

# SOIL-ADSORPTION

*Report of the Proceedings of the Second Commission,  
Groningen, 1926*

*By*

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*Dr. D. J. Hissink, Referee*

At the final meeting of the Second Commission, held in May 1924, during the conference at Rome, the duty of reporting on the questions of soil adsorption was entrusted to me. I have already partly fulfilled this duty, during the Groningen Meeting in April 1926, and refer, so far as this is concerned, to Volumes A and B.

I have already treated the questions of soil adsorption theoretically in Volume B (1) and also in my Faraday lecture (2) and would therefore confine myself here to a few remarks on this point.

In his paper on "Replaceable Bases in Soils," page 34, Kelley makes the following remark:

"Hissink also found that a lesser amount of leaching with salt solutions is required to remove the replaceable monovalent bases than the divalent bases. Our experience is in agreement with theirs. It is difficult to harmonize these facts with the absorption hypothesis of Hissink. If every atom of a given base is located on the exposed surface of particles, as he assumes, one should be as readily displaced as another."

Kelley is inclined to think that the explanation is that more than one chemical compound is involved. I hardly think this can be the case. I made my tests with artificially prepared sodium and calcium soils, in which all the bases were replaced by sodium and calcium, respectively, so that I worked both times with soils of the same chemical constitution, except for the fact that one soil contained exchangeable sodium and the other exchangeable calcium. May there not be some relation between the displaceability of the univalent and bivalent bases on the one hand, and the solubility of their silicates and humates on the other hand? I shall be glad to hear the views of my colleagues and especially of Kelley and Brown on this point.

It was only my intention to study in general the proposed methods as originally laid down; it was not my intention to ascertain whether any modifications were advisable.

The proposed methods are to be found in Volume B (p. 175). It will be noted that the number of these has been increased, and that I have included, among others, Hutchinson's method. I tried out these methods on a series of Dutch soils of widely different types. I chose for this purpose eight different experimental fields of six different types, and from each field I took one sample from a limed plot and one from an unlimed one.

## DESCRIPTION OF THE SOIL SAMPLES

B 1690 and 1691. Two samples of surface soil (0-23 cm.) from the Experimental Garden at Sappemeer (Province of Groningen); mixture of sand and very well humified high peat; about 23 per cent humus. B 1690 was taken from Plots A 1 and A 3, which received only stable manure; B 1691, from Plots C 2 and C 4, which received only artificial fertilizers (potash, superphosphate and sulfate of ammonia).

B 1718 and 1724. Two samples of surface soil (0-15 cm.) from the Experimental Field at Harkstede (Province of Groningen); well humified low peat; very rich in humus (about 50 per cent), with some clay. B 1718 was taken from Plot B 10, which received 6000 kg. CaO per ha. in the form of limecake; B 1724 from Plot C 6, which received no lime. Both plots received potash and phosphate, but no nitrogen.

B 2145 and 2146. Two samples of surface soil (0-22 cm.) from the Experimental Field at Eelderwolde (Province of Groningen); well humified low peat; very rich in humus (about 45 to 50 per cent), with a little clay. B 2145 was taken from half of Plot 2, which received 2300 kg. CaO per ha. in the form of limecake; B 2146 from the other half, which was not limed. The whole plot received stable manure, but no artificial fertilizers.

B 2329 and 2330. Two samples of surface soil from an Experimental Field at Eersel (Province of North Brabant); humus sandy soils, poor in humus (about 5 to 6 per cent humus). B 2329 received liquid manure and Thomas slag; B 2330 the very small amount of about 480 kg. CaO per ha. and further stable manure, superphosphate and potash.

B 1697 and 1698. Two samples of surface soil from an Experimental Field at Schildwolde (Province of Groningen); heavy clay soil, relatively rich in humus (about 9 to 12 per cent). B 1698 was taken from the limed half of the field, which received 20,000 kg. limecake per ha. (about 4000 kg. CaO); B 1697 from the unlimed half. Both parts of the field were manured with artificial fertilizers.

B 2335 and 2337. Heavy loamy soils, practically without humus, from two spots on moorland at Roden (Province of Drenthe). B 2335 (depth 30-50 cm.) is covered with low peat; B 2337 (depth 75-100 cm.) with sandy loam. The soils were never manured.

B 1937 and 1939. Two samples of surface soil (0-23 cm.) from an Experimental Field in Overlangbroek (Province of Utrecht); grassland; very heavy river clay, relatively rich in humus (8 to 9 per cent). B 1937 was taken from the limed plot, which received in 1915, 1920 and 1923 each time 10,000 kg. slaked lime per ha.; B 1939 from the unlimed plot.

B 1944 and 1946. Two samples of surface soil (0-23 cm.) from an Experimental Field at Amsweer (Province of Groningen); arable land;

heavy marine clay with little humus (about 2 per cent). B 1944 received 12,000 kg. CaO in the form of lime cake; B 1946 was not limed.

With the exception of 2329, 2330, 2335 and 2337 all the soil samples were taken from fields already described in Volume A (p. 175; p. 198).

B 1690 and 1691 were, however, taken again in October 1924; and B 1718 and 1724 were taken again in October 1926. B 2145 corresponds to B 1858 and B 2146 to B 1859, but they were taken in May 1926.

#### COMPOSITION OF THE SOIL SAMPLES

Table 1 shows the composition of these 16 soils. The pH was determined by the Biilmann electrode in water suspensions (10 g. soil with 25 cc. of water). The exchangeable CaO was determined according to Hissink (with sodium chloride); the exchangeable MgO, K<sub>2</sub>O and Na<sub>2</sub>O by leaching 25 g. of air-dried soil with one liter of N NH<sub>4</sub>Cl solution (Kelley's method). For the value *V* (degree of saturation according to Hissink) see also Table 2 ( $V = 100 S : T$ ).

According to Table 1 the soil samples 1718, 1724, 2145 and 2146 all contain small amounts of calcium carbonate. It is strange that such acid soil as B 1724 (pH of 4.58), which never received any lime, should contain calcium carbonate. It is not impossible that when determining calcium carbonate (boiling of the soil with hydrochloric acid) in soils such as these four, which are very rich in humus, a small quantity of carbon dioxide is formed by the oxidation of carbon (see also Volume A, p. 197, remark 2).

