

Dit proefschrift met stellingen van
RUDOLF HUBERT JOHAN ROBORGH
landbouwkundig ingenieur, geboren te
's-Hertogenbosch den 28sten September 1908, is
goedgekeurd door den promotor: Ir J. HUDIG,
hoogleraar in de Scheikunde ende Bemestingsleer.

De Rector-Magnificus der Landbouwhoogeschool
DR D. L. BAKKER.

Wageningen, 25 Januari 1935.

A STUDY ON THE NATURE OF CLAY

PROEFSCHRIFT

TER VERKRIJGING VAN DEN GRAAD VAN
DOCTOR IN DE LANDBOUWKUNDE
OP GEZAG VAN DEN RECTOR-MAGNIFICUS
DR D. L. BAKKER, HOOGLEERAAR IN DE VEE-
TEELTWETENSCHAP, TE VERDEDIGEN VOOR
EEN DAARTOE BENOEMDE COMMISSIE UIT
DEN SENAAAT DER LANDBOUWHOOGESCHOOL
OP VRIJDAG 1 MAART 1935 TE DRIE UUR DOOR

R. H. J. ROBORGH



H. VEENMAN & ZONEN — WAGENINGEN — 1935

STELLINGEN

I

Uit theoretische en praktische overwegingen is het gewenscht de gebruikelijke bepaling van de „totale adsorptie capaciteit” (T) van de grond, volgens HISSINK, te vervangen door de bepaling van de adsorptie capaciteit met een bufferoplossing van pH 6.5.

HISSINK, Versl. Landb.k. Onderz. R. L. P., 30, 115 (1925);
NIKOLSKY, Pedology, 2, 180 (1934).

II

Voor de bepaling van de colloïdale bodembestanddeelen is de methode VAN BEMMELEN-HISSINK onbruikbaar.

Verh. IIten Komm. d. Intern. Bod. k. Ges. Budapest, A, 6 (1929).

III

De methode NEUBAUER geeft geen uitkomst omtrent de kali-behoefte van de grond, daar zij geen rekening houdt met de ionen-bezetting van het adsorptie-complex.

NEUBAUER, Handb. d. Pfl. Ernähr. u. Düng. Lehre, Honcamp, 1, 882 (1931).

IV

De resultaten van adsorptie-proeven met permutieten en zeolieten zijn niet algemeen geldend voor de adsorptie-verschijnselen aan klei.

V

De adsorptie-verschijnselen in de Nederlandsche kleigronden worden voornamelijk veroorzaakt door de verweeringsproducten der in de kleifractie aanwezige mineralen.

VI

Het is principieel onjuist aan een stof een van het oplosmiddel onafhankelijke „specifieke” adsorptie-affiniteit toe te kennen.

LUNDELIUS, Koll. Ztschr. 26, 145 (1920).
HEINE und POLANYI, Ztschr. f. physik. Chem. 132, 384 (1928).
BERGER, Rec. d. Trav. Chim. 50, 377 (1931).

VII

Uit de experimenten van LANGENBECK en BALTES kan niet worden afgeleid, dat hun esterase-model: benzoyl-methanol, inderdaad katalytisch werkt bij de verzeeping van methyl-butyraat.

LANGENBECK und BALTES, Ber. 67, 387 (1934).

VIII

De vetbepaling, in het bijzonder in dierlijke producten, behoort — in tegenstelling met de meening van de Redactie van de Chemiker Zeitung — te worden uitgevoerd volgens de gewijzigde methode Berntrop.

Chem. Zeit. 57, 363 (1933).

IX

Verbetering van de bodemstructuur is de belangrijkste maatregel ter bestrijding van de Tarwehalmdooder (*Ophiobolus graminis* Sacc.).

X

De bloemkleur heeft voor de voedselzoekende honingbij (*Apis mellifica*) geen primaire beteekenis; zij kan slechts dienen als herkenningsteeken.

XI

Het niet-bloeien van „korte-dag-planten” (GARNER en ALLARD), in noordelijke streken, wordt niet veroorzaakt door te lange dagen, maar door te korte nachten.

XII

De natuurlijke dag-en-nacht afwisseling is voor de levensverrichtingen van de plant niet noodzakelijk.

XIII

De discontinue pH-bepaling van bietsuikersappen met behulp van de electrode van VAN DAM, is in de suikerfabricage te prefereren boven de continue pH-bepaling met de H_2 -electrode.

VAN OORT, Automatische pH-bepaling in de suikerfabricage (1930).

Bij de voleinding van mijn studie aan de Landbouwhoogeschool met de publicatie van dit werkstuk, biedt zich de welkome gelegenheid mijn dank te betuigen aan allen, die tot mijn wetenschappelijke vorming hebben bijgedragen.

Meer in het bijzonder richt ik mij daarbij tot U, hooggeleerde HUDIG, hooggeachte promotor, die — mede door Uwe hoge interesse in dit onderzoek — mij Uwe wetenschappelijke steun, in ruime mate, hebt willen geven. Uwe critische medewerking, die ik gedurende het geheele onderzoek mocht ondervinden, wordt door mij op hoogen prijs gesteld.

Hooggeleerde ABERSON: Gij waart het, die mij de eerste beginnelen der Bodemkunde hebt bijgebracht waaruit zich mijne belangstelling voor deze wetenschap ontwikkelde; Uwe colleges zullen mij steeds in aangename herinnering blijven.

Hooggeleerde EDELMAN: De geanimeerde gedachtenwisseling waartoe U mij herhaaldelijk in de gelegenheid stelde was mij bij de samenstelling van dit proefschrift van hooge waarde. Ik ben U ook grooten dank verschuldigd voor Uwe bijdrage tot dit onderzoek betreffende de mineralogische analyse van de zandfracties van de door mij onderzochte gronden.

Het was mij een aangename taak, hooggeleerde OLIVIER, als college-assistent op Uw laboratorium werkzaam te zijn, gedurende de jaren, die ik voor de bewerking van mijn dissertatie behoefde. U, en ook U, zeergeleerde BERGER, breng ik gaarne dank voor Uwe voortdurende belangstelling voor mijne experimenten.

Hooggeleerde VAN UVEN: Voorzoover mijn wiskunde-kennis tekort schoot waart Gij zoo bereidwillig de oppervlakteberekening van de kleifracties der gronden uit te voeren; ik ben U daar zeer erkentelijk voor.

Groote waardeering heb ik voor Uwe medewerking, collega SCHUFFELEN, die U ten allen tijde beijverde mij Uwe vriendschap-

pelijke assistentie te verleen en met mij medeleefde in de uitslagen van mijne onderzoekingen.

Den Heeren: M. M. H. EVERS, cand. l.i., die de „analoge onderzoekingen aan mineralen” uitvoerde en J. P. PLANJE, cand. l.i., die de analyses volgens de methode Van Bemmelen-Hissink verrichtte, breng ik voor hunne toewijding mijn oprechten dank.

Ten slotte dank ik het personeel van het Landbouwscheikundig Laboratorium voor de betoonde hulpvaardigheid.

I. INTRODUCTION AND PURPOSE

In 1819 GAZZERI discovered that dungwater was decolourised by clay ¹⁾, a fact that afterwards appeared to be of fundamental significance for the knowledge of soil processes.

