the New Zealand area throughout this lapse of geological time It is noticeable that where the basement beds are of greatest age, as at the Clarence Valley, and also at Batley, in the north of Auckland, the overlying limestone member of the series is a deep-sea ooze—globigerina, diatomaceous, or radiolarian.

While the palaeontological evidence at present available strongly supports the conclusions stated, it is certain that much still remains to be done. The collections that have already been made are capable of much extension even from the same localities, while doubtless other localities will yet be found that will add greatly to our knowledge of the fauna of the lowest members of this system of younger rocks.

Art. XL.—*On the Absorption of Lime by Soils: An Investigation of the Hutchinson-MacLennan Method of determining the Lime Requirements of Soils.*

By Leonard J. Wild, M.A., B.Sc., F.G.S., and James G. Anderson, M.Sc.

[*Read before the Canterbury Philosophical Institute, 6th December, 1916; received by Editors, 30th December, 1916; issued separately, 7th December, 1917.*]

Contents

In a paper* read by one of us before this Society last year the Hutchinson-MacLennan method of determining the lime requirement of soils was described, and some preliminary trials of its reliability were recorded It was stated that "a more practical test of the method would be to determine by it the lime requirements of two similar and adjacent soils, one of which had received a known dressing of lime at a sufficient time previously to allow of its being incorporated with the soil." It was also shown that "the result for any given soil varies with the strength of the solution."

The present paper consists of two parts: (1) A practical test of the method on lines indicated in the first quotation; (2) an investigation of the reason for the variable absorption.

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* L. J. Wild, Studies on the Lime Requirements of certain Soils, *Trans. N.Z. Inst.*, vol. 48, 1916, pp. 513–17

PART I.—PRACTICAL TEST OF THE METHOD.

This part includes a brief summary of the results already published* by one of us in the *Journal of Agricultural Science* (which periodical is not generally available to New Zealand readers), together with some additional matter.

In the summer of 1915–16 a soil-collecting tour was made in Southland, and a large number of pairs of adjacent limed and unlimed soils was obtained. Southland is a district where the farmers have no doubt as to the efficacy of lime—in fact, in some districts it is impossible to farm without it. The practice of liming was first introduced by the New Zealand Land Company on their Edendale Estate about 1890, after which the custom rapidly became popular. An excellent account of the history and practical methods of liming is given by W. D. Hunt in the New Zealand *Journal of Agriculture* for August, 1916.

In the following table we give the lime requirements indicated for pairs of adjacent limed and unlimed soils, together with the amount of lime put on, and the date of application. The conditions of experiment were: Weight of soil, 10 grammes; time of treatment, three to four hours; strength of bicarbonate solution, 0·02 normal.

TABLE I.—THE LIME REQUIREMENTS OF SOME ADJACENT LIMED AND UNLIMED SOUTHLAND SOILS

No.	Locality	Treatment.	Lime Requirement (Percentage)	Difference from Adjacent Unlimed Soil	
				Percentage	Pounds per Acre
S 3	Wallacetown	No lime	0·248	..	..
S 4	,,	1 ton lime, 1909	0·226	0·022	300
S 7	,,	1 ton lime, 1906 1 ton lime, 1915	.. 0·184	.. 0·064	.. 880
S 9	Branxholm	No lime	0·205	..	..
S 8	,,	1 ton lime, 1901	0·113	0·092	1,250
S 20	Edendale	No lime	0·270	..	..
S 18	,,	2 tons lime, 1896	0·250	0·016	220
S 19	,,	2 tons lime, 1910	0·243	0·027	370
S 23	Lochiel	Limed twenty years ago	0·221	..	..
S 21	,,	8 cwt. lime, 1915	0·153	0·068	925
S 22	,,	6 cwt. lime, 1914	0·196	0·025	340
S 62	Longbush	No lime	0·188	..	..
S 61	,,	8 cwt. carbonate, 1914	0·160	0·028	380
S 65	Morton Mains	No lime	0·208	..	..
S 64	,,	10 cwt. carbonate, 1915	0·192	0·016	220
S 63	,,	30 cwt. lime, 1914	0·125	0·083	1,030
S 17	Woodlands	No lime	0·180	..	..
S 16	,,	1 ton lime, 1915	0·159	0·021	290

Out of these results the following conclusions emerge: (1) That an application of lime to a soil in the field is reflected in a diminution of the lime requirement, as indicated by the method under consideration; (2) that the diminution in the indicated lime requirement is not commensurate with the amount of lime added; (3) since practical experience shows that the applications of lime recorded above were sufficient to convert

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* L. J. WILD, On some Soils of the South Island of New Zealand, with Special Reference to their Lime Requirements, *Journ. Ag. Sci.*, vol. 8, 1917.

unhealthy, infertile soils into healthy, fertile ones, then either (*a*) the Hutchinson-MacLennan method gives excessive estimates of the lime requirements of soils, or (*b*) it gives an optimum value that is greatly in excess of practical, or at all events of economical, requirements.