For the potential adsorption see Volume A, p. 183. It is the amount of calcium oxide that can be absorbed by the clay-humus-substance under natural conditions. This figure depends on the one hand on the clay and humus contents of the soil, and on the other hand on the degree of saturation (*V*) of the clay-humus-substance and on the maximum *V* that this substance can reach under natural conditions. I have calculated this amount assuming that the highest *K* values under Dutch climatic conditions are:

$$K (\text{clay}) = 1.1 \text{ and } K (\text{humus}) = 5.0^1.$$

The calculation is as follows: With *K* values respectively 5.0 and 1.1 100 g. dried soil B 1690 (with 23.1 per cent humus and 8.4 per cent clay) contains  $(23.1 \times 5 + 8.4 \times 1.1) : 100 = 1.247$  g. CaO. Since B 1690 contained 0.653 per cent CaO, the clay-humus-substance of 100 g. dried soil (105° C.) can take up under the prevailing climatic conditions  $1.247 - 0.653 = 0.594$  g. CaO. This figure is introduced as the *potential adsorption*.

<sup>1</sup> As can be seen from these figures, it is especially the humus which adsorbes the CaO. In well saturated Dutch soils, in a natural condition, 100 g. of humus contain *about* 5 g. CaO and 100 g. clay (I+II) *about* 1.1 g. CaO. These figures are of course to be regarded as a first approximation.

TABLE 1—Composition of soil samples

Soil sample No. B	Percent of H <sub>2</sub> O in air-dried soil	pH	CaCO <sub>3</sub>	Organic matter	Clay (I+II)	Sand (III+IV)	Percentages in dried soil (105° C.)				Total bases in milligr. equivalent per 100 g. soil (S)	Potential adsorption (calculated)	Degree of saturation (V)	Per 100 parts exchangeable bases are present (relative proportion of bases)			
							CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O				Ca	Mg	K	Na
Sappemeer	16.9 13.6	5.03 4.22		23.1 22.9	8.4 7.7	68.5 69.4	0.653 0.359	0.062 0.077	0.043 0.055	0.064 0.104	29.4 21.2	0.594 0.871	21.5 14.9	79 60	11 18	3 6	7 16
Harkstede	30.9 31.4	5.90 4.58	0.76 0.60	48.2 48.0	33.1 31.9	18.7 20.1	1.867 1.079	0.105 0.104	0.048 0.033	0.103 0.085	76.2 47.1	0.907 1.672	28.0 15.9	88 82	7 11	1 1	4 6
Eelderwolde	31.6 38.1	5.26 5.10	0.53 0.51	45.4 49.2	17.2 20.2	37.4 30.6	1.512 1.430	0.073 0.081	0.072 0.087	0.060 0.089	61.1 60.3	0.947 1.252	25.7 23.4	88 85	6 7	3 3	3 5
Eersel	1.8 1.9	5.03 4.13		5.0 5.8	10.1 9.3	84.9 84.9	0.093 0.055	0.009 0.020	0.009 0.009	0.007 0.017	4.0 3.7	0.268 0.337	11.9 9.7	82 54	13 27	5 5	14
Schildwolde	8.2 8.8	6.83 4.83		9.7 12.6	59.2 63.7	31.1 23.7	0.791 0.366	0.017 0.023	0.012 0.018	0.027 0.047	30.4 16.1	0.345 0.965	34.9 16.5	93 81	3 7	1 3	3 9
Roden	7.3 7.4	6.28 5.07		1.5 1.7	86.2 78.2	12.3 20.1	0.809 0.507	0.129 0.151	0.019 0.048	0.049 0.074	37.4 29.1	0.254 0.438	50.9 41.9	77 62	18 26	1 4	4 8
Overlangbroek	5.4 5.8	7.35 6.19	1.49 0.19	8.5 8.8	70.0 73.2	20.0 17.8	1.139 0.849	0.117 0.128	0.034 0.024	0.022 0.039	48.0 38.5	0.056 0.396	48.3 40.6	85 79	13 17	1 1	3 3
Amweeer	4.0 4.6	7.83 7.56	1.29 0.57	2.2 1.8	54.3 56.8	42.2 40.8	0.665 0.608	0.081 0.103	0.023 0.029	0.035 0.034	29.5 28.6	0.042 0.107	53.2 53.1	80 76	14 18	2 2	3 4

## SOME EXPLANATORY REMARKS ON THE FIGURES IN TABLES 2 AND 3

All values in Table 2 are expressed in milligram equivalents (me.) on 100 g. dried soil (105° C.) and will here be calculated for the first sample B 1690.

The *S*-values of Kelley (total bases and  $\text{NH}_4$ -adsorbed), Hissink, and Bobko-Askinasi (28.9—29.3—22.3—32.8), require no further explanation.

The titration according to Gedroiz gave, for B 1690, in 3 liters:  $1.86+1.31+0.78=3.95$ , in round figures, 4.0 me. Assuming that in the place of the replaced H an equivalent amount of Ba is adsorbed by the clay-humus-substance, the soil will contain after the leaching with barium chloride:  $29.4$  (*S*-Hissink)  $+4.0=33.4$  me. bases in the adsorbed condition.

With Hutchinson's method 10 g. of air-dried soil B 1690 were shaken with 200 cc. of calcium bicarbonate, 100 cc. of which titrated 20.6 cc. 0.1 *N* HCl, whilst 100 cc. of the soil filtrate titrated 16.6, so that per 5 g. of air-dried soil  $(20.6-16.6)\times 2.8$  mg. CaO was adsorbed or 0.224 g. CaO per 100 g. air-dried soil. Now the air-dried soil contains 16.9 per cent water (see Table 2). If this is taken into account, then 0.272 g. CaO is adsorbed per 100 g. dried soil. The duplicate determination gave 0.258, the average being 0.265 g. CaO=9.5 me. CaO. The original soil contained 29.4 me. (*S*-Hissink); after the treatment with calcium bicarbonate the soil contained adsorbed:  $29.4+9.5=38.9$  me. bases.

