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> BIGLICH INSTITUUT VCC BODEMVRUCHTBAARHL GRONINGEN

A STUDY OF THE ADSORPTION COMPLEX OF MINERAL 9 SOILS

D. J. HISSINK, JAC. VAN DER SPEK, and S. B. HOOGHOUDT (Institute of Soil Science, Groningen, Holland)

1. Object of the investigation. The investigation was instituted to study the nature of the adsorbing capacity for bases and water in different types of mineral soils.

2. Mechanical composition of the soils tested. The following four Dutch soils were employed.

			Particles smaller than			
Type of soil	CaCOa	Humus (C x 1·7)	16µ (clay-fraction)	16-2000µ (sand-fraction)		
Heavy marine alluvial clay soil	0	3.7	65-4	30-9		
Heavy river alluvial clay soil	0	$2 \cdot 3$. 90-9	6.8		
Heavy loam soil*	0	1.4	81.6	17.0		
Boulder clay	0	0.2	23.5	76.3		

3. Preparation of the fractions. The particles of the above soils smaller than 2μ (fraction a), $2-8\mu$ (fraction b), $8-16\mu$ (fraction c) were obtained by treating the soils according to the International method for the mechanical analysis $(H_2O_2 - HCl - NH_4OH + NaOH)$ A and decanting with Atterberg cylinders (fractions a: 10 cm., 8 hours;fraction b: 10 cm., 30 min.; fraction c: 10 cm., 7.5 min.). The fraction of 16-43 μ (fraction d) was obtained with the aid of the Ro-Tap Testing Sieve Shaker (Tyler-system). The aqueous suspensions of these fractions were electrodialysed until all the bases were removed (the liquid from the cathode-chamber being no longer coloured by phenolphtalein). To prevent decomposition of the alumino-silicate complex it is absolutely necessary that the suspension to be dialysed should not contain any humic matter. During dialysis, at most 0.2% SiO, and 0.02% Al₂O₈ were removed, while during the preliminary treatment by boiling with HCl at most 0.9% SiO₂, 1.2% Al₂O₃ and 0.15% Fe₂O₃ were dissolved, these being likewise removed.

4. Methods of examination of the fractions. Determinations were made in the first place of the chemical composition, the adsorption capacity for bases and the acidity of the fractions. A total analysis of the fractions was made by fusing with sodium carbonate, whilst van Bemmelen's weathering silicate A (boiling with 25% HCl and subsequent treatment with NaOH) and van Bemmelen's weathering silicate B (boiling the residue of A with H_2SO_4 and subsequent treatment with

* In all probability this soil is not loam, but a river or stream deposit.

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Heavy marine alluvial clay soil	0	3.7	65-4	30.9		
Heavy river alluvial clay soil	0	2.3	90-9	6· 8		
Heavy loam soil*	0	14	81·6	17.0		
Boulder clay	0	0.2	23.5	76 ·3		

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NaOH) were also determined. The adsorption capacity for bases was determined by the baryta method (see: Base Exchange in Soils. A general discussion held by the Faraday Society, December, 1924. Transactions of the Faraday Society, Volume XX, page 556, etc.). This method determines the T-S value; but since the fractions have been quite freed from exchangeable bases by means of electrodialysis (S=0), T-S is equal to T.

5. Some results of the investigation obtained up to the present. The marine clay soil contains per 100 g soil (105°C.) 42.0 g of the fraction a; in 100 g of this fraction are found 74.0 g weathering silicate A, so that from 100 g soil, the fraction a yields $42.0 \times 74.0 \div 100 = 31.1$ g weathering silicate A. The 4 fractions (a+b+c+d) contain -per 100 g soil-31.1+1.9+1.0+1.6=35.6 g silicate A; that is per 100 g silicate A, respectively 87.4+5.3+2.8+4.5=100 (see Table I).

