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THE TOTAL BASE EXCHANGE CAPACITY OF THE SOIL AND ITS RELATION TO THE HUMUS AND CLAY CONTENT

BY

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The base exchange capacity of the clay and humus particles of the soil has been studied by a number of investigators. When a salt solution is added to a soil suspension, an equivalent exchange takes place between the cations that are fixed adsorptively by the soil, and the cations of the solution; the equilibrium that is finally reached depends first of all upon the ratio of the ion concentrations. Verwey has emphasized the fact that this type of adsorption is a common property of colloids [1]) [2]). Gedroiz, amongst others, pointed out the fact that, next to the exchangeable basic cations, hydrogen ions are present in the soil and that they possess a much greater adsorption energy [3]). Consequently the hydrogen ions of a moderately acid soil practically cannot be exchanged against the cations of a salt derived from a strong acid, because the $H^{\cdot}$-ion concentration of the solution very soon reaches a value where further exchange does not take place. An exchange, however, is possible to a certain extent in very acid soils [4]) [5]). The exchangeable $H^{\cdot}$-ions can, of course, be replaced to a far greater extent when they are removed from the solution by OH^{-}-ions or by the anions of a weak acid. Not only because of the very different function performed by the basic cations and by the $H^{\cdot}$-ions respectively, with regard to plant growth, but also because of the very large difference in adsorption energy, it may be easily understood that in problems of agricultural chemistry and soil science a differentiation is made between these two types of cations, distinguishing exchangeable bases and exchangeable

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[1]) E. J. W. Verwey, Dubbellaag en stabiliteit van lyophobe kolloïden, Diss. Groningen (1934). (English summary).

[2]) E. J. W. Verwey, The electrical double layer and the stability of lyophobic colloids. Chem. Rev. 16, 363 (1935).

[3]) K. K. Gedroiz, Die Lehre vom Absorptionsvermögen der Böden, Theodor Steinkopff, Dresden, 1931.

[4]) H. W. v. d. Marel, Bijdrage tot de kennis van de kationen- en anionen-adsorptie van Tropische en Nederlandsche gronden, Diss. Wageningen, 1935.

[5]) D. J. Hissink, Trans. Faraday Soc. 20, 551 (1924—'25).

hydrogen. Hissink introduced symbols for these two groups, which are now in common use in literature. The content of exchangeable bases is expressed by the S-value, and the amount of exchangeable hydrogen by the T—S figure. T is the sum of S and T—S, and represents the total base exchange capacity of the soil. The values are given in milligram equivalents per 100 g of dry soil. The V-value represents the degree of saturation by exchangeable bases $\left(V = \frac{100\ S}{T}\right)$ [5] [6] [7]. It should be borne in mind that Hissink based his considerations mainly on the assumption of humus and clay acids in the soil [8].

Methods for the determination of S and T—S are numerous [9]. The result obtained depends to a large degree upon the method followed, especially for T—S, and to a smaller extent also for S.

The *S-value* is determined by replacing all the exchangeable bases by the same cation. In effecting this exchange we are on the one hand concerned with the question, whether a state of equilibrium representing complete exchange of the exchangeable bases has indeed been reached, whereas on the other hand the possibility must be kept in mind that mineral particles from the soil are attacked and involved in the exchange reaction. The latter point may become important when extraction by acid is used. When comparing results of agrochemical studies by different workers, due attention should be paid to differences brought about by the method of determining the S-value.

The *T—S-value* is determined by treating the soil with bases, salt solutions or salts in order to exchange the exchangeable hydrogen against other cations. The differences in the T—S figures depend on the pH, the concentrations of electrolytes in the solution, and further upon the exchanging ion etc. [10].

The choice of a method for the determination of T—S depends upon the purpose aimed at and upon the fundamental point of view with regard to the problem of exchangeable hydrogen. In the first place we can distinguish between an agrochemical and a purely chemical treatment of the question.