With Kappen's method 100 g. of air-dried soil B 1690 were shaken with 250 cc. *N* Ca ( $\text{C}_2\text{H}_3\text{O}_2$ )<sub>2</sub> solution; 125 cc. of the filtrate titrated 37.5 cc. 0.1 *N* NaOH solution. Per 100 g. air-dried soil was thus adsorbed:  $2\times 37.5\times 2.8=210$  mg. $\times 0.210$  g. CaO. The duplicate determination titrated 39.5 cc. 0.1 *N* NaOH, that is 0.221 per cent CaO adsorbed, the average being 38.5 cc. or 0.2156 per cent CaO adsorbed. Allowing for the water content of the air-dried soil (16.9 per cent) then 0.277 g. CaO =9.9 me. was adsorbed per 100 g. dried soil. The original soil contained 29.4 me. (*S*-Hissink); after the treatment with calcium acetate the soil contained adsorbed:  $29.4+9.9=39.3$  me. bases.

As is known, Kappen employs the factor  $1\frac{1}{2}$ . Taking this factor into account, and assuming also that  $1\frac{1}{2}$  times the amount of CaO is actually adsorbed by the soil (i.e.  $1.5\times 0.277=0.4155$  per cent), the soil contains in this case:  $29.4+(1\frac{1}{2}\times 9.9)=44.2$  me. adsorbed. This figure is not included in Table 2.

According to Kappen (Volume B, p. 179) a sufficiently accurate measure of the amount of lime needed to bring the soil to neutrality is provided by multiplying the alkali titer 38.5 by the factor 4.5. This gives the number of double centriers of pure  $\text{CaCO}_3$  needed per ha. (3,000,000 kg.) i.e. in this case:  $38.5\times 4.5=173.2$  double centriers = 17,320 kg.  $\text{CaCO}_3$ . This figure can also, of course, be obtained in this way:  $10,000\times (0.2156\times 1\frac{1}{2})$

TABLE 2—Milligram equivalents

Soil sample No.	pH	S-Kelley		S-Hissink (see Table A)	Bobko and Askinst	Gedrois	Hutchison and MacLennan		Kappen	Gehring and Webermann			Hissink		Titration with CaO till pH =			Potential adsorption (see Table 1)								
		Total bases	NH <sub>4</sub> Cl sorbed				25, resp. 10 g. of soil	10, resp. 5 g. of soil		T-S	T	6.0	6.5	7.0												
1690	5.03	28.9	22.3	29.4	32.8	4.0	33.4	9.5	38.9	9.9	39.3	11.0	40.4	24.6	54.0	107.5	136.9	5.0	34.4	10.8	40.2	18.9	48.3	21.2	50.6	
1691	4.22	21.4	18.0	21.2	27.3	6.2	27.4	16.7	37.9	17.1	38.3	17.8	39.0	31.6	52.8	120.8	142.0	13.8	35.0	22.5	43.7	32.1	53.3	31.1	52.3	
1718	5.90	71.0	61.8	76.2	77.5	2.2	78.4	8.9	85.1	9.5	85.7	17.6	93.8	55.9	132.1	196.2	272.4									
1724	4.58	43.8	41.4	47.1	55.4	11.2	58.3	27.5	74.6	26.9	74.0	37.5	84.6	68.7	115.8	248.9	296.0	21.3	68.4	38.6	85.7	60.0	107.1	59.7	106.8	
2145	5.26	62.0	45.3	61.1	66.0	2.3	63.4	11.9	73.0	12.6	73.7	23.0	84.1	64.5	125.6	176.7	237.8	5.5	66.6	14.3	75.4	26.8	87.9	33.8	94.9	
2146	5.10	57.9	45.3	60.3	65.1	4.2	64.5	18.4	78.7	19.2	79.5	33.2	93.5	81.1	141.4	197.5	257.8	11.2	71.5	21.6	81.9	35.7	96.0	44.7	105.0	
2829	5.01	4.4	3.8	4.0	6.5	1.9	5.9	4.9	8.9	4.5	8.5	13.3	17.3	22.1	26.1	29.7	33.7	2.6	6.6	5.1	9.1	8.4	12.4	9.6	13.6	
2830	4.11	3.8	3.8	3.7	7.7	4.1	7.8	6.7	10.4	6.1	9.8	13.8	17.5	26.6	30.3	34.4	38.1	5.8	9.5	8.4	12.1	11.5	15.2	12.0	15.7	
1698	6.83	32.2	25.1	30.4	31.0	-1.0		0.1	30.5	1.8	32.2	9.6	40.0	28.1	58.5	66.8	87.2									
1697	4.81	18.4	18.1	16.1	24.5	3.5	19.6	10.6	26.7	10.0	26.1	17.3	33.4	32.3	48.4	81.2	97.3	7.2	23.3	14.2	30.3	21.4	37.5	34.5	50.6	
2835	6.28	36.9	33.5	37.4	37.0	0.7	38.1	1.5	38.9	1.4	38.8	13.4	50.8													
2837	5.07	28.3	27.7	29.1	28.6	0.7	29.8	6.8	35.9	4.8	33.9	18.0	47.1													
1937	7.35	66.7	34.5	48.0	45.9	-7.3		-1.4		1.3	49.3	4.2	52.2	14.0	62.0	51.3	99.3									
1939	6.19	40.4	32.0	38.5	39.0	0.2	38.7	2.8	41.3	3.5	42.0	12.5	51.0	27.9	66.4	66.4	94.9	0.9	39.4	5.9	44.4	5.9	44.4	14.1	52.6	
1944	7.83	40.9	18.1	29.5	21.8	-7.9		-6.5		0.6	30.1	4.0	33.5													
1946	7.56	31.9	19.4	28.6	22.0	-2.6		-0.8		0.7	29.3	6.2	34.8													

\* Corrected.



$\times 3$ ):  $56 = 173.2$ . When, however, the moisture content is taken into account, we obtain:  $10,000 \times (0.277 \times 1\frac{1}{2} \times 3) : 56 = 222.6$ .

This shows that the water content of soils like these, which contain a great deal of water in an air-dried condition, has a great influence on the results, and must therefore be taken into account.

Twenty-five grams of soil B 1690, treated according to Gehring, gave on leaching with sodium chloride 0.960 per cent CaO (in dried soil); the content of exchangeable CaO in the original soil being 0.653 per cent CaO,  $0.960 - 0.653 = 0.307$  per cent CaO = 11.0 me. was adsorbed per 100 g. dried soil. The original soil contained 29.4 me. (S-Hissink) adsorbed bases; after the treatment according to Gehring the soil contained adsorbed  $29.4 + 11.0 = 40.4$  me. bases. If 10 g. of soil is treated, the result is:  $29.4 + 24.6 = 54.0$ .