In 1850, the fixation of chemically defined substances was established by HUXTABLE and by THOMSON and SPENCE ²⁾ and in the following years J. THOMAS WAY ³⁾ published the scientific basis of the exchange-reactions of the soil.

WAY discovered that when clay was treated with a solution of a neutral salt only the cation of the salt was fixed up to a certain quantity, whereas the anion was found again quantitatively in the filtrate of the suspension. Instead of the cations which had disappeared out of the electrolyte-solution, an equivalent quantity of the cations of the clay was yielded to the filtrate.

WAY ascribed this exchange-reaction, which he distinguished from „physical adsorption”, because not the whole of the salt-molecule but only the cation reacted, to the water-containing double-silicates present in the soil. The exchange-reaction was characterized by: little influence of temperature, a quick attainment of equilibrium, and the quantity of the cations of the electrolyte-solution exchanging with those of the clay, being a complicated function of the concentration of the electrolyte-solution: from a more-concentrated solution relatively less was bound than from a more dilute one.

The conclusions of WAY, being opposed to the chemical insights holding good at that time, were called into question by J. VON LIEBIG. He saw the phenomenon as a pure physical surface-

¹⁾ Cited from HEIDEN, Landw. Versuchsstat. 57 (1873).

²⁾ Cited from WIEGNER, Journ. für Landw. Sch., 60, 111 (1912).

³⁾ J. THOMAS WAY, Journ. of the Roy. Soc. of Engl., 11, 313 (1850); 13, 123 (1852); 15, 491 (1854).

attraction. The experiments of WAY however had roused interest for this important soil-property and a great number of investigators coming after him e.g.: BRUSTLEIN, PETERS, HENNEBERG and STOHMANN, HEIDEN ¹⁾ and MULDER ²⁾ affirmed and extended his experiments.

About 1880 J. M. VAN BEMMELEN succeeded by means of the newer theories of chemistry and colloid-chemistry in locating and explaining the exchange-reactions of the soil ³⁾. He ascribed the exchange-reaction to amorphous complexes of alumina-(iron-) and silica with varying quantities of water and bases, which were supposed to be present in the soil in a colloidal state. These so-called „adsorption-compounds according to VAN BEMMELEN” are therefore not to be understood as constant chemical compounds, but as mixtures of aluminium-hydroxide and iron-hydroxide with silica. They originate in the soil by mutual adsorption of the components in the colloidal state and are capable of absorbing crystalloids which in their turn can be chemically substituted by others.

With regard to the equivalent ion-exchange these soil-particles resemble the crystalline zeolites, water-containing double-silicates; so, in analogy with these compounds, the Al-Fe-Si-complex of the soil is wrongly called: the „zeolitic” soil-complex. The structure of these zeolites however differs greatly from that of the soil-colloids ⁴⁾ with the result that the exchange-reaction also differs essentially from that of clay.

The exchange-reaction was studied especially on so-called permutites which according to WIEGNER ⁵⁾, STREMME ⁶⁾, MATTSON ⁷⁾ etc. are to be looked on as artificial mixed-gels of silica, alumina, bases and water in variable proportions ⁸⁾. From the experiments of WIEGNER the exchange-reaction in permutites appears to be a

¹⁾ J. M. VAN BEMMELEN, Landw. Versuchsstat. 21, 136 (1878). (Uebersicht der früheren Versuchen).

²⁾ G. J. MULDER, De scheikunde der bouwbare aarde, 2, 47 (1860).

³⁾ J. M. VAN BEMMELEN, Landw. Versuchsstat., 21, 135 (1878); 23, 265 (1879); 35, 69 (1888); 37, 79, 347 (1890).

⁴⁾ N. CERNESCU, Kationenumtausch und Struktur. Diss. Zürich, 83 (1933).

⁵⁾ G. WIEGNER, Boden und Bodenbildung, 39 (1929).

⁶⁾ H. STREMME, Zentr. Blt. f. Min. Geol. u. Paleont., 622, 661 (1908).

⁷⁾ S. MATTSON, Soil Sci., 25, 289 (1929).

⁸⁾ According to R. GANSEN, H. KAPPEN, K. UTESCHER, etc. these compounds are to be looked on as „Aluminat-Silikate”, i.e. as chemical compounds. The exchange-reaction should be a real chemical-one. G. WIEGNER however has sufficiently refuted this conception. The controversy between these opponents may be found in: Zentr. Blt. f. Min. Geol. u. Paleont., 699 (1913), 262 (1914), 273 (1914), 299 (1914).

ion-reaction which takes place under chemical and physical influences ¹⁾).

It is possible to explain the reaction as a physical phenomenon in so far that it corresponds to an adsorption-reaction according to FREUNDLICH, i.e. there is a low negative temperature-coefficient, a quick attainment of equilibrium and also with regard to the quantitative concentration-proportions. On the other hand the equivalence of the exchange however indicates an analogy with the chemical reaction. ²⁾

WIEGNER ³⁾ is of opinion that the adsorption-reactions in the soil are caused by gels which resemble these permutites.

GEDROIZ ⁴⁾ also considers the exchange-reaction as a physico-chemical reaction because it is made possible on the one hand by the existence of the surface-energy, while on the other hand the cations of the soil-solution are attracted by the surfaces of the negatively charged colloidal particles of the soil, after which the chemical reaction occurs because these cations react by exchange with those of the existing surface-molecules of the clay. With regard to the colloidal part of the soil he develops the idea that it consists of two compounds different in origin and structure: „Das Ergebnis der Einwirkung atmosphärischer und biologischer Agenzien auf die in Boden vorhandenen Mineralien sind einerseits einfache mineralische Verbindungen in kolloider Zerteilung, anderseits zugleich kolloide Verwitterungsreste verwickelter Zusammensetzung.”

Besides this complex-formation by decomposition he also expects a synthesis out of the free colloids SiO_2 , Al_2O_3 and Fe_2O_3 , originating in the weathering by mutual coagulation. According to him, however, this new complex-formation should not be understood to be a simple gel-mixture, but an adsorption-compound ⁵⁾).

¹⁾ The studies on permutites appear to be of a great importance, especially with regard to the knowledge of the mechanism of ion-exchange.

²⁾ G. WIEGNER, Journ. f. Ldwsch., 60, 221, (1922). WIEGNER has the following idea of the reaction: „Dasz eine Adsorption von Ionen und zwar von Kationen vorliegt, die aus elektrostatischen Ursachen unter Verdrängung einer Menge äquivalenter Kationen aus dem Gel der sogenannten Aluminium-Kieselsäure verläuft.”

³⁾ G. WIEGNER, Boden und Bodenbildung, 42 (1929), „Die praktische Wirkung des s.g. Basenaustausches ist die, dasz die mit Basen gesättigten gemengten Gele von Aluminiumhydroxid und Kieselsäure, die einen groszen Teil unserer Tone bilden, NH_4 -kation und K-kation fester als Na- und Ca-ion halten.

⁴⁾ K. K. GEDROIZ, Die Lehre vom Adsorptionsvermögen der Böden, 405 etc. (1931).

⁵⁾ K. K. GEDROIZ, loc. cit. says: „Die so entstehenden Neubildungen sind aber nicht als einfaches Gelgemisch anzusehen, denn hier, wie bei anderen Kolloidreaktionen, liegt im Grunde eine chemische Reaktion vor, blosz da sie nur zwischen den Molekeln an der Oberfläche der Kolloidteilchen stattfindet und ausserdem lediglich an den Berührungsstellen so können hier keine stöchiometrische Verhältnisse für die gesamte Teilchenmasse bestehen.”

