be attributed to the included comparatively small amount of organic lime and other bases. That the lime of such manure treatments is readily available, and that it is conserved and repeatedly used as a neutralizer in the cycle which it follows, is shown most admirably by Hall in his treatise, "Some secondary actions of manures upon soils." The conservation of lime from treatments of barnyard manure is also emphasized by results obtained by the writer on the manure plots of the Pennsylvania Station.<sup>1</sup>

As a further convincing argument that so-called free "humic acid" is not to be considered as a reason, except colloidal, for soil acidity, a subsoil is usually more acid than its organic-matter-containing surface soil, where undisintegrated rock particles and close proximity of original carbonate rock do not interfere. Sandy soils and those soils especially low in their lime requirements usually contain relatively small amounts of clay. Conversely, a heavy clay soil is usually acid and high in its lime requirement, even when very low in organic matter. In other words, excessive soil acidity, as measured by the ability of a soil to effect decomposition of  $\text{CaCO}_3$ , is coincident with occurrences of clay, or acid silicates.

1. Pa. Station, Report, 1911-1912, p. 640.



The existence of determinable temporary soil acidity or lime requirement, and the presence of carbonate of lime as a solid mineral in soil, are not compatible, save in such cases as glacial clay. However, as previously stated, a soil may be strongly acid in its effect upon carbonate of lime, when following the various procedures offered for determining the extent of this acidity, and yet its extract, or leaching, will often be strongly alkaline and impregnated with  $\text{CaCO}_3$ . The writer has analyzed many hundreds of surface and deep waters, and many of them from sections considered to be devoid of any native carbonate rocks, but he has never found an earth water which was not distinctly alkaline, save in two instances of waters which flowed through very extensive swamps. Unusual occurrences of excessive mineral sulphides might, however, in some instances overcome this alkalinity. In some sections such alkalinity must in the main be derived from the hydrolyzation of soil silicates. As bearing on this point, drainage waters collected in leaching experiments at this Station are invariably alkaline, though coming from acid soils, devoid of carbonates. This alkalinity is sometimes increased by the passage of drainage waters through additional depths, up to 5 feet, of strongly acid clay subsoil. The alkalinity of leachings varies appreciably. At times leachings are heavily impregnated with  $\text{CaCO}_3$ , and at other times they contain a preponderance of alkali carbonates. This is readily shown by boiling the leachings at various times and making alkalinity determinations before and after the removal of precipitated  $\text{CaCO}_3$ . It might be expected that during the winter the water of lower temperature would be more heavily charged with  $\text{CO}_2$ , and having less crop growth to assimilate the dissolved  $\text{CaCO}_3$ , the leachings might consequently be more alkaline than under conditions of higher temperature and greater plant growth. The increase of temperature during the growing season would tend to expel the gas from solution near the surface, thus giving a weaker solvent, though in the soil atmosphere there would probably be greater quantities of  $\text{CO}_2$  than would be found under colder conditions. The reactions involved in the decomposition of applied carbonate and the hydrolysis of silicates and leaching of bases may be shown with ease in the laboratory. Untreated, highly acid clay subsoil, and the same after treatment and evaporation with a little less  $\text{CaCO}_3$  than that represented by its lime requirement, may be used. Both of the carbonate-free soils are then extracted for a few hours with carbonated water. Thus we find the carbonate is first decomposed by its reaction with both  $\text{H}_2\text{SiO}_4$  and acid silicates in the absence of dissolved  $\text{CO}_2$ , and then the reaction is reversed in the presence of carbonated water. This may be quantitatively shown by the titration of the easily filtered carbonated water solution. Gentle suction through a Buchner funnel gives a quick filtration. This explains, in part, why maximum decomposition of added carbonates in solution is not obtained in the Hutchinson-MacLennan method. Either a forcing back of the lime-silica reaction is effected by the excess of  $\text{CO}_2$  or else a secondary hydrolysis and recarbonation reaction takes place.