$T - S$  according to Hissink is 107.5, which gives  $T = 107.5 + 29.4 = 136.9$ .

The result of the titration with CaO is that 5 me. CaO per 100 g. dried soil B 1690 are required to reach a pH of 6. With a pH of 6 this soil therefore contains  $29.4 + 5.0 = 34.4$  me. bases adsorbed. With a pH of 6.5 the figures are:  $29.4 + 10.8 = 40.2$ ; with a pH of 7:  $29.4 + 18.9 = 48.3$ .

According to Table 1 the potential adsorption of B 1690 is 0.594 g. CaO, that is 21.2 me. CaO. When the soil has fixed this amount, it contains  $29.4 + 21.2 = 50.6$  me. bases in the adsorbed condition, i.e. adsorbed in the clay-humus-substance.

Table 3 shows in the first place the pH of the water soil suspension (see Table 1). It further shows the pH of the KCl soil suspension (100 g. air-dried soil per 250 cc. *N* KCl solution); the pH of the filtrate of this suspension and also the pH of the soil on the filter, after it had been washed with and shaken in water. Finally the number of mg.  $Al_2O_3 + Fe_2O_3$  per 125 cc. of the filtrate (i.e. per 50 g. air-dried soil) is also given. The same data as for potassium chloride are also given for the calcium acetate solution (Kap-pen's method). I also tried to get the same data for calcium bicarbonate (Hutchinson's method) but the agreement between the duplicate determinations was not very satisfactory (Tables 1 and 3).

#### DISCUSSION OF THE METHODS

*S-value*.—In soils containing no calcium carbonate the determination of the *S-value* presents relatively little difficulty, the only question in this case being the amount of soil to be leached out. Generally speaking, less substance should be taken of soils rich in exchangeable bases, that is, especially, soils which are slightly acid to alkaline and rich in humus. In the case of these soils also, of course, two liters may be leached out at each leaching instead of one.

That the differences in the *S-value* of these soils are but slight, whatever method is used, may be seen by comparing Kelley's figures (total bases) with mine: for instance B 1690: 28.9 and 29.4. If, however, the soil con-

TABLE 3.—Comparison of hydrogen ion concentration as determined by Kelley's and Kappen's methods

Soil sample No. B	pH of the water suspension (see Table I)	Potassium chloride solution				Calcium acetate solution			
		pH of the KCl soil-suspension	pH of the filtrate of this suspension	pH of the water soil suspension after the treatment with KCl	mg. $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ per 125 cc. of the filtrate; i.e. per 50 g. air-dried soil	pH of the calcium-acetate-soil-suspension	pH of the filtrate of this suspension	pH of the water soil suspension after the treatment with calcium acetate	mg. $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ per 125 cc. of the filtrate; i.e. per 50 g. air-dried soil
1690	5.03	4.55	4.96	6.05	1.5	5.78	5.78	6.44	3.0
1691	4.22	3.55	3.65	5.53	9.6	5.51	5.51	6.34	3.8
1718	5.90	5.45	6.25	6.76		5.85	5.88	7.05	
1724	4.58	3.89	4.05	5.34	7.3	5.41	5.41	6.40	6.4
2145	5.26	4.94	5.64	6.60		5.80	5.83	6.57	
2146	5.10	4.58	5.64	6.14	1.2	5.67	5.67	6.57	1.2
2329	5.03	4.34	4.90	6.34	2.5	6.04	6.04	6.57	2.0
2330	4.13	3.85	4.31	5.70	7.3	5.91	5.91	6.60	1.0
1698	6.83	6.03	6.63	7.50		6.49	6.52	7.05	
1697	4.83	3.88	4.22	5.70	14.8	5.72	5.73	6.44	2.5
2335	6.28	5.26	6.48	6.32		6.53	6.66	6.91	
2337	5.07	4.00	4.33	6.03	33.3	6.03	6.11	6.22	2.7
1937	7.35	6.83	7.11	8.16		6.59	6.73	7.85	
1939	6.19	5.19	5.25	7.05		6.19	6.25	6.96	
1944	7.83	7.24	7.18	8.72		6.99	7.15	8.46	
1946	7.56	7.54	6.73	8.30		6.85	7.08	7.56	

tains calcium carbonate, some difficulties are encountered, since part of the calcium carbonate is brought into solution by the neutral salts used for leaching. In my opinion a sodium chloride solution can be used in this case as sodium chloride dissolves practically the same amount of calcium carbonate in the first liter as in the second. The soil might also, according to Gedroiz, be leached with sodium chloride and the amount of calcium carbonate that has gone into solution be determined by testing the leached soil. It will be advisable to compare these two methods, but I have not yet had time to do so.

At any rate leaching with ammonium chloride gives, in the case of soils containing calcium carbonate, too high results, as can be seen by comparing Kelley's figures (total bases) with mine; for instance B 1944 (with 1.29 per cent  $\text{CaCO}_3$ ); *S*-Kelley 40.9 and *S*-Hissink, 29.5; etc.

*Kelley (total bases and NH<sub>4</sub>-adsorbed).*—The blank was determined by boiling the original soil with sodium hydroxide. Table 4 shows the results of the blank determinations in milligram equivalents per 100 g. soil, together with the *S*-value Kelley, NH<sub>4</sub>-adsorbed uncorrected and corrected and the *S*-value Hissink. As will be seen from Table 4, there is some relation between the blank and the humus content of the soil. In the case of the soils very rich in humus, the blank reaches very high values.