Whereas, according to WIEGNER, STREMMER, MATTSON, GEDROIZ and also HISSINK ¹⁾, STEBUTT ²⁾ the compounds causing the exchange-reactions in the soil are essentially identical with the „absorption-compounds according to VAN BEMMELEN“, GEDROIZ sees the necessity of the existence of more complicated, colloidal weathering-residues being formed because at the time of the weathering, not only final products SiO_2 , Al_2O_3 and Fe_2O_3 , but also complexes of silicate-molecules have been dissociated from the surfaces of the minerals. ³⁾

Finally it is accepted by a number of American investigators on the basis of röntgenographic analysis that the clay-fraction consists principally of „crystalline compounds“. ROSS ⁴⁾, HENDRICKS and FRY ⁵⁾, KELLEY, DORE and BROWN ⁶⁾ therefore suggest the existence of special „clay-minerals“ such as montmorillonite, bentonite, halloysite and beidellite, which must be of secondary origin, because they are not present in the crystalline rocks. According to their opinions these minerals are frequently found in the clay-fractions of different soils and ROBINSON ⁷⁾ therefore considers that the valid hypothesis of the composition of the clay out of „absorption-compounds according to VAN BEMMELEN“ should make place for the conception of the adsorption-complex being composed of some minerals of a definite crystalline structure.

SCHLUNZ ⁸⁾, who submitted the different fractions $> 1 \mu$ of a diluvial and of a tertiary clay to a mineralogical- and chemical-analysis, found going in the direction of the smaller fractions, a decrease in the contents of quartz and feldspath, on the contrary an increase in muscovite. From the diluvial clay 65 % and from the tertiary only 26 % was $> 1 \mu$. From the chemical composition of the fraction $< 1 \mu$ he deduced that the mineralogical compo-

¹⁾ D. J. HISSINK, Landw. Versuchsstat., 81, 377 (1913).

²⁾ A. STEBUTT, Lehrb. der allgem. Bod. k, 211 (1930).

³⁾ K. K. GEDROIZ, Die Lehre vom Adsorptionsvermögen der Böden 403 (1931): „Es besteht kein Grund die Möglichkeit auszuschließen das Teilchen kolloider Großenordnung bei der Verwitterung der Alumino-Silikate, namentlich aus den Verwitterungsprodukten entstehen: Irgend ein Mineral das an der Oberfläche der vereinten Wirkung verschiedener Verwitterungsfaktoren ausgesetzt ist, kann einerseits einfaches SiO_2 , Al_2O_3 und Fe_2O_3 , anderseits feine Teilchen verwickelterer Zusammensetzung von seiner Oberfläche abspalten.“

⁴⁾ C. ROSS, Proc. 1st Intern. Congr. Soil Sci., 551 (1928).

⁵⁾ S. HENDRICKS and W. FRY, Soil Sci., 29, 457 (1930).

⁶⁾ P. KELLEY, W. DORE and S. BROWN, Soil Sci., 31, 25 (1931).

⁷⁾ G. W. ROBINSON, Soils, Their Origin, Constitution and Classification, 89 (1932).

⁸⁾ E. SCHLUNZ, Chemie der Erde, 8, 167 (1933).

sition of this fraction probably corresponded to that of the fractions $> 1 \mu$, except that muscovite would be replaced at least partly, by another muscovite-like mineral: in the tertiary clay however, below 1μ , colloids should prevail which could be partly amorphous.

By pedologists, it is generally accepted that the adsorption-phenomena of the soil are practically limited to the clay-fraction.

In the European classification, the soil-parts with a diameter $< 10 \mu$ belong to the clay-fraction ¹⁾, whereas the American scale puts the limit at 2μ .

While contradictory opinions exist as to the structure of the clay-fraction, this fraction is generally taken as a unit with regard to the exchange-reaction: STEBUTT ²⁾ assigns the soil-particles $< 10 \mu$ to the clay-fraction; GEDROIZ ³⁾ calls the sum of the particles with a distinctly expressed exchange capacity: the adsorption-complex. He puts the limit between clay and sand at $0,25 \mu$; according to ROBINSON ⁴⁾ the clay-fraction is identical with the weathering-complex, excepting only those soils that have been formed chiefly under physical influences.

VAN BEMMELEN ⁵⁾ however distinguished in the soil one part which is soluble in HCl and another which is soluble in H₂SO₄, of which, according to him, only the part soluble in HCl accounts

¹⁾ K. K. GEDROIZ, Die Lehre vom Adsorptionsvermögen der Böden, 413 (1929). „Es darf demnach festgestellt werden dasz das Austauschvermögen des Bodens hauptsächlich der Schlammfraktion zukommt, dasz die Bedeutung der übrigen Fraktionen für die physiko-chemische Adsorption sehr klein ist, und dasz in Fraktionen $> 5 \mu$ ein Kationen-Austausch überhaupt fehlt.“

P. PRILLWITZ, De invloed van den Basentoestand van den grond op de ontwikkeling van de Theeplant. Diss. Wageningen, 34 (1932): He found that for volcanic tuff-soils the fractions up to 500μ still showed important adsorption capacities. This proved that these fractions for the greater part consisted of aggregates („pseudo-zand“).

M. ANDERSON, W. FRY, P. GILE, H. MIDDLETON and W. ROBINSON, U. S. Dept. Agr. Bull. 1122 (1922) stated that at the utmost 5% of the total adsorption capacity is caused by parts $> 1 \mu$ (muscovite- and biotite-soils excepted).

²⁾ A. STEBUTT, Lehrb. der Alg. Bod. k., 65, 67 (1930). „Wir wissen dasz es (Ton) Bestandteile $< 10 \mu$ sind. Ton ist eine chemische Neuschöpfung des Bodens. Ton ist das Protoplasma des Bodenorganismus. Die Tonteilchen besitzen folgende für die Bodenbildung wichtige Eigenschaften: Bildsamkeit und Verwitterungsvermögen, Dispersions-, Quellungs-, Adsorptions- und Substitutions-Fähigkeit.“

³⁾ K. K. GEDROIZ, Die Lehre v. Ads. verm. d. B., 411 (1931).

⁴⁾ G. ROBINSON, Soils, etc. pag. 73. „In other words can we assume that the clay-fraction contains all the chemically reactive colloidal inorganic material of the soil and that this is identical with the fraction which has resulted from the chemical weathering of mineral silicates? Whilst we cannot assume the complete identity of these groups, there is probably no great error for ordinary soils in the assumption.“

⁵⁾ J. M. VAN BEMMELEN, Ztschr. f. anorg. Chemie, 42, 287 (1904). „Das sogenannten Adsorptionsvermögen des Bodens kommt denselben (das in verdünnten Säuren löslichen Teil des Verwitterungssilikat) in erster Stelle zu.“

for the exchange-reactions in the soil. Besides MULDER ¹⁾ had said earlier that only the part soluble in HCl was of importance as regards the vegetation. A further differentiation of the clay-fraction into a part soluble in HCl and into a part that is not soluble in HCl appears to be necessary. After that it still remains possible that only a part of the compounds, that are soluble in HCl and which are present in the clay-fraction, is related to the exchange-reaction.