In problems of agricultural chemistry one of the chief points is, whether a correlation exists between a certain chemical property of the soil and the yield. The V-figure, for instance, proves to be a useful indicator for the lime deficiency of a soil; it is to a certain degree proportional to the pH, which has proved itself a very useful figure in a number of agricultural problems [11]. In these problems the

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[6] D. J. Hissink, Verslag. landb. Onderzoek. Rijkslandbouwproefstat. 30, 115 (1925).

[7] D. J. Hissink, Z. Pflanzenernähr. Düngung Bodenk. A 4, 137 (1925).

[8] D. J. Hissink, Trans. 3rd Intern. Congr. Soil Sci. II, 60 (1935).

[9] Imp. Bur. Soil Sci. Tech. Communication No. 12 (1930).

[10] P. Bruin, Landbouwk. T. 47, 502 (1935).

[11] O. de Vries, Landbouwk. T. 36, 401 (1934).

significance of a correlation between V and, say, the yield is not influenced by the question whether a certain method for the determination of T—S gives values of a well defined chemical meaning. The T-value has a certain agricultural meaning, to a certain extent independent of the method by which it has been determined, because it is a measure for the buffering capacity of the soil. It will be clear that, in general, in problems of agricultural soil research many terms have a relative rather than an absolute meaning.

When dealing with the more purely chemical side of the problem the method of determination of the exchangeable hydrogen has to be selected according to more fundamental considerations. So Hissink, in using his $Ba(OH)_2$ method, tried to replace all the hydrogen ions of the weak soil acids by basic cations. A solution of $Ba(OH)_2$ is added until the relation between the amount of $Ba(OH)_2$ added and the non-absorbed part becomes rectilinear. Extrapolation to a concentration of $Ba(OH)_2$, equal to zero, gives the T—S value. When using this method a pH of about 11 is reached. In his last publication (1935) Hissink expresses his view that the state of equilibrium reached by this method may be regarded as a "theoretical or total saturation" [8]). Various authors have discussed the method of determination proposed by Hissink, and make remarks of a critical nature. Some point out that one has to distinguish between polar and non-polar binding (base exchange and molecular adsorption respectively) [12]); others call attention to an adsorption of alkali which should occur at this high pH [4]) [13]). Vageler rightly pointed out that the T-S value according to Hissink does not represent a maximum of saturation, because the angle between the straight part of the curve and the abscissa is less than 45° [14]) (the amounts of added $Ba(OH)_2$ are indicated on the abscissa and the non-absorbed part on the ordinate). According to Vageler the upper end of the adsorption curve only seems to be straight. Another consideration of fundamental importance has been put forward by Verwey who, for the adsorption phenomena of clay, calls attention to the possibility that the OH^--ions should be considered as potential determining ions; in that case a functional relation should exist between the charge of the double-layer and the concentration of the OH^--ions in the solution [15]). Bär and Tendeloo gave some experimental facts which, according to these authors, give a confirmation of this view [16]).

From this summary we may conclude that in the present state of

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[12]) A. A. J. von Sigmond, Verhandl. 2. Komm. Intern. Bodenk. Ges. 1933 A, p. 92.

[13]) J. Hudig, E. Biewenga, J. B. v. d. Meulen, Meded. Landbouwhoogeschool, Wageningen, 37, 3, p. 20.

[14]) P. Vageler, Der Kationen- und Wasserhaushalt des Mineralbodens, Julius Springer, Berlin, p. 46 (1932).

[15]) E. J. W. Verwey, Chem. Weekblad **31**, 789 (1934).

[16]) A. L. S. Bär, H. J. C. Tendeloo, Rec. trav. chim. **53**, 1128 (1934); **54**, 566 (1935).

our knowledge it is not possible to speak about a "theoretical or total saturation" of the soil. Whether a certain method of determination gives values which have a fundamental importance, depends upon the details of the method, which determine the equilibrium that is reached by it; the practical importance of the method depends upon whether it is able to differentiate between different types of soil. When a useful type of equilibrium is reached, the T-value may be very suitable for characterizing the type of clay and humus in the soil as regards their adsorption capacity.