TABLE 4.—*S*-value as determined by Kelley's and Hissink's methods

Soil sample No. B	Per cent of organic matter (Table 1)	Milligram-equivalents			<i>S</i> -value Hissink (Table 2)
		Method Kelley NH <sub>4</sub> -ad- sorbed, blank	<i>S</i> -value Kelley NH <sub>4</sub> -adsorbed		
			Uncorrected	Corrected (Table 2)	
1690	23.1	7.0	29.3	22.3	29.4
1691	22.9	6.7	24.7	18.0	21.2
1718	48.2	12.1	73.9	61.8	76.2
1724	48.0	11.3	52.7	41.4	47.1
2145	45.4	19.2	64.5	45.3	61.1
2146	49.2	19.2	64.5	45.3	60.3
2329	5.0	2.3	6.1	3.8	4.0
2330	5.8	2.6	6.4	3.8	3.7
1698	9.7	5.7	30.8	25.1	30.4
1697	12.6	6.6	24.7	18.1	16.1
2335	1.5	0.3	33.8	33.5	37.4
2337	1.7	0.3	28.0	27.7	29.1
1937	8.5	5.3	39.8	34.5	48.0
1939	8.8	5.7	37.7	32.0	38.5
1944	2.2	2.1	20.2	18.1	29.5
1946	1.8	2.1	21.5	19.4	28.6

As will be seen from Table 2, the corrected *S*-values of Kelley (NH<sub>4</sub>-adsorbed) are a good deal smaller than the *S*-values Kelley-total bases and Hissink (28.9–22.3–29.4), except in the case of two very acid soils with not much humus, viz., B 2330 (3.8–3.8–3.7) and B 1697 (18.4–18.1–16.1). Two factors play a rôle here. In the first place some hydrogen from the soil is replaced by NH<sub>4</sub>; this makes the value NH<sub>4</sub>-adsorbed greater than the value for total bases. The more acid the soils

the more this factor will make itself felt. But I think, this influence will not be great, even in the case of very acid soils.

The second factor, which seems to me to be of much more importance, is that when the  $\text{NH}_4$ -soil is leached with distilled water, a peptisation of the  $\text{NH}_4$ -clay-humus formed takes place, especially in heavy clay and loam soils and in soils rich in humus, in consequence of which some  $\text{NH}_4$ -clay-humus-substance comes into colloidal solution, so that some  $\text{NH}_4$  is leached out with the leaching water. The water leachates of the humus soils were more or less colored, whilst in the leachate of the clay soils there was present per 100 g. dried soil the following quantities of clay substance; B 2335, 1.74; B 2337, 0.48; B 1937, 0.47; B 1939, 0.29; B 1944, 0.34; B 1946, 0.49 g.

In consequence of the fact that some  $\text{NH}_4$  is washed away, the value  $\text{NH}_4$ -adsorbed becomes smaller than the value total-bases. This latter factor makes itself felt especially in the case of soils rich in humus and clay; the less acid the soils are, the greater will be the effect of this factor; B 1718 (pH 5.90), for instance, with  $S\text{-NH}_4$ -adsorbed = 61.8 to  $S$ -Hissink = 76.2 and B 1724 (pH 4.58) with 41.4 to 47.1.

*Bobko and Askinasi.*—These methods were combined with the method of Gedroiz. With the method of Bobko and Askinasi the same remarks are to be made as with the method of Kelley  $\text{NH}_4$ -adsorbed. As a part of the hydrogen of the soil is replaced by the barium of the barium chloride, the  $S$ -values according to Bobko and Askinasi must be somewhat greater than the  $S$ -Hissink values and the more acid the soils are, the more this will be so. On the other hand, some of the barium adsorbed by the soil may be leached out with leaching water. As in the case of  $\text{NH}_4$  this factor will make itself felt especially with heavy clay soils but in soils rich in humus, of a slightly acid to alkaline reaction, it will, however, be much less.

We therefore see a difference when comparing the two  $S$ -values (Hissink and Bobko-Askinasi) of the acid soils and the alkaline soils. For instance: B 1891 (pH 4.22): 29.4 smaller than 32.8; B 1946 (pH 7.56): 28.6 greater than 22.0; B 1718 (pH 5.90): 77.5 - 76.2 = 1.3, and B 1724 (pH 4.58): 55.4 - 47.1 = 8.3.

*Gedroiz.*—To obtain a neutral filtrate by leaching the soil with barium chloride solution the following quantities were required:

B 1690 and B 2330, 3 l.; for 1691 and B 1724, 4 l.; for the remaining 12 samples 2 l. of barium chloride solution. The correction for the barium chloride was determined in the following manner; 450 cc.  $\text{BaCl}_2$  were put into a half liter flask, 3 cc. 0.02  $N$   $\text{NaOH}$  and 10 drops methyl orange were added; after standing overnight, the flask was filled with water to 500 cc., filtered, and 200 cc. of the filtrate was titrated to a certain tint. The soil extract was treated in the same manner and titrated to the same tint. Working in this way, a fairly good agreement was found between duplicate determinations.

The *S*-values according to Gedroiz (see Table 2, second column) are necessarily about as high as those of Bobko and Askinasi. For instance, with B 1690, Bobko and Askinasi find  $S = 32.8$  and Gedroiz =  $4.0 + 29.4$  or 33.4.

In accordance with this, Gedroiz finds a positive titration value in the case of soils, where the *S*-Bobko-Askinasi is greater than the *S*-Hissink and a negative titration value in the case of soils, where the *S*-Bobko-Askinasi is smaller than the *S*-Hissink. Only in case soils have very small titration values according to Gedroiz, there may be some small deviations from this rule. The *S*-values, according to Kelley (total bases), Hissink, Bobko, and Askinasi, and Gedroiz will then be about the same; for instance; B 2335, 2337, and 1939.

Gedroiz says that the degree of saturation (or of unsaturation) of the soil is determined by his method. He supposes that by leaching the soil with barium chloride solution the barium replaces so much hydrogen that the treated soil reaches the *state of saturation*. B 1724, for instance, with  $S = 47.1$ , adsorbs 11.2 me. barium from the  $BaCl_2$  solution and its *S*-value becomes  $47.1 + 11.2 = 58.3$ . Gedroiz expresses the degree of saturation of this soil in the following terms:

$$\frac{47.1}{47 + 11.2} = \frac{47.1}{58.3} = 0.81 \text{ or } 81 \text{ per cent.}$$

If these ideas of Gedroiz are right, then this peat soil B 1728 should be in a wholly saturated state, when containing  $47.1 + 11.2 = 58.3$  me. bases adsorbed.