It is namely accepted by GEDROIZ ²⁾, HISSINK ³⁾ VAN DER SPEK ⁴⁾, CERNESCU ⁵⁾, etc. that the exchange-reactions take place at the surfaces of the clay-particles so that a very great percentage of weight of the clay-fraction should not contribute to the adsorption of the soil. From the point of view however that the inorganic adsorption-complex, viz. that part of the clay that is responsible for the exchange-reaction, consists only of permutite-like materials, it is necessary to accept this exchange as a process that is carried out throughout the whole substance.

In permutites as well as in zeolites all cations can be exchanged equivalently, because they all are in direct contact with the surrounding electrolyte-solution. CERNESCU ⁶⁾ expresses himself in the following manner regarding the place which is occupied by the cations in permutites and zeolites: „Die Kationen liegen im Permutit wie in den natürlichen Zeolithen an den Wänden der verschiedenen Poren. In diese Poren können die eintauschenden Kationen eindringen und die Kationen des Permutits umtauschen“. As to the clay-colloids, however, he proves that the exchange-reaction is limited to an exterior surface. This result therefore only could agree with the older view of the adsorption-complex if the surface layer of the clay-particles possessed a permutoid-structure ⁷⁾.

¹⁾ G. MULDER, *De scheikunde der bouwbare aarde*, 4, 366 (1860).

²⁾ K. K. GEDROIZ, *loc. cit.*, 400, 408 (1929).

³⁾ D. HISSINK, *Intern. Mitt. f. Bod. k.*, 12, 81 (1922).

⁴⁾ J. VAN DER SPEK, *Versl. Ldbk. Onderz. R. L. P.*, 27, 162 (1922).

⁵⁾ N. CERNESCU, *Kationenumtausch und Struktur*, 20 (1933).

⁶⁾ N. CERNESCU, *loc. cit.* 20 and 85.

⁷⁾ Formerly WIEGNER was of the opinion that the clay-colloids possessed an enormous interior surface and the exchange-reactions would be carried out on these interior surfaces in the same way as on the exterior surfaces (Cited from R. BRADFIELD, *Journ. of Amer. Soc. of Agron.* 17, 262 (1925)).

However, after the investigations of his pupil CERNESCU, WIEGNER changed his older point of view and agreed with the idea that the exchange-reaction of clays was limited to the surface of the clay-colloids (G. WIEGNER, *IX Congr. Intern. de Quim. Pur. y Aplic.* (1934) Madrid).

See also: P. SZIGETI, *Koll. Beih.*, 38, 100 (1933).

The experiments of BRADFIELD ¹⁾ also give rise to doubt as regards the analogy between clay-fraction and permutite. BRADFIELD examined the clay-fractions ($< 0.1 \mu$) of some Missouri-soils in comparison with an artificial gel of alumina, iron and silica. From the conductometric titration with alkali and the stability-factors for the sol-condition, it can be deduced that the structure of these two substances differs in important respects. When comparing the clay-fraction of the soil with an artificial gel of the same total-analysis in respect of the behaviour towards acids and bases, it appears for instance that the clay-fraction, even when treated with concentrated HCl, is only 40% dissolved, while the synthetic colloid-mixture dissolves completely in dilute acids and bases.

From this experiment it seems probable that many colloidal clays do not consist of a mixture of colloidal oxides but are composed to an important extent of complex alumino-silicates ²⁾.

BOUYOUCOS ³⁾, who compared the heat of reaction of soil-colloids with NaOH and KOH, with that of artificial gel-mixtures similarly treated, also found very different behaviour in these two compounds.

Finally, by X-ray-analysis, the permutites show no X-ray-pattern as contrasted with the soil-colloids ⁴⁾.

Summarizing one gets the impression, that in spite of many investigations, still very divergent opinions prevail as to the structure of the inorganic part of the so-called adsorbing soil-complex. However all of them lead to the conclusion that it consists of a complex of alumina, (iron), and silica, to which is bound a certain quantity of bases and water.

It seems probable that according to the conception of GEDROIZ only part of the clay-fraction possesses a permutite-like structure.

If the adsorption-phenomena in the soil are caused by this permutoid-part, it then follows from the investigations by VAN BEMMELEN, that this part of the clay-fraction is soluble in HCl.

The part of the clay-fractions which is soluble in HCl or its

¹⁾ R. BRADFIELD, Journ. of Amer. Soc. of Agron. 17, 253 (1925).

²⁾ However, it may be possible, that the complex gels used by BRADFIELD differed largely from those which are present in clays: It has been stated by WIEGNER that the way of preparation has a great influence on the structure and exchange capacity of a gel. (Private communication Prof. G. WIEGNER).

³⁾ G. BOUYOUCOS, Soil Sci., 23, 243 (1927).

⁴⁾ W. KELLEY, W. DORE and S. BROWN, loc. cit., pag. 12.

surface should then be the cause of the adsorption-phenomena of the soil, while the non-permutoid-part might consist of possibly modified, crystalline weathered-residues of the original crystalline rocks.

The object of this research is to get an insight by means of HCl-extraction into the composition of that part of the clay-fraction, which is essential for the adsorption-phenomena in the soil, and also into its resistance towards attack with HCl.

The intentions of the experiments which were carried out are as follows:

When a clay-soil is extracted under certain conditions with HCl, the permutoid-parts of the Al-Fe-Si-compounds which are present in the soil will be dissolved completely or partly. The decomposition of these compounds may be controlled by the determination of a comparable adsorption-value, before and after the extraction.

If the conditions of the HCl-extraction are chosen, so that the permutoid-part of the Al-Fe-Si-compounds which are present in the soil is completely dissolved, it might be expected that the exchange capacity of the residue would have disappeared entirely.

The Al-Fe-Si-complex, which is responsible for the adsorption-decrease, may be reconstructed from the contents of Al_2O_3 , Fe_2O_3 and SiO_2 of the HCl-extract.

In this method one has to reckon with the appearance of two complications one of which can be deduced from the researches of VAN BEMMELEN into the composition of the so-called „weathering-complex” while the other is apparent from the criticism his method met with afterwards.

J. M. VAN BEMMELEN ¹⁾ succeeded, by treating the soil with H_2SO_4 , in dissolving the „amorphous colloidal weathering-silicate”. This weathering-silicate consisted of a „weathering-silicate A”, which was soluble in HCl and a „weathering-silicate B” which was soluble in H_2SO_4 . For the first silicate in alluvial clays a SiO_2 : Al_2O_3 ratio of 3 to 5 was characteristic and for the second silicate a SiO_2 : Al_2O_3 ratio of about 2.

The silicate A, which is soluble in HCl, was the cause of almost the total adsorption capacity of the soil, at least when it contained no organic complex, a fact which had been formulated already by

¹⁾ J. M. VAN BEMMELEN, Ztschr. f. anorg. Chemie, 42 (1904).

G. J. MULDER: „De klei als onrein kaolien is voor den plantengroei chemisch zoo indifferent als het zand; het is het in HCl-oplosbare hetwelk actief is bij de vegetatie.” ¹⁾

BRUSTLEIN ²⁾ found that a clay-soil which contained CaCO_3 , after extraction with dilute HCl fixed no NH_4^+ from a NH_4Cl -solution and PETERS ³⁾ also stated that after extraction with HCl, the HCl-residue only fixed a minimum quantity of K^+ from a KCl-solution.