Since we admit that the soil's solution is the medium through which a plant absorbs its mineral supply, we are compelled to conclude that a plant's source of nutrition is almost always alkaline, but of varying degrees



of alkalinity. Thus we have lime-loving plants which do not thrive, *not because their nutrient solutions are acid, but because the available solutions are not sufficiently concentrated in their  $\text{CaCO}_3$  content*, or possibly in neutral salts of root-formed acids which act directly upon the bases of unhydrolyzed silicates. It is conceivable that rapidly growing plants would extract lime and also other bases from a soil solution more rapidly than the soil moisture could effect the hydrolysis of the silicates, from which an acid soil principally derives the bases which are offered to the plants. This would of course give a soil solution approaching very nearly to neutrality. The soil solution would not become acid, however, even under this condition, for any nitric or organic acid formed after removal of bases from solution by plants would be quickly neutralized through direct reaction of acids upon the various bases of the silicates.

A point in field practice readily illustrates the foregoing hypothesis. Alfalfa, for instance, may be sown upon a soil needing lime, after the soil has lain fallow during the summer. The young plants appear to thrive in the fall, when the temperature is fairly low and the conserved soil moisture is heavily impregnated with  $\text{CO}_2$ , and therefore correspondingly high in carbonates from the hydrolyzed silicates. At this stage of their growth they are receiving lime sufficient for their needs, though they may later die from the lack of lime. There is of course the factor of a store of nitrates to feed upon—nitrates formed by the action of carbonated soil water upon the nitric acid, resulting from soil nitrification processes. Though stimulating, this nitrate offering will not replace needed lime, and as the plants grow and require more lime, the meager supply in the soil solution is consumed. If the soil solution's alkalinity were greater—if it were sufficient to offer requisite plant-food requirements of lime and also to afford an acceptable medium for nodule bacteria—the plants would continue to thrive, and themselves solve the question of nitrogen supply.

## PROPOSED METHOD<sup>1</sup>

### PREPARATION OF $\text{CaCO}_3$ STOCK SOLUTION

Pass purified  $\text{CO}_2$  into one or more 4-liter cylinders containing distilled water and about 20 grams of "fluffy" C. P. precipitated  $\text{CaCO}_3$  for 4 hours. Permit the  $\text{CO}_2$  to enter with sufficient rapidity to keep considerable of the carbonate in suspension. At the same time prepare carbonated distilled water to the amount of about one-tenth that of the carbonate solution. Filter the carbonate solution through large gravity filters into the carbonated water. A large stock of 16 liters may be made and kept indefinitely without determinable change by use of the pressure-syphon bottle shown in Fig. 1. Upon withdrawal of each aliquot, pressure is maintained by blowing through the tube *A*. The  $\text{CaCO}_3$  value of the solution is determined by first boiling and then liberating the  $\text{CO}_2$  of the precipitated carbonate. *The value of the  $\text{CaCO}_3$  solution should not be determined by direct titration, if the liquid absorption procedure be followed.*

<sup>1</sup> This method was published in Jour. Ind. and Eng. Chem., Oct. 1915.

The HCl used in generator to liberate  $\text{CO}_2$  for preparation of  $\text{CaCO}_3$  solution should not exceed 1-1 in strength. To insure complete removal of hydrochloric acid from the rapid flow of gas, it is necessary to force the gas through the several columns of sodium carbonate solution when making large stock solutions of carbonate. A "Kipp" generator may be fitted with a 2-hole rubber stopper, a stand tube being inserted in one hole and in the other a stopcock-controlled tube for blowing to obtain pressure. A simple and more useful form of apparatus is that of Fig. 2.