Pairs of soils were also obtained in Canterbury, and dealt with in like manner. The following table gives some results :—

TABLE II.—THE LIME REQUIREMENTS OF SOME ADJACENT LIMED AND UNLIMED CANTERBURY SOILS

No	Locality	Treatment	Lime Requirement (Percentage)	Difference from Adjacent Unlimed Soil	
				Percentage	Pounds Per Acre*
L 21B	Lincoln	No lime	0·139	0·036	500
L 21A	,,	6 cwt lime, 1915	0·103		
C 129	Ashley Dene	No lime	0·156	0·043	590
C 128	,,	1 ton carbonate, 1915	0·113		
C 220	Morven	No lime	0·104	0·019	260
C 219	,,	1 ton lime, 1913	0·085		
C 122	Longbeach	No lime	0·120	Nil	Nil
C 123	,,	Limed twenty years ago	0·120		

Taking these results in conjunction with the fact that liming has never "taken on" among the farmers of Canterbury (though the soils give an acid reaction to litmus), the high so-called lime requirement is noteworthy, though it is certainly much less than in the case of Southland soils. Liming here also seems to reduce the indicated lime requirement, but not to a degree commensurate with the quantity of lime applied.

There are, however, some areas in Southland where farming is successfully practised without the use of lime—namely, the flats of the Oreti and Aparima Rivers, especially the Dipton Flat and Bayswater. We do not say that lime will not give payable results, but merely that these soils do not demand lime in the insistent manner of, say, the Edendale soils.

In the next table we give the lime requirements of some of these different types of soils.

TABLE III.—LIME REQUIREMENTS OF SOME SOUTHLAND SOILS

(*a*) Soils demanding Lime			(*b*) Soils not requiring Lime		
No	Locality	Lime Requirement (Percentage)	No	Locality	Lime Requirement (Percentage)
S 3	Wallacetown	0·25	S 6	Wallacetown Flat	0·18
S 9	Branxholm	0·21	S 24	Winton	0·16
S 14	Rakahouka	0·22	S 26	Lady Barkly	0·14
S 17	Woodlands	0·18	S 29	Centre Bush	0·13
S 18	Edendale	0·25	S 30	Kauana	0·13
S 20	,,	0·27	S 31	,,	0·12
S 62	Longbush	0·19	S 36	Dipton	0·14
S 65	Morton Mains	0·21	S 69	Bayswater	0·14
S 22	Lochiel	0·20	S 70	Upper Bayswater	0·14
S 23	,,	0·22	S 71	Lower Bayswater	0·11
	Average	0·22		Average	0·139

In the next table we give the lime requirements of some typical Canterbury Plains soils. These, it will be remembered, give an acid reaction to litmus, but do not markedly respond to lime.

TABLE IV.—LIME REQUIREMENTS OF ACID BUT UNRESPONSIVE CANTERBURY PLAINS SOILS

No.	Locality.	Lime Requirement (Percentage).	No.	Locality.	Lime Requirement (Percentage).
L 21	Lincoln College	0·10	C 141	Lincoln	0·14
C 142	Weedon's	0·09	E 1	Ladbrook's	0·06
C 143	,,	0·15	C 217	Willowbridge	0·06
C 218	Waihao Flat	0·09	C 221	,,	0·09
C 219	Morven	0·11	E 2	Prebbleton	0·05
C 220	,,	0·09	E 8	Springston	0·10
C 109	Rakaia (West)	0·11	C 111	Overdale	0·14
C 110	,, (East)	0·12	C 112	Chertsey	0·14
C 120	Eiffelton	0·09	C 122	Longbeach	0·12
C 124	Waterton	0·12	C 125	Greenstreet	0·11

Average lime requirement, 0·104 per cent.