Methods of determining T, clay and humus, used by the Government Agricultural Eperimental Station at Groningen. From the preceding it is clear that as a rule methods for the determination of the T-value must be called conventional. The same is the case with the methods used to determine the clay and humus contents.

For the determination of the percentage of *clay* the so-called mechanical analysis of the soil is very often used, by which the percentage of particles of various diameter is determined; the material with a diameter below a certain value is then called clay. The choice of this latter value as well as the way in which the soil is treated before the mechanical analysis is conventional. Novak has given a summary of the various methods for the mechanical analysis of the soil at the 3rd Intern. Congress of Soil Science at Oxford [17]).

The following method is used in our laboratory. 10 g of soil are treated with H_2O_2 (27½ %) until even on heating no more reaction occurs. The surplus H_2O_2 is destroyed by some drops of ammonia. The suspension is then boiled for a moment, after adding HCl (1 n); the liquid containing the electrolytes is removed by repeated decantation. For peptisation ammonia (0.2 n) is then added; the suspension is stirred a few times and is left standing over night. Finally the elementary particles are separated by a flowing solution of 0.2 n ammonia, using the apparatus of Kopecky; NaOH is added to this ammonia solution in the storage tank up to 0.01 n to remove the bivalent ions; the temperature is about 17° C. For the separation between clay and fine sand a flow velocity of 0.2 mm per second is chosen; according to the calculation proposed by the Int. Soc. of Soil Science the particles removed at this velocity of flow have a diameter below 15.2 micron [18]).

The *humus* content of the soil is determined by oxidation. The result is influenced first of all by the strength of the oxidising reagents. The following methods are used in our laboratory.

In sandy and peaty soils the humus content is determined in the form of loss on ignition; from this figure the moisture content (determined at 105° C) and, when carbonates are present also the loss of CO_2 have first to be subtracted. The same method is used

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[17]) V. Novak, Trans. 3rd Intern. Congr. Soil Sci. 1935 II, p. 23.

[18]) V. Novak, Proc. Intern. Soc. Soil Sci. **5**, 15 (1930).

for clay soils containing more than 5 % humus; an additional subtraction of 6 % of the clay content has then to be made for the moisture bound by the clay. The humus content of soils from arable land on marine and river clay is always very low; in such cases, and in other cases where the humus content is less than 5 %, the method of Istscherekow is used for determining the humus figure [19]). To 500 mg of soil, disintegrated in a mortar, 100 cm³ of a $KMnO_4$ solution (0.1 n) and 2 cm³ of H_2SO_4 (1 : 10) are added. The mass is heated in a boiling water bath for 50 minutes and shaken a few times. Then 50 cm³ of oxalic acid (0.2 n) and 15 cm³ H_2SO_4 (1 : 10) are added and the MnO_2 is dissolved by boiling the solution. After cooling the remainder of the oxalic acid is titrated with a solution of $KMnO_4$. The carbon content of the humus is assumed at 58 %.

The *T-value* is calculated as the sum of S and T—S as determined in the following way.

The *value S* (sum of exchangeable bases) is found by extraction with HCl (0.1 n). The soil is extracted only once at a ratio of 5 g of soil and 100 cm³ of HCl. The mixture is shaken by hand and left standing over night. The hydrochloric acid added is titrated, and afterwards the extract, using phenolphtaleïn as an indicator. At the end of the titration the red colour of the indicator should remain for ten seconds; the salts of iron and aluminium do not interfere under these circumstances. Neutral salts have no influence upon the S-value, whereas the tertiary phosphates of calcium do not neutralize the hydrochloric acid. As a further check on the correctness of the method used for extraction, we have extracted the soil not only once but four times with and without additions of different amounts of calcium carbonate; twelve soils of different types have been treated in this way. A single extraction has given on the average 98 per cent (93—100 %) of the amount obtained by repeated extraction. Finally we should mention the fact that the mineral particles of the soil may be slightly attacked by 0.1 n hydrochloric acid; when this is the case, the acid is neutralized to some extent by cations which do not belong to the exchangeable bases, so that the value found for S is too high.