Now, a method for determining the saturated state of a soil must always give about the same result in the case of a given soil. This means the following: B 1718 and 1724 are the same soils, respectively limed and unlimed, and accordingly their *S*-values differ, being 76.2 and 47.1, respectively. But in the saturated state, both soils should have about the same *S*-values. This is not the case by using the Gedroiz method, which gives 78.4 and 58.3, respectively, the ratio between these two figures being 1.35.

The results, according to Gehring and Hissink, satisfy much better the above mentioned condition and so it is also the case with the *S*-values with a pH of 7 and with the *S* of the potential adsorption, as may be shown by the following data:

	<i>S</i> -values		
	B 1718	B 1724	Ratio
Gedroiz	78.4	58.3	1.35
Gehring	132.1	115.8	1.14
Hissink	272.4	296.0	1.08
pH 7	96.7	107.1	1.11
Potential adsorption	108.6	106.8	1.01

From the above it follows that the Gedroiz reagent only replaces from the soil a part of the hydrogen which is saturated by a base, and not only in the laboratory, but also in natural condition in the field.

*Gehring's method.*—Gehring prescribes the addition of 100 cc. of saturated  $\text{Ca}(\text{OH})_2$  to 25 g. of air-dried soil. Acid soils, rich in humus, such as B 1724, treated in this manner, gave with phenolphthalein no red color. In the case of B 1718, 1724, 2145 and 2146, therefore, 10 and 5 g. respectively air-dried soil and for the other samples 25 and 10 g. respectively were used. As shown in Table 2 the results depend largely on the amount of soil used. The leaching of clay-humus-soils with sodium chloride after the treatment with calcium hydroxide takes a long time, apparently for the following reason. When treated with calcium hydroxide clay-humus- $\text{CaO}$  is formed (adsorption), and is transformed by the leaching with sodium chloride into clay-humus- $\text{Na}_2\text{O}$ , which peptizes a little.

With regard to the methods of Hutchinson-McLennan, Kappen and myself, I will merely remark that the results also depend on the ratio: grams clay-humus-substance to cubic centimeters of solution, whilst the concentration of the solution is also of influence. For the Gehring method this influence of the ratio is shown in Table 2. We could also observe fairly great differences with the Hutchinson method, by using more or less soil or a more or less concentrated bicarbonate solution. So far, we could find no time to study this subject for the Kappen method, but I suppose that the use of more or less soil will be of no great influence here, because Kappen uses a rather strong calcium acetate solution. As will be seen from Volume B (p. 187, Addendum), I have proposed in my own method to always use the same quantity of clay-humus-substance and because I use highly concentrated barium hydroxide solutions, my method is subject to only slight errors on this point.

*Titration with  $\text{CaO}$ .*—The titration with  $\text{CaO}$  took place as described in Volume A, p. 76 (shaken for 72 hours). The same remark about the influence of the proportion of soil to liquid can be made with regard to the results of the titration curves, but no further researches have been made on this subject.

It is recommended that the influence of the ratio: soil to liquid should be further investigated, and also theoretically considered for all the above mentioned methods.

Finally it should be noted that the value: *potential adsorption*, is not subject to this error.

#### CONCLUSIONS

The methods which have been tried, may be divided into two classes. The first class includes the methods for determining the amount of exchangeable bases, that is the value *S*. To this class belong the methods: Kelley (total bases) and Hissink, and, if you like, also the methods Kelley ( $\text{NH}_4$ -adsorbed) and Bobko-Askinasi.

The second class includes the methods for determining the amount of calcium oxide or barium oxide, which is adsorbed by the soil under certain conditions, either from a solution of a neutral salt (Gedroiz barium chloride) or from a solution of a salt of a weak acid (Hutchinson, calcium bicarbonate; Kappen, calcium acetate), or from a solution of calcium hydroxide (Gehring; titration-curves) or barium hydroxide (Hissink).

With the aid of the *S*-value and the amount of calcium oxide or barium oxide adsorbed by the soil, the degree of saturation of the original soil according to each different method can be calculated. Also from the value—potential adsorption—a degree of saturation can be calculated. What I mean is shown in the following table in the case of soil B 1690 (See also Table 2):

TABLE 5.—Comparison of various methods for determining saturation

Method	<i>S</i> (Hissink)		Base adsorbed		Sum	Degree of saturation
Gedroiz	29.4	+	4.0	=	33.4	88
Hutchinson	29.4	+	9.5	=	38.9	76
Kappen	29.4	+	9.9	=	39.3	75
Gehring	29.4	+	11.0	=	40.4	73
Gehring	29.4	+	24.6	=	54.0	54
Hissink	29.4	+	107.5	=	136.9	22
pH=6	29.4	+	5.0	=	34.4	86
pH=6.5	29.4	+	10.8	=	40.2	73
pH=7	29.4	+	18.9	=	48.3	61
potent. ads.	29.4	+	21.2	=	50.6	58

From the above table it is clear that, when referring to the degree of saturation, it is always necessary to mention the method used.

#### DEGREE OF SATURATION ACCORDING TO HISSINK (*V*-VALUE)

My method for determining the degree of saturation ( $V=100 S:T$ ) has been attacked on different grounds. Some are of the opinion that the strong solution of barium hydroxide would partly be transformed into barium carbonate by absorbing carbon dioxide either from the air or from the decomposition of the humus substances. Others have pointed out the possibility of the formation of basic salts.

My answer to these objections is in the first place that all the barium oxide which has been supplied with my method, remains in the soil in an exchangeable form. In the second place I wish to point out the following: Weak acids are saturated at very alkaline reaction; boric acid, for instance, by pH of about 10.5. We may, therefore, expect the weak acids present in the soil to be likewise saturated by a rather alkaline pH. Now I found that the reaction of soil suspensions containing as much barium oxide as is

indicated by my  $T$ - $S$ -value was very alkaline (pH about 10.5). In this very alkaline pH value at  $V=100$  I see a theoretical support of my method.

I was accordingly very pleased to hear in Dr. Truog's and Dr. Kerr's lecture that they found a pH of about 10.5 in the case of wholly saturated permutites also. In this connection I wish to refer to one of my papers in Volume A (p. 198), in which I pointed out that there is a certain relationship between the values pH and  $V$ .