These figures merely confirm what has already been observed—namely, that while the Hutchinson-MacLennan method enables us to distinguish between soils demanding lime and soils not requiring it so urgently, yet we cannot agree to the statement that a complete failure of crop is the accompaniment of an absorption of 0·18 per cent. For there are Southland soils naturally requiring lime that, after a dressing of lime that experience shows to be sufficient for the practical purpose of soil-amelioration, may still show as high an absorption as 0·24 per cent.; while those of the Canterbury Plains and of the Southland river-flats, though having an absorption of 0·104 and 0·139 per cent. respectively, have nevertheless not shown any marked demand for lime, and certainly are being farmed very profitably without it. Hutchinson and MacLennan would apparently, in the light of their experience, lime a soil till its absorption is reduced to nil. In connection with field experiments at Woburn Station they say, "Without necessarily indicating that the controlling factor in crop-production of these (barley) plots is one of physiological resistance to soil acidity, there is still a very close agreement between yields and soil reaction. In all cases where the soil is neutral in reaction high returns are obtained; where the requirement is more than 0·18 per cent. the crop shows almost if not complete failure. . . . Somewhat similar data were obtained with the soils from the permanent wheat plots, although in this case the crop was more resistant to acid conditions, and persisted until the soil showed an absorption of over 0·22 per cent."

Unfortunately, we have not in this country a series of experimental results bearing on this matter, but practical farm methods in the districts we have visited appear to indicate that the limits suggested in the above statement are too narrow for adoption here. Thus, to take the case of the Wallacetown soil, one giving a markedly acid reaction and with an indicated lime requirement of 0·265 per cent., it is found that a dressing of even 1 ton — and certainly of not more than 1½ tons — of burnt lime is ample for the practical purpose of putting the soil into condition to yield an abundant harvest, while, owing to the high price of lime, a phenomenal return would be required for a further application to prove profitable Another point is that the effect of lime is seen rather in the pastures than in the cereal or root crops. At Edendale they say that a want of something in the soil was seen not so much by low yields of oats or turnips as in the ill health and lack of condition of stock depastured in these fields.

Taking into consideration these facts, as well as observations of the absorption of average Canterbury Plains soils, we have come to the conclusion that, while lime is no doubt urgently needed where the absorption is greater than about 0·20 per cent., there is no proof from the point of view of crop-production that it is required where the absorption is less than about 0·10 per cent. To translate the indication of the Hutchinson-MacLennan method into practical terms, therefore, we suggest the use of this figure as a correcting value to be deducted from the actual indication in order to get the probable practical requirement. The quantity 0·10 per cent. is selected as being the present lime requirement indicated for field 21 of the Lincoln College Farm, which received 6 cwt of lime in the winter of 1915, and which is now in an entirely satisfactory productive condition. A higher value—say, 0·14 per cent —may perhaps be allowed for Southland soils.

Our conclusions, however, must be taken strictly in the sense in which they are here recorded. We do not attempt to insist that liming the soils of the Canterbury Plains will not pay; but it is certainly the case that while the benefits of liming have thrust themselves under the notice of Southland farmers, they have not been sufficiently obvious to those farmers in Canterbury who have made the experiment. Nor is it necessary for us to say that we fully recognize that a manurial application may be more than paying its way though the fact may not be obvious simply by viewing the plots without measurements. Our conservative attitude is dictated by the considerations — first, that there is as yet no positive experimental evidence proving the economic importance of lime to these soils, secondly, that satisfactory results are being obtained without liming; thirdly, that whereas a kind of natural selection operating among methods of farming the Southland Plains soils brought about the evolution of the practice of liming, the same processes have not achieved similar results in Canterbury.

Reason for greater acidity of Southland Plains soils: A search for reasons for the greater lime requirements of Southland Plains soils on the one hand, and those of the river-flats and of Canterbury Plains on the other, led to the conclusion that the greater acidity and higher lime requirement of the soils of the Southland Plains appears to be due to a combination of lack of natural under-drainage (owing to more or less impervious clay subsoil) and high rainfall, which together prevent aeration and oxidation of organic matter, so that "sour" humus accumulates in the soil The reasons for this conclusion are set forth in the article in the *Journal of Agricultural Science* already mentioned.

PART II.—AN INVESTIGATION OF THE THEORY OF THE METHOD.