The *T—S value* (exchangeable hydrogen) is determined in the following way. A soil paste is formed by adding distilled water to 20 g of soil mixed with 400 mg of precipitated calcium carbonate. The mixture is left standing at room temperature; after one day the watery soil paste is stirred again and after two days the contents are dried thoroughly at about 100° C. The amount of calcium carbonate left is determined by measuring the volume of CO_2 evolved after adding acetic acid. In a Scheibler apparatus this amount of CO_2 is compared with the amount evolved from a known quantity of pure calcium carbonate at the same room temperature and atmospheric pressure. The amount of $CaCO_3$ bound by the soil is then calculated

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[19]) W. Istscherekow, J. Exp. Landw. 67 (1904); Jahresbericht über Agriculturchemie, 1904, p. 653.

and expressed in milligram equivalents per 100 g of dry soil. A correction is made for $CaCO_3$ already present in the soil, which has to be determined separately. When after the reaction less than 200 mg of $CaCO_3$ is found to be left, a repeat test is made with a smaller amount of soil or a larger quantity of $CaCO_3$.

Table I.

Origin	Type of soil	pH	Content of		T—S after drying		Diff.	pH after drying		Diff.
			clay.	hum.	at 18°	at 100°		at 18°	at 100°	
Kolham (Gr.)	sandy soil	4.2	—	5.9	16.6	13.0	+ 3.6	7.45	7.2	+ 0.25
Heino (O.)	„	5.6	—	6.2	13.0	11.6	+ 1.4	7.45	7.5	—0.05
*) Gov. m. Agr. Exp. St.	„	5.0	—	6.4	10.0	9.8	+ 0.2	7.4	7.25	+ 0.15
Kolham (Gr.).	„	5.0	—	7.3	15.5	15.5	0	7.5	7.5	0
Nw. Compagnie (Gr.) .	**) old „dalgrond"	4.25	—	12.2	24.9	19.5	+ 5.4	7.35	7.25	+ 0.1
Grootegast (Gr.) . . .	sandy soil	4.35	—	12.5	25.8	23.5	+ 2.3	7.25	7.15	+ 0.1
Elsloo (Fr.)	„	4.6	—	14.9	26.8	25.1	+ 1.7	7.3	7.0	+ 0.3
Scharmer (Gr.)	old „dalgrond"	4.7	—	22.4	37.5	36.1	+ 1.4	7.25	7.05	+ 0.2
Scheemda (Gr.)	marine clay	5.5	52	2.9	13.0	13.2	—0.2	7.45	7.4	+ 0.05
Blijham (Gr.).	„	4.7	77	3.9	15.3	16.8	—1.5	7.25	7.35	—0.1
Garmerwolde (Gr.) . .	peaty marine clay	5.8	58	10.8	15.6	19.3	—3.7	7.3	7.2	+ 0.1
Geffen (N.-Br.)	river clay	5.5	52	11.8	11.4	15.2	—3.8	7.25	7.3	—0.05
Meeden (Gr.)	***) „roodoorn"	5.8	36	12.7	15.5	18.6	—3.1	7.35	7.35	0
Zevenhoven (Z.-H.) . .	peaty marine clay	4.1	48	39.6	102	99.7	+ 2.3	6.9	6.95	— 0.05
Harkstede.	„	5.25	38	45.5	69.2	72.7	—3.5	7.15	7.1	+ 0.05

*) Soil carried from Vries (D) in 1904.