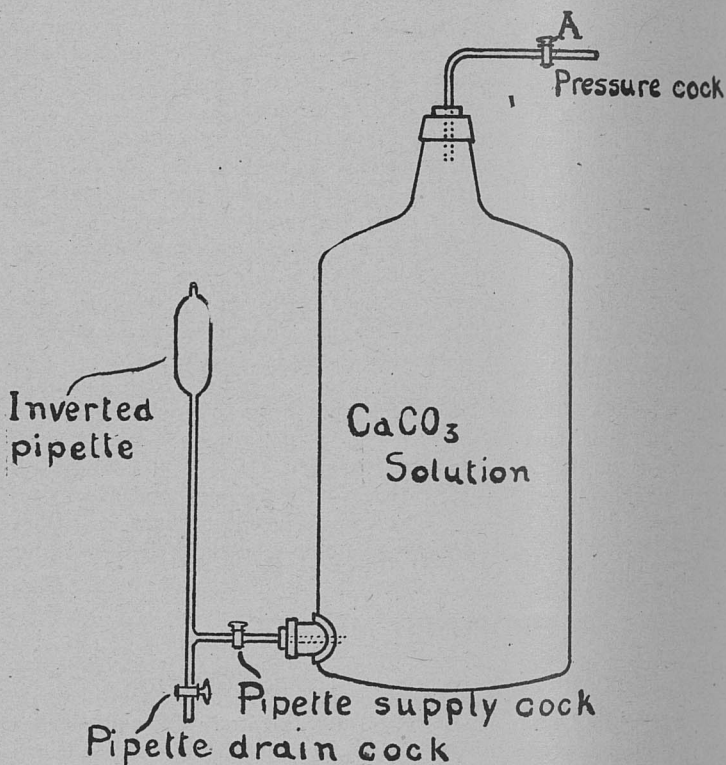


FIG. 1—PRESSURE CONTAINER FOR  $\text{CaCO}_3$  SOLUTION

### PROCEDURE FOR THE DETERMINATION OF THE IMMEDIATE LIME REQUIREMENT OF SOILS

For the average soil, take 10-gram charges of soil and 150 cc of  $\text{CaCO}_3$  solution. This volume usually represents about .1500 gram of  $\text{CaCO}_3$ . For very heavy clays, or peaty or swamp soils, reduce the charge to 5 grams. Evaporate to a paste in 150-cc porcelain evaporating dishes. Transfer paste to a 300-cc Erlenmeyer flask, by means of  $\text{CO}_2$ -free distilled water, delivered by gravity from reservoir. (Such water may be easily

obtained in considerable quantities by slowly syphoning off boiling water, the volume of which is maintained by a gravity constant-level supply). Do not have volume of transferring water to exceed 60 to 70 cc. In unusual cases of adhesion of soil to dish, scour with a little  $\text{CaCO}_3$ -free sand. The tendency of the carbonate is sometimes to precipitate in a ring marked by the initial level of aliquot. Determine  $\text{CO}_2$  by agitation and aspiration for 30 minutes, at room temperature, with 4 inches vacuum, using 5 cc concentrated  $\text{H}_3\text{PO}_4$  to effect liberation of gas. Description of apparatus and detailed directions for manipulation of this determination were given in Tennessee Station Bulletin 100 and in the March (1915) number of the Journal of Industrial and Engineering Chemistry. Hydrochloric acid may be used instead of  $\text{H}_3\text{PO}_4$ , if proper precautions be taken for collection of volatile acid. The gravimetric method of absorption is decidedly preferable unless the analyst is thoroughly conversant with the technic of the liquid absorption and double titration procedure. Although absolute theoretical recovery of  $\text{CO}_2$  in large amounts cannot be secured by the volumetric absorption, at room temperature, the factor is apparently uniform. However, the differential  $\text{CO}_2$  values in the small charges used in the method may be accurately determined at ordinary temperatures if proper precautions be observed. (See Lincoln and Walton, *El. Quant. Chem.*, p. 64).