The principal object of this investigation was to ascertain, if possible, the nature of the action by which lime is taken up by the soil. At least two explanations have been offered—

(1.) The phenomenon is a mass-action effect, the calcium base combining with the so-called humous acid of the soil.

(2.) The interaction between calcium salts and soil is due to "adsorption" by soil colloids.

The first explanation is put out of court by the consideration that if we were concerned only with a mass action, then the amount of lime withdrawn from solution by a given weight of the same soil would always be the same, provided always that sufficient time were allowed for the completion of the action. Variations in the concentration of the solution would not affect the result, provided that the solution has enough lime to satisfy the soil. Now, we have determined by preliminary experiments (see *Journ. Ag. Sci.*, vol. 8; also this article, p. 475) the time necessary for the completion of the action; but, even allowing this time, we have found a variable absorption of the kind already described. Within fairly wide limits, the greater the initial concentration of the solution the greater is the absorption.

We turn, therefore, to the second suggestion. The literature of "adsorption" by soils has been summarized by Patten and Waggaman* and more recently by Prescott.† The following is from Russell's *Soil Conditions and Plant Growth*, p. 58 (new ed., 1915):—

> "Van Bemmelen has demonstrated a close parallelism between the various interchanges and absorptions shown by the soil and those shown by colloids; and there is considerable evidence in other directions that some of the soil constituents, especially the clay, possess all the properties of colloids. Now, the adsorption by colloids can generally be represented by the equation—
>
> $$\frac{y}{m} = kc^{\frac{1}{n}}$$
>
> where y = amount absorbed by quantity m of adsorbent; c = equilibrium concentration of dissolved substance; k and n are constants depending on the nature of the solution and the adsorbent. Wiegner has shown that the interaction between ammonium salts and soil accords entirely with this reaction, and Prescott finds the same holds true with adsorption of phosphates from their solution by soil."

In this paper an attempt is made to test the applicability of this formula to the absorption of lime by soil. Table V shows some results obtained with the soil from field 21 (Lincoln College)—

Table V—Absorption of Lime by Soil No L 21 from Calcium-bicarbonate Solutions of varying Concentrations

Initial concentration	0·0246N	0·0227N	0·0211N	0·0197N	0·0184N	0·0174N	0·0164N	0·0155N
Lime absorbed (grammes)	0·161	0·160	0·157	0·143	0·134	0·133	0·131	0·120

These results are plotted in fig. 1. It is evident that the part of the curve that embraces the results with higher concentrations is of the parabolic type, and would presumably approach that form more nearly if determinations had been made with solutions of greater strength.

In order, therefore, to experiment with a solution richer in lime a saturated solution of lime-water was employed; and as with caustic lime a

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* H. E. Patten and W. H. Waggaman, Absorption by Soils, *U.S. Dept. of Agric., Bureau of Soils, Bull. No. 52,* 1908.

† J. A Prescott, The Phenomenon of Absorption in its Relation to Soils, *Journ. Ag Sci*, vol. 8, 1916, p 111

disturbing effect would be created by a high percentage of humus, we took a clay subsoil poor in organic matter. The conditions of the experiment were as follows: A saturated solution of $Ca(OH)_2$ was carefully prepared and kept in a stoppered bottle. In order to obviate the formation of $CaCO_3$ by the action of atmospheric CO_2 the air was displaced by coal-gas. Titration with standard acid gave the initial concentration as 1·7 grammes per litre. Ten grammes of soil was used in all the experiments, and the volume of solution was 300 c.c. in each case. After a preliminary shaking the contents were allowed to digest for three hours, after which 5 c.c. to 20 c.c. of the supernatant liquid were pipetted off and titrated with standard acid, phenol-phthalein being used as indicator. The end point was in all cases quite distinct. The equilibrium concentration of $Ca(OH)_2$ was then calculated, and the diminution in concentration so deduced.