**) Peat moor from which the peat has been removed and the upper layer has been mixed with sand from the underground.

***) A thin layer of clay (about 50 cm), very often reddish through iron compounds.

Some critical remarks on the $CaCO_3$ method for the determination of T—S. The question in how far the equilibrium reached in our above described method may be called a true equilibrium is an important one. Maschhaupt and ten Have published details about this method used for clay soils [20]. We have later on applied this method to sandy and peaty soils. From a number of results obtained by the authors just mentioned we concluded that a true equilibrium had been reached in contact with $CaCO_3$ as a solid phase. We compared the T—S results obtained by the method described above in different types of soil with the results obtained when wetting and then drying the soil at room temperature, two times in succession, instead of drying at 100° C. In Table I the figures for T—S are mentioned, and also the pH figures found after the two treatments (pH is determined in a suspension of about 10 g of soil and 50 cm^3 of distilled water, using the quinhydrone electrode). It is remarkable that the sandy and peaty soils (first series) as a rule show a lower T—S value when using the ordinary method, than after drying at room temperature, while the clay soils show the opposite behaviour (second series). The final pH of the sandy and peaty soils, reached after our ordinary method of T—S determination, is lower than after the treatment at room temperature, whereas with the clay soils no difference in any direction is predominant. Maschhaupt and ten Have found the same results for their clay soils (l.c. page 755). Furthermore we did not find an influence upon the T—S value of the concentration of electrolytes in the soil solution, nor of the proportion between the different exchangeable bases bound by the soil [10]. From these facts and from many other data which cannot be discussed in this paper, we concluded that the method described above could be used for practical agricultural work, although we were not fully satisfied with the T—S value obtained by it, as such.

In the first place the question arises how it is possible that the pH of soil in contact with a surplus of very fine $CaCO_3$ never reaches a value higher than 7.4, even after drying at 100° C (decomposition of the bicarbonates). The soil from Zevenhoven (Table I), which is very rich in humus, even has a pH lower than 7. The pH of a suspension of $CaCO_3$, in equilibrium with CO_2 of the atmosphere, is 8.4. Clay soils naturally saturated with $CaCO_3$ often show a pH figure of about 8. Thus the pH figures mentioned in the 10th column of Table I are lower than would be expected from the data just mentioned. These considerations led us to try to get a higher value for the $CaCO_3$ that enters into reaction with the soil and in connection with it a higher pH.

We left the sandy soil from Grootegast standing as a soil paste for a longer period, with the same ratio of soil to $CaCO_3$ (20 g of soil and 600 mg of $CaCO_3$). The soil was then dried at 100° C, and the

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[20] J. G. Maschhaupt, J. ten Have, Verslag. landb. Onderzoek. Rijkslandbouwproefstat. **40**, 695 (1934).

following values for T—S were found: 1 day 23.1 — 3 days 21.8 — 5 days 23.5. The length of time of the reaction therefore seems to have no influence; this agrees with the results of Maschhaupt and ten Have.

We then added a greater surplus of $CaCO_3$, and found as a rule a higher value for T—S. In the following experiments we checked this point more accurately by determining the amount of $CaCO_3$ by weighing CO_2 instead of using the Scheibler apparatus. In Table II the various amounts of $CaCO_3$ are expressed in mg per gram of soil. For these experiments we used 10 or 20 g of soil; in each case more than 1 % $CaCO_3$ remained after the reaction. The further treatment was as usual. In the experiments of the second series of Table II we added $CaCO_3$ in successive small quantities and dried the soil after every addition at 100° C. In one experiment we first oxidized the "roodoorn" soil with H_2O_2 (27½ %) to destroy the humus.

Table II.

T—S figures expressed in milligram equivalents per 100 g of dry soil *).

mg of $CaCO_3$ added per 1 g of soil	Grootegast. **)	Nw. Compagnie.	Meeden	oxidised soil Meeden ***)	Zevenhoven.	Scheemda.	Nw. Beerta. ****)
20			17.4	17.4		12.7	6.0
30	19.0	20.3	17.3	18.0		12.3	6.5
40	20.8	21.8	18.3	18.6		12.9	6.7
50	—	—	18.4	18.8			
60	21.3	21.0					
80	22.1	22.5			104.8		
100					106.1		
125					108.7		
150					109.8		
2 × 10						14.4	
2 × 15						14.0	
2 × 20						14.4	
2 × 25			21.5				
2 × 62½					117.7		
2 × 75					120.1		
4 × 12½			21.6				
5 × 12½			23.7				

*) See Table 1 for description of the type of soil.