There is a third point which supports my views and that is the results which we get by calculating the equivalent weight of the humus-substance and of the clay-substance. I did this in the following manner: Soil B 1690 contains 23.1 per cent of organic matter, whilst  $T=136.9$ ; that means that 23,100 mg. organic matter are saturated by 136.9 me. bases; the equivalent weight of the organic matter being therefore 23,100:136.9=169. And my various types of humus soils (without clay); sandy humus soils, low peat soils, high peat soils, all give an equivalent weight of the humus substance of about 170.

I may add that I found about the same equivalent weight for the humus-substance in a sample of Dappleriet (practically pure humic acid).

In my Faraday Society paper (2) I calculated the equivalent weights of the clay-substance in some clay soils, the average being 1250. I should be the last person to deny that the two figures (about 170 and 1250) are open to criticism and that they are only provisional.<sup>1</sup>

It has been contended that it was my intention to recommend liming the soil to such an extent that it would reach a degree of saturation (His-sink) = 100. My answer to this objection is that *all* the proposed methods merely determine certain values of the soil, which characterize the soil more or less, and that recommendations for the lime-requirement of the soil can be based only upon the results of these methods in conjunction with the results of field experiments.

That my  $V$ -value characterized the soil in a very good manner, may be shown by the following: the degree of saturation of the original soil B 1690 = 100  $S$ :  $T=100 \times 29.4$ : 136.9 (see Table 2) = 21.5 (see Table 1).

I have calculated the  $V$ -values of this soil after it has adsorbed as much calcium oxide as is indicated by each of the various methods. For instance, the  $V$  of B 1690 in the state of saturation, according to Hutchinson =  $100 \times 38.9$ : 136.9 = 28.4; according to Gehring (highest value) =  $100 \times 54.0$ : 136.9 = 39.4; with a pH of 7,  $V=100 \times 48.3$ : 136.9 = 35.3 and

<sup>1</sup> Although these values for the equivalent weight are only provisional, they do show very clearly that the humus-substance has a far greater power of base-adsorption than the clay-substance. This follows also from my  $K$ -values of the humus substance and the clay-substance. I found in the Dutch Soils which were in a practically well saturated state, under the natural climatic conditions in Holland, that 100 g. clay (I+II) contain about 1.1 g. CaO and 100 g. humus, about 5.0 g. CaO.



according to the potential adsorption =  $100 \times 50.6 : 136.9 = 36.9$ . These *V*-values for all the 16 soils are shown in Table 6. From these results we can draw the following conclusions:

A. *Humus Soils* (B 1690–B 2330).—First let us consider the first eight humus soils. It will then be seen that the 8 *V*-values according to Hutchinson, Kappen, with pH 7 and with the potential adsorption, agree fairly closely, so that average *V*-values may be calculated for these four columns. The *V*-values, according to Gehring, however, differ too much to enable one to calculate an average *V*-value.

TABLE 6.—*V*-values as determined by various methods  
(*V*, calculated with *T*-Hissink)

No. B	Original soil	Hutchinson	Kappen	With pH 7	Potential adsorption	Gehring (highest value)
1690	21.5	28.4	28.7	35.3	36.9	39.4
91	14.9	26.7	26.9	37.5	36.8	37.2
1718	28.0	31.2	31.4	35.5	39.9	48.5
24	15.9	25.2	25.0	36.2	36.1	39.1
2145	25.7	30.7	31.0	36.9	39.9	52.8
46	23.4	30.5	30.8	37.2	40.7	54.8
2329	11.9	26.4	25.2	36.8	40.4	77.4
30	9.7	27.3	25.7	39.9	41.2	79.5
Average humus soils		28.3	28.1	36.9	39.9	
1698	34.9	35.0	36.9	35.8	48.9	67.1
97	16.5	27.4	26.8	38.5	52.0	49.7
2335	50.9	52.9	52.8	52.8	61.2	69.1
37	41.9	51.7	48.8	42.0	64.4	68.0
1937	48.3		49.6		50.4	62.5
39	40.6	43.5	44.3	46.8	55.4	70.0
1944	53.2		54.3		55.9	60.5
46	53.1		54.4		66.1	64.6

From this result I may draw the following conclusions: (1). For the tested types of humus soils, my *V*-value possesses a certain general significance and characterizes these types of humus soils very well; (2). The latter conclusions refer also to the results of the four methods: Hutchinson, Kappen, pH 7, potential adsorption. Judging from my results this latter statement cannot be made with regard to the Gehring methods. Further experiments, especially with regard to the proportion: soil (clay-humus-substance): CaO-solution may bring results that agree more closely with one another.

B. *Mineral Soils*.—There are only four real mineral soils, with practically no humus, namely the clay soils 1944/46 and the loamy soil 2335/37. The *V*-values according to Hutchinson and Kappen for these soils are

about 50 and 54; with pH 7 about 52 and 53; according to the potential adsorption about 56 and 64, and according to Gehring about 60 and 70.

These  $V$ -values are higher than the corresponding values of the humus soils. The result of this will be that for the four soils 1698/97 and 1937/39 with a fair amount of humus the corresponding  $V$ -values are between those of the humus soils and the mineral soils.

For the present I will confine myself to these few observations. More mineral soils have to be examined, before we can draw other conclusions with regard to these soils.

#### THE LIME-REQUIREMENT OF THE SOIL

I repeat that all of the proposed methods merely determine certain values of the soil, which characterize the soil more or less.

How far recommendations for the lime-requirement of the soil can be based upon the results of these methods, can be determined only with the aid of field experiments. As it was not my intention to treat these fertilization questions in my lecture, I will confine myself to the following remarks on this subject.

The question as to whether a soil must be limed is either a question of improving the structure of the soil (heavy clay soils) or relates to the acidity of the soil.

Heavy clay soils can have a slightly alkaline reaction, but nevertheless they may be in great need of lime for the improvement of their structure. Neither the method of Hutchinson nor that of Kappen, can tell us anything about the lime-requirement of these soils. The results of Gehring's method and of my own method, and also the potential adsorption can give us some indication of the necessary amount of lime of these heavy soils.

In Holland it is the custom to give these heavy clay soils, poor in humus, about 10,000 kg. CaO per ha. and somewhat less CaO for less heavy soils. From experience we know that under the Dutch climatic conditions, we must repeat this on heavy clay soils about every 12 or 14 years.