VAN BEMMELEN ⁴⁾ himself concludes in consequence of his experiments with „Erde B” i.e. with the soil boiled with strongly concentrated HCl: „Werden die basischen Silikate in einer Ackererde durch Auskochen mit starker Salzsäure zerstört und die basischen Oxyde durch Auswaschen entfernt, so dass nur die sauren Silikate des Tons, Quartz-körnchen, die abgeschiedene Kieselsäure und Humus-reste zurückbleiben, dann hört ihre Absorption von basischen Oxiden aus den Lösungen der Alkali- und alkalischen Erd-Salze mit starken Säuren fast ganz auf.”

However, it also appeared to be possible to regenerate to a certain value the exchange capacity of the soil-residue which had disappeared after the extraction with HCl. When to „Erde B” of VAN BEMMELEN a salt of a weak acid and a strong base was added, e.g. CaCO_3 and this mixture was treated with KCl-solution, K^+ again disappeared from the solution.

VAN BEMMELEN ascribes this adsorption to the SiO_2 -gel which is present in the HCl-residue and explains the reaction by the fact that in the KCl-solution CaCO_3 goes into solution and the K_2CO_3 which is formed by that reaction is hydrolized into KOH and KHCO_3 . The KOH is then fixed by the SiO_2 , the equilibrium between the ions in the solution is disturbed and K_2CO_3 is again hydrolized. This action is then repeated till equilibrium is reached. VAN BEMMELEN supports this interpretation with the fact that never more than half the quantity of the cations is absorbed: Half of it is found again in the filtrate as KHCO_3 and further because by experiments with pure SiO_2 -gel, this substance appears to be able to bind a variable quantity of bases: as more bases are bound, the compound becomes more unstable, more soluble, and when to one molecule SiO_2 one molecule KOH is added, the SiO_2 -gel is

¹⁾ G. J. MULDER, *De scheikunde der bouwbare aarde*, 4, 366. (1860).

²⁾ BRUSTLEIN, *Ann. de Ch. et de Phys. Sér. III*, 56, 157 (1859) (cited from VAN BEMMELEN).

³⁾ E. PETERS, *Landw. Versuchsstat.*, 2, 145 (1860).

⁴⁾ J. M. VAN BEMMELEN, *Landw. Versuchsstat.*, 23, 296 (1879).

completely dissolved; before that an equilibrium is established: one part of the SiO_2 -gel is dissolved and another is left as an insoluble alkali-silicate.

As the adsorption capacity in these experiments is determined by percolation of the HCl-residue with a $(\text{CH}_3\text{COO-})_2\text{Ca}$ -solution ¹⁾, the value which is found will be too high, owing to the SiO_2 -gel which remains in the HCl-residue after the HCl-extraction.

The influence of the SiO_2 -gel-adsorption on the adsorption-value of the HCl-residue may be ascertained in two ways. The SiO_2 -gel may be dissolved by treatment of the HCl-residue for 5 minutes at 50°C , with NaOH, sp. gr. 1.04, according to VAN BEMMELEN. The exchange capacity of the HCl-NaOH-residue may be determined in the same way as the HCl-residue. Besides the influence of the SiO_2 -gel-adsorption may be limited by determining the adsorption capacity of the HCl-residue of an artificial permutite. This residue consists almost entirely of the SiO_2 -gel, which has been separated in the same way. The adsorption capacity per unit-weight SiO_2 -gel may then be calculated and it thus becomes possible to define the correction for the SiO_2 -gel which is present in the HCl-residue of the soil.

A second complication is caused by the fact that besides the amorphous colloidal alumina-iron-silica-compounds in the soil crystalline mineral-fragments are also found in colloidal state, such as: muscovite, biotite, feldspath, augite and a few rarer minerals; and it is for this reason that by the extraction of the soil with HCl not only the alumina-iron-silica-compounds, which are the cause of the exchange-reaction are dissolved: these minerals are also partly or completely dissolved so that a reconstruction of the amorphous colloidal weathering-silicate from the composition of the HCl-extract becomes impossible. ²⁾

This was also the most principal objection that was raised against the determination of the soil-colloids by the extraction with HCl, by STREMME, GLINKA, ATTERBERG, etc., at the Agrogeologic Conference of Stockholm in 1910 ³⁾.

Indeed some unweathered minerals appear to be very attackable to, some of them even completely soluble in boiling HCl, as

¹⁾ See: Methods pag. 30.

²⁾ O. TAMM, Meddelanden från Statens Skogs-Försöksanstalt, 25, 1 (1929).

³⁾ D. J. HISSINK, Verh. der zweiten Agro-geol. Konf. Stockholm, 43 (1910).

was proved by STREMME and AARNIO ¹⁾, DE 'SIGMOND ²⁾, RINDEL ³⁾, VESTERBERG ³⁾ and UTESCHER ⁴⁾ and afterwards by a more extensive investigation of THIÉBAUT ⁵⁾.

The contributions which these mineral-fragments that are hard to dissolve in HCl, yield to the HCl-extract, may be determined by repeated extraction of the residue under the same conditions.

In this way it seems possible to determine the permutoid-part of the clay-fraction apart from the Al-(Fe-)Si-compounds of lower solubility.

After these preliminary investigations, which will be performed on one of the clay-soils, which are included in this research, a hypothesis will be made as to the composition of the inorganic part of the so-called „adsorption-complex”. This hypothesis will be tested on a dozen Dutch clay-soils. Afterwards experiments to show how far the quantity of Al-(Fe-)Si-complex, which is dissolved out of the different soils by the HCl-extraction, depends on the clay-contents of the soils in question and how far the clay-fractions of the humus-free, original soils define the adsorption capacities of them, will be carried out.

From this will appear whether the whole clay-fractions, or possibly only variable parts of the clay-fractions, for the different soils, are concerned in the adsorption-phenomena of the soils.

The mechanical compositions of the soils will be defined by means of the pipette-analysis of OLMSTEAD. Moreover the mechanical compositions of the HCl-residues of the different soils will be determined in the same way in order to show how far the original mechanical compositions of the soils have been changed by the HCl-extraction, and also to show to what degree the adsorption capacities of the HCl-residues are dependent on the mechanical compositions of these residues.

Finally some minerals, possibly present or supposed to be present in the clay-fractions of the soils by several investigators, are treated in the same way. Before starting the research it seemed desirable to give a summary of the methods applied.

¹⁾ H. STREMME, Ztsch. f. prakt. Geol., 19, 329 (1911).

²⁾ A. DE SIGMOND, Intern. Mitt. f. Bod.k. 4, (1914).

³⁾ Protokoll der Tagung der intern. Komm. f. d. Chem. Bod. Anal. München (1914). Intern. Mitt. f. Bod.k., 5, 25 (1915).

⁴⁾ K. UTESCHER, Ztschr. f. Pfl. Ernähr. D. u. Bod.k., 11, 275 (1923).

⁵⁾ J. LUCIEN THIÉBAUT, Contrib. à l'Etude d. Sedim. Argilo-Calc. (1925).

II. ORIGIN, DESCRIPTION AND SAMPLING OF THE SOILS

The soils were collected in the clay-regions of the Netherlands. They all represent Dutch clay-soils which have been reclaimed.

Figure I shows the places where the samples were drawn and the following table indicates their cadastral data:

TABLE 1.