**) With this experiment a new very finely ground sample was used.

***) These values are expressed in milligram equivalents per 100 g of oxidised soil. After the oxidation the S-value decreased from 27.4 to 3.9, so that the T-values are respectively 44.8 and 21.3

****) Marine clay soil — clay 71 % — humus 4.2 % — pH of the unlimed soil 6.25.

From the results mentioned in Table II we may conclude that a greater surplus of $CaCO_3$ causes a higher T—S value; this is particularly obvious when the $CaCO_3$ is added in two or more equal portions. The results obtained with an oxidised soil show that this increase cannot be ascribed to changes in the humus only.

In a few cases we also determined the pH of the soil when increasing amounts of $CaCO_3$ had been added. The following values for the pH were found when the increasing amounts of $CaCO_3$ mentioned in Table II were added to the sandy soil from Grootegast: 7.2, 7.17, 7.21, 7.20 respectively. When adding small portions of respectively 2, 3, 4 and 5 times 250 mg of $CaCO_3$ to 20 g of the soil from Meeden and drying the soil at 100° after each application, we found the following values for the pH: 7.34, 7.43, 7.40 and 7.44. We may therefore conclude that the pH does not change appreciably.

We further examined this question by an experiment in small plots with different types of soil. Increasing amounts of ground chalk were added to the soil. The soil was left uncropped. The average results of two series of samples, taken 3½ and 16½ months after liming respectively, are given in Table III. The results of the two series of samples were practically the same. In Table III the T-values are mentioned. When $CaCO_3$ is absent or when only a small amount is present, the T-value is calculated as the sum of the S and T—S values. When a large surplus of $CaCO_3$ is present, the soil is already saturated by exchangeable bases, at least after our definition; in such a case the T-value is equal to the S-value. We ought to mention here,

Table III.

Grootegast			Kolham			Heino		
pH of the	$CaCO_3$ % limed soil	T	pH of the	$CaCO_3$ % limed soil	T	pH of the	$CaCO_3$ % limed soil	T
4.7	0	30.3	4.63	0	16.3	5.79	0	18.4
5.55	0	29.1	5.46	0	15.7	6.62	0	18.1
6.52	0	29.5	6.29	0	16.3	7.21	0	18.2
7.23	0	32.3	6.19	0	17.1	7.57	0.14	18.9
7.67	0.86	38.9	7.64	0.85	17.9	7.77	1.23	19.7
7.76	2.84	35.5	7.78	2.87	21.0	7.83	3.50	23.5
7.74	4.70	35.3	7.79	5.00	20.9	7.82	5.46	22.8
7.78	7.97	39.6	7.83	7.96	28.1	7.84	8.63	29.6

Zevenhoven			Meeden			Blijham		
pH of the	$CaCO_3$ % limed soil	T	pH of the	$CaCO_3$ % limed soil	T	pH of the	$CaCO_3$ % limed soil	T
4.53	0	110	5.98	0	48.1	4.7	0	42.0
5.53	0	113	6.61	0	47.5	7.77	3.14	41.9
6.29	0	115	7.14	0	49.1	7.79	5.30	39.0
7.26	0.32	122	7.48	0.12	50.0	7.79	8.72	45.2
7.39	1.32	125	7.71	1.07	50.7			
7.51	3.34	131	7.79	3.14	54.5			
7.53	5.72	132	7.79	5.35	58.3			
7.54	8.86	—	7.82	8.55	56.4			

The amounts of $CaCO_3$ and the T figures are expressed on the dry and $CaCO_3$-free soil.