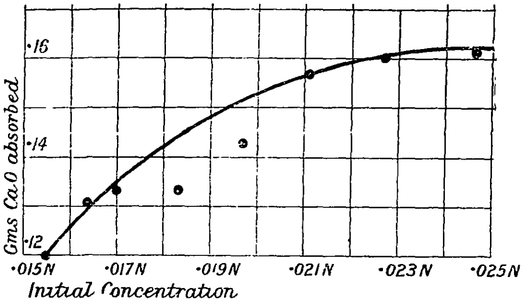

FIG 1

Results: Several series were repeated, and very good agreement was obtained. The following set of values may be taken as typical:—

TABLE VI—ABSORPTION OF LIME FROM LIME-WATER BY CLAY SUBSOIL

Initial Concentration. Grammes $Ca(OH)_2$ per Litre	Final Concentration: Grammes $Ca(OH)_2$ per Litre	Loss of Concentration: Grammes $Ca(OH)_2$ per Litre	Constant: 4*a*
1·7	1·0	0·7	0·49
1·475	0·834	0·64	0·49
1·14	0·59	0·55	0·51
0·875	0·46	0·44	0·42
0·575	0·235	0·34	0·49
0·28	0·08	0·20	0·50

The derivation of the figure in the last column (4*a*) will be explained later

Graphical representation: From these values two curves may be drawn—(1) diminution in concentration of $Ca(OH)_2$ against initial concentration; (2) loss in concentration against final concentration of dissolved substance. Both these curves were found to be perfectly general in form, and it will be noticed that the majority of the points lie on the curves.

Evaluation of constant 4*a*: Examination of the curve in fig 2 will show that it is of the parabolic type. Now, the general equation for the parabola is $y^2 = 4ax$, where a is a constant From this curve the values given in the last column of Table VI were calculated, and here with one exception excellent agreement is obtained, the mean value being 0·49.

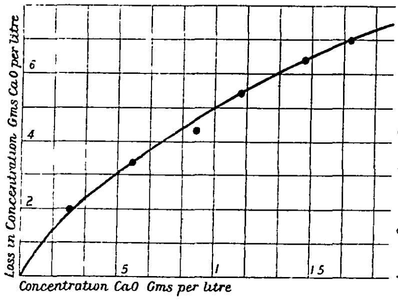

FIG. 2.

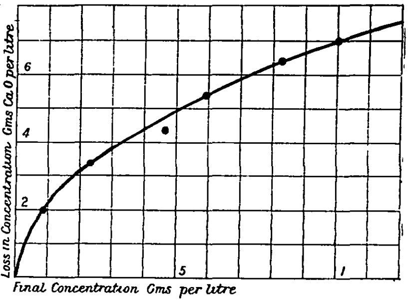

FIG 3

The equation for the parabola may now be compared with that for colloidal adsorption.

The general formula representing colloidal adsorption is—

$$\frac{y}{m} = kc^{\frac{1}{n}}$$

where the symbols have the significance given above (p. 471). Now, this may be transformed as follows :—

By squaring $\frac{y^2}{m^2} = k^2 c^{\frac{2}{n}}$

let $n = 2$ (see observation below) ;

then $\frac{y^2}{m^2} = k^2 c,$

therefore $y^2 = m^2 k^2 c,$ analogous to

$y^2 = 4ax$ the equation for the parabola.

Therefore we may equate

$m^2 k^2 = 4a;$

but $m = 10,$

therefore $k^2 = \frac{1}{100} 4a,$

therefore $k = \frac{1}{10} \sqrt{4a}$

$= \frac{1}{10} \sqrt{\cdot 49}$

$= \cdot 07$

For this particular soil, therefore, the connection between the absorption of $Ca(OH)_2$ and the equilibrium concentration may be expressed—

$$\frac{y}{m} = \cdot 07\, c^{\frac{1}{2}}.$$

Observation : The selection of the value $n = 2$ is more or less arbitrary, and on it, of course, the value of k depends. It is well known, however, that in the case of colloids adsorption varies with the valency of the ion that is being adsorbed. Calcium functions as a dyad ; and for that reason, as well as for the consequent conformity with the general parabolic equation which the experimental curve seems to postulate, 2 has been adopted provisionally as the value of this constant.

Further trials of a similar nature were made with other soils, and the results of these were of the same general form. Two typical sets of results are given below—

TABLE VII.—ABSORPTION OF LIME FROM LIME-WATER BY WANGANUI SOILS.

Initial Concentration: Grammes $Ca(OH)_2$ per Litre	Final Concentration: Grammes $Ca(OH)_2$ per Litre	Loss of Concentration: Grammes $Ca(OH)_2$ per Litre	Constant: k
	Soil A		
1·558	0·7479	0·8101	0·095
1·2984	0·5651	0·7333	0·096
1·0388	0·3513	0·6575	0·111
0·7792	0·2440	0·5352	0·109
0·5196	0·1300	0·3896	0·108
0·2600	0·0444	0·2156	0·103
	Soil B		
1·558	0·7759	0·7821	0·089
1·2984	0·5590	0·7394	0·098
1·0388	0·4490	0·5898	0·089
0·7792	0·2658	0·5134	0·100
0·5196	0·1483	0·3713	0·096
0·2600	0·0214	0·2386	0·152 ?