In this laboratory we have secured very satisfactory results, even on large amounts of  $\text{CO}_2$ , by the

procedure of precipitating the alkali carbonate formed in the absorbent solution with a constant maximum amount of neutral  $\text{BaCl}_2$ , and making to 500-cc volume with  $\text{CO}_2$ -free distilled water. An aliquot of 250 cc of the clear supernatant caustic liquid or the entire volume is then titrated directly with standard acid, using phenolphthalein as an indicator. From the

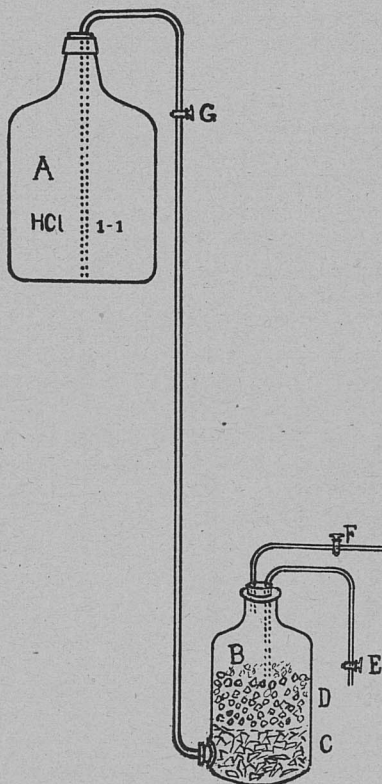


FIG. 2— $\text{CO}_2$  GENERATOR

- a—16-Liter Acid Reservoir
- b—4-Liter Generator
- c—Broken Pottery
- d—Marble-Sized Limestone Lumps
- e—Geisler Cock Outlet for Spent Acid
- f—Outlet for  $\text{CO}_2$  to Purifiers
- g—Safety Cock

determined strength of the absorbent is then deducted the blank obtained in the same manner upon the original solution.\*

Ten cc of approximately half normal NaOH or KOH, diluted to 50 cc with CO<sub>2</sub>-free water, is sufficient to absorb the liberated CO<sub>2</sub>. If the double titration procedure be followed, the number of cc of N/20 acid used in the methyl orange titration of the blank, minus that of the determined residual, will give, in terms of N/20 acid, the CaCO<sub>3</sub> decomposed by the soil. This number, multiplied by .005 gram and divided by the charge and multiplied by 100, will give the per cent of lime requirement in terms of carbonate of lime. If the barium chloride precipitation procedure be followed the difference between cc of titration of one-half of original absorbent solution after its treatment with BaCl<sub>2</sub> and that of 250-cc aliquot after absorbing CO<sub>2</sub> multiplied by the CaCO<sub>3</sub> value of titration-acid and divided by charge will give CaCO<sub>3</sub> requirement.

The small and nearly constant atmosphere blank of the apparatus is included in that of the added CaCO<sub>3</sub> and absorbent solution. This eliminates the necessity of rinsing the apparatus before each determination in order to remove any acid residual from the preceding determinations. This, together with the elimination of necessity for sweeping the apparatus free of atmospheric CO<sub>2</sub> prior to each analysis, greatly facilitates speed when making a large number of determinations. In very accurate work the slight action of the acid upon the soil organic matter in the cold should be recorded. The blank would then be run simultaneously upon the aggregate of a charge of the original soil equivalent to that used in the evaporation, the boiled CaCO<sub>3</sub> solution, the apparatus atmosphere, and the absorbent solution, if the volumetric absorbent method were used.

If the apparatus above specified for determination of residual carbonates at room temperature be not available, residual carbonates may be determined by bringing the soil and acid to boiling and continuing the boiling for *one minute*, with passage of purified air during boiling and for 30 minutes subsequently. A blank should then be run upon the acid soil in the same manner and correction made therefor. The boiling necessitates great care in order to prevent moisture being carried through the sulphuric acid into the soda-lime tubes. Camp absorption towers will be found to be very efficient in the drying of the evolved gas.

It is emphasized that the method here given is the result of an attempt to ascertain the conditions effecting the maximum laboratory decomposition of CaCO<sub>3</sub> by soils, and that its relationship to the question of crop response is a problem separate and distinct.

\* For larger amounts of CO<sub>2</sub> as in the determination of CaCO<sub>3</sub> in highly calcareous soils this procedure is decidedly superior to that of double titration.