however, that soils such as those from Zevenhoven and Meeden fixed some $CaCO_3$ added under the lime conditions of the T—S determination, although a large surplus of chalk was present. This fact may possibly be caused by decomposition of the humus during the determination. When using a large surplus of $CaCO_3$ we found as a rule an S-value in the soil treated by $CaCO_3$ (mentioned as T in Table III), higher than the T-value which could be calculated from the T—S values determined in the unlimed soils; the soil from Blijham did not show this phenomenon very distinctly. Sometimes the S-value, obtained in this way, increases when increasing the surplus of $CaCO_3$. The pH figures of the soils in the plots became higher than the pH values found in these soils at the close of the T—S determination in the laboratory. All these results seem to point to the fact, that the equilibrium reached during our T—S determination is not an equilibrium which exists in contact with a surplus of $CaCO_3$ and with CO_2 of the atmosphere. The fact that after 3½ and 16½ months respectively, the same amount of $CaCO_3$ is found to have reacted with the soil, indicates that no decomposition of humus has taken place during the interval.

The results of an analogous experiment (on the so-called "marl plot") are mentioned in Table IV; in this experiment increasing amounts of marl were added to a sandy soil (6 % humus, pH 5.8).

Table IV.

pH	$CaCO_3$ % *)	*)
of the	limed soil	T
6.05	0	15.2
7.15	0.17	15.8
7.38	0.52	15.6
7.51	1.09	15.1
7.53	3.37	13.1
7.59	5.33	12.0
7.59	7.42	13.8

*) The figures are expressed on the dry and $CaCO_3$-free soil.

In this case we do not see any increase of the S-value above the T-value determined in the laboratory. The samples were taken 6 and 10 months after liming respectively. It is remarkable that this result does not agree with the results mentioned above. We should mention two points in which the latter experiment differed from the others: instead of very fine chalk, ground marl of a rather bad quality was used, and oats were grown instead of leaving the soil fallow.

The question now arises what T-value is reached on arable land under ordinary field conditions when the soil is limed to a V-value of 100 %. On sandy and peaty soils this state of saturation (V = 100) is never found, except on dune sand. Nor did we attempt to reach this degree of saturation on experimental fields laid out on these types of soil, because under these conditions the so-called "grey speck disease" is likely to occur, which causes serious damage to the crops. The results from clay soils are mentioned in Table V. We did not take soils that had a natural surplus of $CaCO_3$; Maschhaupt and ten Have found some indications that the T-value of Dollard clay soils (North East Groningen) with such a natural content of $CaCO_3$, is some milligram equivalents higher than the T-value found after liming to a V-value of 100 older clay soils of the same type that are free from $CaCO_3$.

Table V gives, for acid soils, a comparison between the T-values found by the laboratory method and the T-values found in the field

Table V.

	humus	clay	Unlimed soil			Limed soil			
			pH	V	T	pH	$CaCO_3$	V	T
Pr. 79-Experimental field at Nieuw-Beerta. (1931). (marine clay)	3.6	70	5.9	75	38	7.7	1.97	100	40
Pr. 90-Exp. field at Scheemda (marine clay) (1931)	3.0	51	5.3	54	31	7.3	1.41	96	33
*) N. Ge 21. Exp. field at Didam (river clay (1934)	1.8	17	4.75	25	12	7.45	0.43	97	15
*) N. Ge 23. Exp. field at Gendringen (river clay) (1934)	1.3	43	6.7	71	18	8.10	1.68	98	18
*) N. Ge 24. Exp. field at Etten (river clay) (1934)	2.3	52	7.15	89	29	7.7	1.3	100	29
*) N. Ge 27. Exp. field at Rha (river clay) (1934)	1.4	36	5.6	57	19	8.2	1.26	100	21

When the humus and clay content of the unlimed plots differed from those of the limed plots a correction was made on the T-value, so that these "values" could be compared.

*) On the "unlimed" plots small amounts of lime or of sulphur were applied.

after liming with a surplus of $CaCO_3$. The figures show that the T-value determined by our laboratory method is equal to or lower than the results from the field. From this fact may be concluded that by our method, in various cases, the equilibrium in contact with a surplus of $CaCO_3$ and with CO_2 of the atmosphere is not reached; but the question also arises in how far a limed soil changes its T-value after liming. We intend to come back to this problem in the second part of this paper.