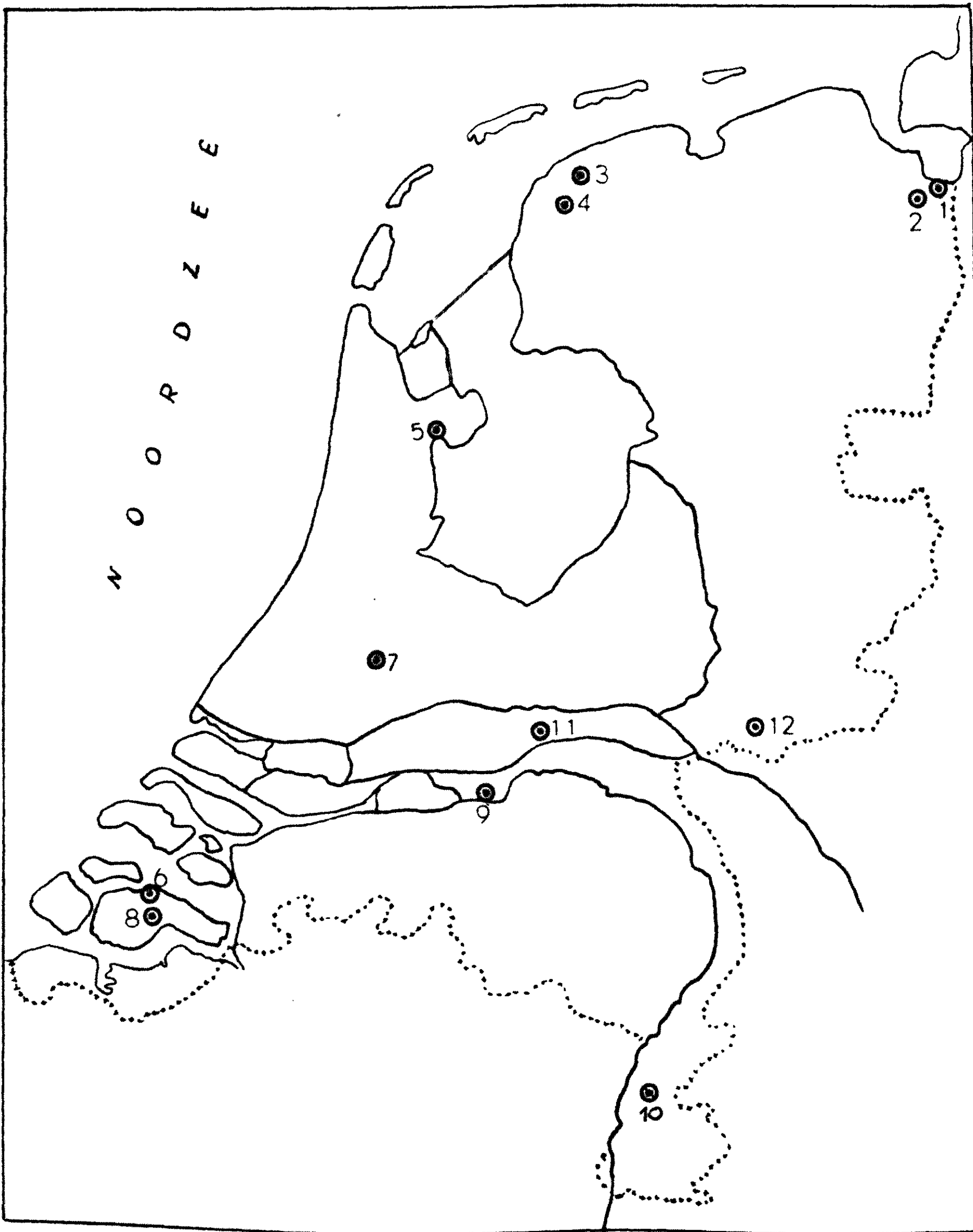
CADASTRAL DATA OF THE SOILS

Indication:	Cadastral community:
1. Drieborg	Beerta, Section B, nr. 95
2. Ulsda	Beerta, Section G, nr. 259
3. St. Anna Parochie	St. Anna Parochie, Section C, nr. 1604
4. Menaldum	Beetgum, Section C, nr. 1728
5. Zwaag	Zwaag, Section A, nr. 2023
6. Wilhelminadorp	Kattendyke, Section G, nr. 285
7. Rietveld	Rietveld, Section B, nr. 767
8. 's-Heere Abtskerke	's-Heere Abtskerke, Section A, nr. 7
9. Hedel	Hedel, Section C, nr. 173
10. Susteren	Nieuwstad, Section C, nr. 2085
11. IJzendoorn	Kesteren, Section B, nr. 955
12. Etten	Etten, Section B, nr. 148

Soils 1 (Drieborg), 2 (Ulsda), 3 (St. Anna Parochie), 4 (Menaldum), 5 (Zwaag), 6 (Wilhelminadorp) and 8 ('s-Heere Abtskerke) are sea-clays, which have been reclaimed for different periods of time. For example the soils 4 (Menaldum) and 8 ('s-Heere Abtskerke) are very old deposits, whereas the soils 1 (Drieborg) and 6 (Wilhelminadorp) are very young polder-soils ¹⁾

¹⁾ Soil 1 (Drieborg) is situated in the „Stad-polder”, which was dyked in 1740. Soil 6 (Wilhelminadorp) is situated in the „Wilhelmina-polder”, which was dyked in the 17-th century. A. BEEKMAN, Nederland als Polderland, Ite Druk, pag. 353, 249.

FIGURE I



Soils 9 (Hedel), 11 (IJzendoorn) and 12 (Etten) are river-clays, respectively from the Meuse, the Rhine, and the Ysel and soil 10 (Susteren) is a brook-clay. Finally soil 7 (Rietveld) represents a so-called potter's clay.

Soils 7 (Rietveld) and 10 (Susteren) were only cultivated as meadow-land, whereas the other soils were all cultivated as plough-land.

The sampling was performed in the soil-layer from 5 to 20 cm. below the ground-level, in April 1933.

After having been passed through a 2 mm-sieve, the samples were dried in the air.

TABLE 2.

GENERAL DATA FOR THE SOILS

Soil Nr	Description of the soil	Moisture- content in % of the air-dry soil (105° C.)	CaCO ₃ in % of the air-dry soil	Organic matter in % of the air-dry soil	pH of the suspension (quinhydrone- electrode).
1	light-grey, heavy clay-soil	4.6	4.4	5.4	7.8
2	grey, heavy clay-soil	4.8	0.1	4.9	7.3
3	grey, sandy clay-soil	2.7	2.5	5.5	7.5
4	grey, loamy clay-soil	4.0	1.5	5.5	7.5
5	dark-grey clay-soil	1.9	4.6	4.2	7.7
6	light-grey clay-soil	3.1	11.2	3.4	7.6
7	dark-grey, humus-rich, heavy clay- soil	7.5	0.1	15.4	5.8
8	grey, loamy clay-soil	2.5	—	4.2	6.3
9	light-grey, sandy clay-soil	1.3	—	3.2	6.9
10	brownish-grey, loamy clay-soil . .	3.7	—	5.9	6.4
11	brownish-grey, sandy clay-soil . .	2.7	0.6	3.8	8.0
12	ruddy-brown, heavy clay-soil . . .	3.9	—	4.6	5.4

III. EXPERIMENTS

I. METHODS

A. The Pre-treatment of the Soil

The soils which are concerned in this research all contain small amounts of organic matter originating from the decomposition of plant-rests and from the micro-flora and -fauna that is living in the soil.