As for the other soils (sandy soils, sandy humus soils, humus soils) the results of all the proposed methods can be used for determining the lime-requirement of a given soil (and a given crop, under given climatic conditions), when the lime-requirement of this soil type (for the given crop, etc.) has previously been fixed with the aid of experimental fields. I will try to make my meaning clear.

Let us suppose that for a given humus soil (and a given crop under certain climatic conditions), the Hutchinson-Kappen methods give a fairly good indication of the lime-requirement of this soil. This means that the degree of saturation of this given soil (the  $V$ -value according to Hissink) must be brought up to about 28 (see Table 6, average humus soils). The lime which must be given per 100 g. of soil can then be calculated further from the  $S$ - and  $T$ -values of the original soil.

It may be said that the Hutchinson-Kappen methods are in any case simpler than the determination of the *S*- and *T*-values. This doubtless is the case, but the result of my researches, which are that the *V*-values according to Hutchinson and Kappen of the light tested humus soils are about the same (average 28.3, see Table 6), tends to give a wider scope to Hutchinson's and Kappen's results. It leads to the supposition that the results for one of the tested types of humus soils can be applied to the other types.

In this connection it is also important to state which pH the soil reaches, by absorbing so much calcium oxide as is found by the Hutchinson-Kappen methods. This pH can be fixed by the aid of the results of the titration curves (see Table 2).<sup>1</sup>

TABLE 7.—Comparison of Hutchinson's and Kappen's method on acid soil

No. B	V (Hissink)		
	Hutchinson	Kappen	pH about
1690	28.4	28.7	6.5
91	26.7	26.9	6.5
1718	31.2	31.4	6.5
24	25.2	25.0	6.5
2145	30.7	31.0	6-6.5
46	30.5	30.8	6-6.5
2329	26.4	25.2	6.5
30	27.3	25.7	6.5
1698	35.0	36.9	6.5
97	27.4	26.8	6-6.5
2335	52.9	52.8	6.5
37	51.7	48.8	6.5
1937		49.6	
39	43.5	44.3	6-6.5
1944		54.3	
46		54.4	

The above Table 7 shows that by a treatment according to Hutchinson and Kappen all the acid soils are brought up to a pH of about 6.5. In relation with the results of Table 5 we can also say that when saturating the humus soils to a degree of saturation (according to Hissink) = 28, the pH = 6.5. If, therefore, it has been established for a type of soil that the Hutchinson-Kappen method gives a good indication of the lime-requirement of this soil (for a given crop under certain climatic conditions), it can be further determined by a simple pH determination whether the soil is already in the required condition. So long as its pH lies below about

<sup>1</sup> The pH which the soil reaches, according to Gehring, can be calculated in the same manner. As is known, by a degree of saturation (according to Hissink) = 100, the pH is about 10.5.

6 to 6.5, it is advisable to lime the soil. Of course the simple pH determination does not give any indication of the amount of calcium oxide which is necessary; this amount depends, amongst other things, on the humus content of the soil. Yet the determination of the pH before and after liming the soil is useful as is shown by the following consideration.

As I have already stated in my paper in Volume A: "What happens to the lime, when soil is limed," the object of liming the soil is to increase the amount of calcium oxide adsorbed by the clay-humus-substance. When liming the soil, this purpose is only partly accomplished; only a part of the given lime is adsorbed by the clay-humus-substance (see Volume A, Table E, p. 185). When liming, therefore, with the amount of lime found according to the Hutchinson-Kappen methods, then the pH 6.5 will generally not be reached and the pH determination enables us to state in how far a given amount of lime has been adsorbed by the soil. When this is not the case, we can later add more lime.

#### POTENTIAL ADSORPTION

Finally, I wish to point out the significance of the value: potential adsorption. The potential adsorption is the amount of CaO in grams that the clay-humus-substance of 100 g. of dried soil must adsorb, in exchangeable form, in order that there are contained 5 g. of CaO per 100 g. of humus and 1.1 g. CaO per 100 g. clay. As can be deduced from the results of the titration curves (see Table 2), the reaction of a soil in this state of saturation [ $K(\text{humus}) = 5.0$  and  $K(\text{clay}) = 1.1$ ] is about neutral to slightly alkaline.

For the clay soils the potential adsorption gives some indication of the amount of lime which should be given. So, for instance, for 1939 this value = 14.1 me. (see Table 2); which means that per 100 g. of soil the clay-(humus)-substance of the soil must adsorb  $14.1 \times 28 = 394.8$  mg. CaO, or per ha. (3,000,000 kg.) 11,848 kg. CaO. For 1946 is calculated per 100 g. of soil  $\times 3.828 = 106.4$  mg. CaO, or per ha. 3192 kg. CaO. This latter soil is therefore to be limed with at least 3192 kg. CaO, but while the lime, at least temporarily, remains in the soil partly in the form of  $\text{CaCO}_3$ , it is advisable to add more and, in this case of heavy clay soils, there is no objection to doing this.

With regard to the humus soils, we must be more careful with liming. Assuming that the humus soils must be brought to the saturation state according to Hutchinson or Kappen, it is necessary to lime with  $(28.2:39.9) \times$  the amount of the potential adsorption of these soils.

#### FURTHER RESEARCHES

The main further researches are:

1. Comparison of the methods Gedroiz and Hissink for determining the values  $S$  in the case of soils containing calcium carbonate.

2. Influence of the blank with Kelley's method ( $\text{NH}_4$ -adsorbed) in the case of humus soils.

3. Influence of the ratio soil: solution of and the concentration of the solution with the methods of Hutchinson, Kappen, Gehring, and Hissink.

4. Comparison of the results of laboratory methods for the determination of the lime requirement of soils with the results of field experiments of several years' duration. For the plan of these field experiments, see Dr. Christensen's proposals, Volume B, p. 81.

These remarks, together with what has been published in Volumes A and B, may serve as an introduction to a general discussion on base exchange and soil adsorption.

I only wish to point out that in discussing the matter we must clearly distinguish between facts and theories. And although we need theories, we must quite realize that they are only makeshifts which come and are doomed to pass away. Theories are only intended to give us an idea of the present state of our knowledge and a good theory should lead us as soon as possible to the domain where it does not apply without modification. We must try to bring our researches right up to this frontier. Only then can there be progress in our science.

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