Soil Frac-		Composition of silicate A. mol. ratio Al ₂ O ₃ x SiO ₂ y H ₂ O		% frac- tion per 100 g soil	Weathering silicate A :			T-value in milligram- equivalents (mE) ;		
sample	x=	y=	(105°C)	per 100 g fraction	per 100 g soii	total= 100	per 100 g fraction	per 100 g soil	total= 100	
Marine Clay soil	a b c d	4·11 2 84 2·72 2·04	2.24 2.30 1.98 1.51	$ \begin{array}{r} 42 \ 0 \\ 11 \cdot 7 \\ 11 \cdot 7 \\ 26 \ 6 \end{array} $	74 0 16 2 8 8 6 0	81·1 1·9 1·0 1·6	$87.4 \\ 5.3 \\ 2.8 \\ 4.5$	$100 \\ 16 \\ 9 \\ 4.5$	42.00 1:87 1.05 1.20	$91.1 \\ 4.0 \\ 2.3 \\ 2.6 \\ 2.6$
River clay soil	a b c d	2·96 2·42 2·50 2·56	$2 00 \\ 1 85 \\ 2 00 \\ 2 90$	67·9 19·0 4·0 4·1	$ \begin{array}{c} 68.8\\ 18.8\\ 14.1\\ 25.4 \end{array} $	46 7 3.6 0 6 1.0	$90.0 \\ 6.9 \\ 1.2 \\ 1.9$	88 25 15 30	59.75 4.75 0 52 1.23	90'2 7'2 0'8 1'8
Loam soil	a b c d	3.32 2.09 1.83 2.03	2.01 2.00 2.14 1.51	$\begin{array}{c} 64.7 \\ 14.5 \\ 2.4 \\ 3.5 \end{array}$	70 8 19·7 10·8 4·8	45·8 2·9 0·3 0·2	93·1 5·9 0·6 0·4	87·5 22 7 2·5	56.61 3.19 0.17 0.09	94 3 5·3 0 3 0·1
Boulder clay	a b c d	3·51 2·44 2·24 1·70	1.92 1.93 1.80 0.87	16.7 4.7 2.0 7.9	67·2 14·4 7·4 4·0	11·22 0·68 0·15 0·32	90 7 5·5 1·2 2·6	83 13 75 4	13.86 0.61 0.15 0.32	$92.8 \\ 4.1 \\ 1.0 \\ 2.1$

TABLE I

Table I gives the molecular ratio Al_2O_3 , x SiO₂, y H₂O for the weathering silicate A and the total binding capacity (T-value) expressed in mE. baryta per 100 g fraction. The latter is recalculated per 100 g soil and also for the total=100.

6. Some remarks on the results obtained. The figures of Table I show that the fractions a consist largely of silicate A (74.0% - 68.8% - 70.8% - 67.2%), and that they adsorb the highest quantities of baryta (100 - 88 - 87.5 - 83). The coarser fractions (b, c, d) contain much less of this silicate, the content decreasing with the size of grain (with one exception), whilst at the same time there is a decrease of the T-value. There is a striking relation between the columns 8 (silicate A total per 100) and 11 (T-value total per 100) of Table I. From this it may be concluded that—in the case of the 4 soils—the weathering silicate A dominates the adsorption capacity. It may be remarked here that we found that kaolin and quartz particles smaller than 2μ , purified by means of electrodialysis, have a comparatively slight adsorption capacity (T-value 14 mE, and 9 mE respectively). This proves that more than the mere dimensions of the particles are involved in the adsorption-phenomena; a soil, for instance, with a high content of fine quartz powder will have a relatively low T-value. We confine ourselves here to noting these great differences in T-values between the clay fractions of the 4 soils (fractions *a*, particles smaller than 2μ) and kaolin and quartz particles smaller than 2μ ; it will have to be determined by further investigation whether these differences are to be ascribed to differences in chemical composition or to differences in structure (internal and external surface), or perhaps to both.

Assuming that the bulk of the baryta is adsorbed by the silicate A, it is possible to calculate—at any rate approximately—the T-value per gram silicate A; for instance for fraction a of the first soil: 100/ $74\cdot0=1\cdot35$ mE. These quantities are for the fractions a of the four soils: $1\cdot35-1\cdot28-1\cdot24-1\cdot24$, respectively, and for the four fractions of the marine clay soil $1\cdot35-0\cdot99-1\cdot02-0\cdot75$ mE, resp. It is not impossible that these differences are, at least partly, connected with differences in chemical composition (molecules SiO₂ per 1 Al₂O₃; see Table I, column 3) and perhaps also in structure.

The weathering silicate A of the fraction a probably consists of a magnesium-potassium-aluminium-silicate. The fractions b, c, and d are found to consist largely of quartz.

The acidity of the fractions was determined with the glass electrode and with the quinhydrone method in suspensions of 5 g substance with 12.5 g freshly boiled distilled water. Fraction a of all 4 soils is very acid (pH from 2.6-3.7). Ultrafiltrates of aqueous suspensions of these fractions were found to be *practically neutral* (pH approx. 6.5) with one exception (pH ultrafiltrate boulder clay=3.4). The addition of slight quantities of the fractions a to their neutral ultrafiltrates was found considerably to increase the acidity of these; this points to the acid reaction of the suspension not being caused by the watery solution (ultrafiltrate), but by the particles of fraction a.

7. Further investigation. Whether and to what extent the silicate B and the residue, after removal of the silicate A and B, possess any adsorbing capacity, remains to be investigated. It will further be necessary to test a few coarser fractions than 43μ for their T-value and content of fixed water. It will be determined whether the fractions contain free silicic acid, aluminium oxide, and iron oxide. An attempt will be made to separate the fraction smaller than 2μ still further, and to test the fractions thus obtained in the same way as described here. The determination of the external surfaces of the particles of the fraction smaller than 2μ is also in progress. Finally, it is intended to determine the physical properties (plasticity, etc.) of the various fractions, and to make tests with mixtures of these in order, amongst other things, to fix the limit between sand and clay.