These organic materials principally appear in the colloidal state and thus have an important share in the exchange-reactions of the soil. It is especially in connection with this last quality of the humus that it was desirable to destruct the organic matter in order to restrict the research to soil without the organic complex.

To remove the oxidisable organic matter from the soil, the latter was weighed in portions of 10 g in beakers (of 600 cc) and after adding 40 cc 6% H_2O_2 and covering the beaker with a watch-glass, placed on the steam-bath. At intervals, the beakers were shaken.

After evolution of gas had ceased, a further 40 cc of H_2O_2 were added and this repeated until the supernatant liquid, after the particles had settled, was colourless.

For light clay-soils three, for heavy clay-soils four to five treatments with H_2O_2 were necessary, while to the soils possessing a high content of organic matter (numbers 7 and 10) a further 2—3 additions of 40 cc 30% H_2O_2 were necessary ¹⁾.

The escape of gas having ceased, the watch-glasses were washed and the suspensions heated on the steam-bath for another half hour, to remove the final traces of H_2O_2 .

The treatment on the steam-bath lasted for light clay-soils 3—5 hours, for the heavy samples 6—10 hours.

¹⁾ In the beaker 200 cc solution were then still present so that after addition of 40 cc 30% H_2O_2 the suspension contained about 5% H_2O_2 .

After that, the suspensions were filtered under vacuum through a Zsigmondy-membrane-filter ¹⁾, (10–20 sec., 15 cm diameter), the residues washed with H₂O till no more Fe⁺⁺⁺ was to be found in the filtrate with KCNS. The oxidised soil was quantitatively washed into a porcelain dish ²⁾ and the suspension evaporated to dryness on the steam-bath.

After cooling the soil was brought into an agate mortar by means of a horn spatula and rubbed down under light pressure after which it was spread out in a very thin layer to be dried for 24 hours in the air. Finally the oxidised soil was mixed carefully.

B. *The Extraction of the Soil with HCl*

In the analysis of the Al-Fe-Si-complex of the soil which is soluble in HCl, VAN BEMMELEN extracted the soil with HCl of different concentrations for a fixed time. ³⁾ After the HCl-extraction, the HCl-extract was as far as possible siphoned off and a correction made to account for the small quantity of the extract left in the HCl-residue. Moreover, the extract was filtered and the very small quantity of the soil which remained on the filter taken in account.

This method was not very accurate especially because after the HCl-extraction the residue was treated with NaOH, sp. gr. 1,04, in order to dissolve the SiO₂-gel, which was separated by the HCl-extraction: the SiO₂-content of the small quantity of HCl-residue that was siphoned off, escaped the analysis, while exactly these parts, very probably the finer fraction of the residue, could possess a relatively great SiO₂-content. On the contrary, the inaccuracy which might be caused by the fact that part of the HCl-extract stayed behind in the residue after siphoning, by a possible adsorption of the components brought into solution by the residue, appeared to be very trifling ⁴⁾.

The NaOH-extract, obtained after the NaOH-treatment of the HCl-residue, was also siphoned and filtered and whereas after the HCl-extraction the suspension settled rather quickly so that the extract could be siphoned, it appeared that after the NaOH-

¹⁾ ZSIGMONDY and BACHMANN, *Ztschr. f. anorg. Chemie*, **103** (1918).

²⁾ For heavy clay-soils, it was necessary to use a pencil for this manipulation.

³⁾ J. M. VAN BEMMELEN, *Ztschr. f. anorg. Chemie*, **42**, 266 (1904).

⁴⁾ O. TAMM, *Meddelanden Statens Skogsförsöksanstalt*, **19**, 393 (1922).

treatment the sedimentation wanted much more time and was more incomplete at that. When the turbid NaOH-extract was siphoned afterwards, the finer fraction was eliminated and eventually following repeated HCl-extraction of the residue, could only give an imperfect idea of the part of the soil, soluble in HCl, which was brought into solution by the repeated HCl-extraction ¹⁾).

This method is considerably simplified by the use of Zsigmondy-membrane-filters ²⁾, through which it becomes possible to filter the extracts under vacuum, while the above-mentioned inaccuracies disappear, because the residues are washed with H₂O and the extracts pass through quite clear. ³⁾

a. *Preparation of the HCl-extract.*

10 g of the oxidised soil were put into an erlenmeyer (300 cc) and to this 200 cc HCl of a known concentration was pipetted. The flask was furnished with a thermometer and after shaking the whole was placed in a steam-bath, which had previously been heated to a temperature of 60° C. By frequent shaking, the contents of the erlenmeyer were warmed to 55° C. and from this moment the temperature of the steam-bath was so regulated, that during the extraction it remained at 55° C. (54.5–55.5° C.). The duration of the extraction was calculated from the moment that the extract reached the temperature of 50° C. ⁴⁾

Every five minutes during the extraction the flask was strongly shaken so that the soil-particles continually remained in contact with the solution, because after about 5 minutes the suspension apparently had become completely coagulated.

After the extraction, the erlenmeyer was cooled to 20° C. (under the tap), the thermometer washed, and the extract filtered under vacuum ⁵⁾ through a membrane-filter (10–30 sec., 15 cm diameter), while the HCl-extract was caught in an erlenmeyer which was placed in a filter-apparatus (according to WITT).

¹⁾ By a preliminary experiment with a red lateritic-soil (fraction $< 2 \mu = 32,6\%$) per 5 g soil, 59 mg soil siphoned with the HCl-extract, while 10.1 g HCl-extract remained behind in the residue. By the subsequent NaOH-treatment, 138 mg of the soil siphoned and 14.3 g NaOH-extract remained behind in the residue.

²⁾ See: note 1, pag. 24.

³⁾ By analysis with the ultra-microscope, the extracts appeared to be „optically-empty”. (I am very thankful to Dr. TENDELOO for doing this analysis).

⁴⁾ To reach the temperature of 50° C., under these conditions 5 minutes were required.

⁵⁾ In the filtration of the HCl-extract vacuum-tanks were used.

The residue was washed with H_2O till the filtrate showed no reaction with KCNS. Afterwards it was quantitatively transferred to a porcelain dish ¹⁾ and the suspension evaporated to dryness on the steam-bath.

After cooling the residue was quantitatively taken into an agate mortar by means of a horn spatula and rubbed down under light pressure, after which it was spread out in a very thin layer and dried for 24 hours in the air. Finally the HCl-residue was weighed.

b. Determination of SiO_2 , Al_2O_3 and Fe_2O_3 in the HCl-extract.

The HCl-extract ²⁾ was taken into a 500 cc graduated flask and filled up to the mark.

200 cc of the extract were pipetted off for the SiO_2 -determination, while in the filtrate from the SiO_2 -residue „ $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{P}_2\text{O}_5$ ” were determined.

Fe_2O_3 was determined in 100 cc of the HCl-extract.

Al_2O_3 was found by subtracting from the total precipitate „ $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{P}_2\text{O}_5$ ”, the separately determined quantities Fe_2O_3 and P_2O_5 . ³⁾ P_2O_5 was determined in 100 cc of the HCl-extract.

Determination of SiO_2 .