Average value of soil A, 0·104. Average value of soil B, 0·094.

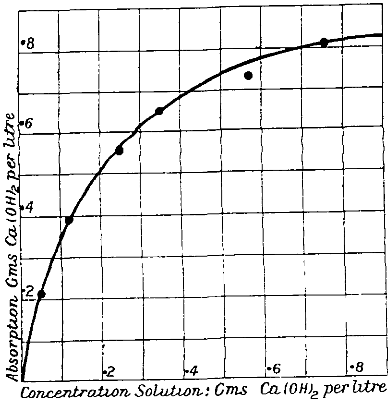

FIG. 4.—Soil A.

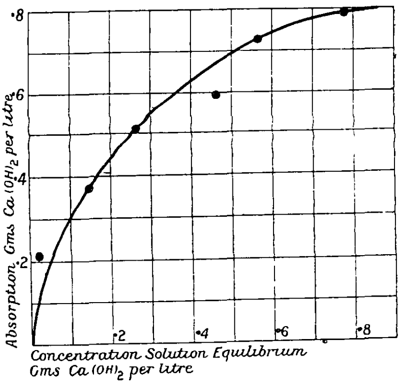

FIG. 5.—Soil B.

It will be noticed that the graphs are of quite similar form to those previously obtained, and the values of the constants for any set show approximate agreement. In certain cases, however, it would seem that this relationship ceases to hold when the concentration becomes very small.

Time curves: In preliminary experimentation we had obtained some information as to the rate at which the reaction proceeds with varying initial concentrations, and it was decided to investigate this more fully in the hope of deducing further confirmatory evidence. Typical sets of values are as follows:—

Set 1.		*Set 2.*	
Time, in Hours	Final Concentration : Grammes per Litre	Time, in Hours.	Final Concentration : Grammes per Litre.
—	1·7	—	0·85
½	1·47	½	0·725
1	1·3	1	0·625
1½	1·17	1½	0·542
2½	1·0	2½	0·380
3½	1·0	3½	0·380

These results are shown graphically in fig. 6, (*a*) and (*b*).

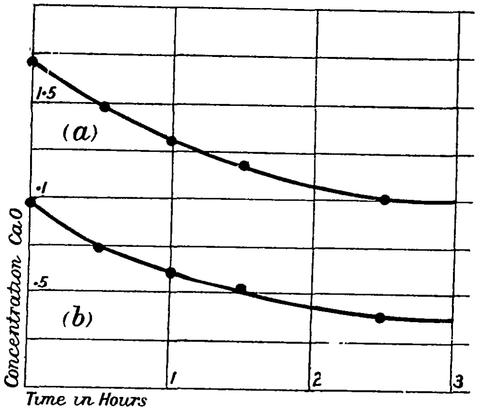

FIG. 6

It will be noticed that the form of the two curves given is almost identical; and, further, that the time taken to complete a certain fraction of the reaction appears, within the limits of the experimental error, to be independent of the initial concentration. For instance, the time taken to complete one-third of the reaction is approximately half an hour in both cases. Now, this is characteristic of reactions of the *first order* (Ostwald)—*i.e.*, reactions where only one substance undergoes any alteration. Many colloidal reactions are of this type, and it may be that here the soil colloid remains of constant activity and that the course of the reaction is conditioned solely by the concentration of the calcium hydroxide.

GENERAL CONCLUSIONS.

The results recorded in this paper appear to us to indicate conclusively that the interaction between soil and solution of calcium bicarbonate or hydrate is a colloidal phenomenon. If this is the case, then it follows that a method of determining the lime requirement of a soil based on this (such as the Hutchinson-MacLennan method) is entirely without scientific foundation. The Hutchinson-MacLennan method, however, taken merely as an empirical method and operated under standard conditions, promises to be of great utility, as has already been shown in the first part of this paper. It is certainly better than any method based on chemical analysis, and compared with other methods of a similar kind hitherto used it has the advantage of ease of manipulation.