From the above it is not yet clear in how far our method of T—S determination leads to the equilibrium of cation exchange which we want to reach, and in how far by-reactions play a role. Other investigators, although working under other circumstances, have met with similar difficulties [21] [22] [23]. As far as our results go as yet the conclusion must be that the final stage that is reached in the reaction does not represent a chemically well defined equilibrium so that the method also on this point is merely conventional.

From a fundamental point of view it seems an attractive feature that the equilibrium of the exchange reaction is fixed by using $CaCO_3$ as a solid phase. Various investigators pronounced themselves in favour of this principle [24] [25]. Bradfield and Allison, in their publication, give the following definition: "soil saturated with bases is one which has reached equilibrium with a surplus of $CaCO_3$ at the partial pressure of CO_2 existing in the atmosphere and at a temperature of 25° C". According to their method a surplus of $Ca(OH)_2$ is added to a suspension of the soil. To accelerate the reaction the suspension is aerated. Afterwards the $Ca(OH)_2$ is changed into carbonate and bicarbonate by a current of CO_2. The $CaCO_3$ left is determined after the method of Schollenberger (the CO_2, evolved when boiling the acidified solution in vacuo, is absorbed by a solution of $Ba(OH)_2$ [26]. The calcium carbonate bound by the soil can be calculated from the amount of $Ca(OH)_2$ added and the amount of $CaCO_3$ left. The method is called: the residual carbonate method. The pH of the equilibrium reached by this method was for various clays higher than 8 and averaged 8.25. When adding $CaCO_3$ directly instead of $Ca(OH)_2$, the same results were found, but the time of reaction was much longer. From the pH figures mentioned by Bradfield and Allison we get the impression that the equilibrium reached by their method is more likely to represent an equilibrium in contact with a surplus of $CaCO_3$ at the partial pressure of CO_2 existing in the atmosphere than the equilibrium reached by our method.

Finally we should like to draw attention to the following experiment by Bradfield and Allison. A surplus of $Ca(OH)_2$ or $CaCO_3$ respectively was mixed thoroughly with a clay soil. During a period of 6 months the soil was, at intervals, moistened and then dried. The results for T—S, obtained in this way, are a little lower than the values found by the method described above; the greatest difference is 1.1 milligram equivalent per 100 g of soil. The lowest value was found when mixing the soil with $CaCO_3$; in this case the pH was

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7.97, whereas a pH of 8.32 was found when using the usual laboratory method described above. In connection with this point an experiment of Maschaupt and ten Have is worth mentioning. They mixed a clay soil with a surplus of $CaCO_3$ or $Ca(OH)_2$ respectively (an amount of 5 % was taken instead of the 2 % taken by Bradfield and Allison). The limed soil was put into bottomless glass vessels, which were under crop and dug into the soil. After a period of three months the amount of CaO bound by the clay soil of the "$Ca(OH)_2$ vessel" was about three times as large as in the "$CaCO_3$ vessel", and after 35 months this ratio was still about two. The amount bound when adding $CaCO_3$ was practically equal to the T—S value found by our method of determination. The method of Bradfield and Allison for treating the soil is different from the method used by Maschhaupt and ten Have because, when the soil is wetted in the laboratory, it is at the same time thoroughly mixed, whereas the soil in the experiment of Maschhaupt and ten Have was only mixed before it was filled into the vessels. Still, it is remarkable that the "$Ca(OH)_2$ soil" of the latter — $Ca(OH)_2$ had, of course, changed into $CaCO_3$ — should maintain such a high S-value, although it had been exposed for three years to all sorts of weather and to the influence of plant roots.

We are now comparing for the same soils the method of T—S determination according to Bradfield and Allison with the method adopted in our laboratory.

(To be concluded)

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