200 cc of the HCl-extract were evaporated to dryness in a porcelain dish (300 cc) on the steam-bath, the residue was sprinkled with 38% HCl till the mass was quite soaked and, after that, it was evaporated to dryness. From this moment the residue was heated for about a quarter of an hour on the steam-bath.

This treatment was repeated twice. Finally the dry-residue was sprinkled once more with HCl, 50 cc. H_2O was added, heated on the steam-bath and filtered directly ⁴⁾. (filter: Delta bruinkruis nr 366, 11 cm).

The filter was now washed with warm H_2O , till the filtrate showed no more Cl' -reaction with AgNO_3 , after which it was

¹⁾ See: note 2, pag. 24.

²⁾ See: methods, pag. 25.

³⁾ This is also the method which is recommended by HILLEBRAND, The analysis of silicate and carbonate Rocks, 100 (1919): „In any event the probable error can hardly be as high as that involved in the direct determination of alumina itself, considering the difficulty of effecting a satisfactory separation of it from the other components of the mixture, an operation which would, moreover, extend immoderately the time required for each analysis.”

⁴⁾ By separating SiO_2 like this, up to 3% of the total quantity SiO_2 may come into the filtrate, according to HILLEBRAND. To separate this last quantity, the filtrate is then once more evaporated and the residue again treated with strong HCl. This second manipulation was omitted here, because of the low SiO_2 -contents of the filtrates.

ignited while still wet in a platinum crucible to constant weight ¹⁾.

After cooling in an desiccator the „impure SiO_2 ” was determined by weighing. Repeated treatment of the ignited residue with NH_4F and determination of the loss in weight, gave the „pure SiO_2 ” ²⁾.

Determination of the total precipitate: „ $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{P}_2\text{O}_5$ ” ³⁾.

To the filtrate from the SiO_2 -determination, 20 cc n. NH_4Cl were added, the solution was neutralized with 10% NH_4OH ⁴⁾ against litmus-paper ⁵⁾, and heated to boiling; after that a few drops of NH_4OH were added and only just boiled. After that the precipitate was settled, was filtered directly through a „Delta-filter” (nr 366, 11 cm) and washed with warm water once ⁶⁾.

200 cc H_2O , 10 cc n. NH_4Cl and 20 cc strong HNO_3 now were put in the same beaker ⁷⁾, the precipitate was dissolved in it ⁸⁾ and then the solution was again treated with NH_4OH in the above mentioned way. The precipitate was washed with warm

¹⁾ W. D. TREADWELL, *Analytische Chemie*, 2, 415 (1927).

²⁾ The SiO_2 which is separated in this way is white and also not visibly contaminated by Fe_2O_3 . The residue after the NH_4F -treatment is also very small and only once amounted to 3% of the quantity „impure- SiO_2 ”; for the other cases the contamination was less.

³⁾ By the neutralization with NH_4OH , Ti also is precipitated as hydroxide and the weight of the „total-precipitate” is too high. By total-analyses of the soils however, on an average only 0.15% TiO_2 could be present (highest value: 0.26%). (See: table 31)

⁴⁾ W. F. HILLEBRAND, *The analysis of silicate and carbonate rocks* 106 (1919), etc. recommends two methods for the precipitation of the „total-precipitate”: the acetate- and the NH_4OH -method. He advises for the first precipitation, the acetate-method: It will occasionally happen that the separation from even very small amounts of manganese is altogether incomplete and the uncertainty of insuring this separation led me to employ the basic-acetate-method for the first precipitation in all cases where manganese is present, and the exceptions are few, even though the precipitation of alumina is sometimes less complete than by ammonia, and in spite of other admitted defects, as for instance a tendency of the precipitate to run through the filter on washing”. Because Mn only occurs in the Dutch clay-soils in small quantities, the NH_4OH -precipitation was preferred (J. M. VAN BEMMELEN, *Landw. Versuchsstat.* 37, 289 (1890)).

⁵⁾ W. F. HILLEBRAND, loc. cit., based on experiments of BLUM, advises one to use for indicator methylred (neutral point pH 6). MC GEORGE, BREAZALE and BURGESS, *Univ. of Arizona techn. Bull.*, 12, 275 (1926), conclude from titration-curves of AlCl_3 with NaOH , $\text{Ca}(\text{OH})_2$, Na_2CO_3 and NaHCO_3 : „The most insoluble range thus lies within the H-ion-concentration represented by pH 7.0—8.0”. Litmuspaper was chosen for indicator in these experiments (neutral point pH 6.6—8.0, J. M. KOLTHOFF, *Der Gebrauch von Farbenindikatoren* 244 (1926)) because the colour-change of methylred was not visible in the presence of organic matter.

⁶⁾ To the filtrate a few drops more of NH_4OH were added and after that the solution was boiled for some minutes; the precipitation appeared to be complete. HILLEBRAND prescribes washing of the precipitate with 2% NH_4NO_3 . According to SIDENER and PETTIJOHN (*Journ. Ind. Eng. Chem.*, 8 (1916) the solubility of $\text{Al}(\text{OH})_3$ in NH_4NO_3 is as great as in H_2O .

⁷⁾ HNO_3 was used because then by washing the precipitate, less H_2O was necessary.

⁸⁾ The filter is attacked by the HNO_3 so that the precipitate is formed in the presence of macerated filterpaper. This is recommended by DIETRICH to prevent the formation of Fe_3O_4 by ignition (*Anl. z. Gesteinsanalyse* 10 (1905)).

H₂O till the filtrate showed no more reaction with AgNO₃. Then the filter was ignited in a porcelain crucible, cooled and sprinkled with strong HNO₃ till the ash was quite soaked. Finally the HNO₃ was evaporated and the precipitate ignited under air-supply to constant weight. After cooling the residue was weighed.

Determination of Fe₂O₃ ¹⁾.

100 cc of the HCl-extract were pipetted into a beaker (400 cc) and evaporated on the steam-bath; after that the beaker was covered with a watch-glass and 20 cc 15% H₂O₂ were added ²⁾.

After evolution of gas had ceased, the watch-glass was washed and the solution evaporated; the residue was moistened with H₂O and once more evaporated ³⁾.

The residue was dissolved in 20 cc 20% HCl and heated to the boiling-point. Out of a burette, SnCl₂ was added to the solution in drops till the yellow colour of the extract had disappeared and one drop was added in excess. The solution was diluted with boiled H₂O up to 100 cc and after 2 minutes, 10 cc of a saturated HgCl₂-solution were added.

After 2 minutes, the solution was diluted up to 500 cc with H₂O, coloured pink by the addition of a few drops of KMnO₄ ⁴⁾ and after adding 6–8 cc. MnSO₄-solution, was titrated with KMnO₄ (0.1 n.) till the pink colour lasted for some seconds. ⁵⁾

Determination of P₂O₅ ⁶⁾.

100 cc of the HCl-extract were evaporated to dryness in a porcelain dish (200 cc) and the SiO₂ was separated and filtered in the same way as indicated for the SiO₂-determination in the HCl-extract ⁷⁾.

The filtrate was evaporated to dryness on the steam-bath ⁸⁾, the residue dissolved in 50 cc of a H₂SO₄-HNO₃-mixture, and after

¹⁾ According to ZIMMERMANN-REINHARDT: W. D. TREADWELL, *Analytische Chemie*, 2, 525 (1927); I. M. KOLTHOFF, *Die Maszanalyse*, 2, 305 (1928).

²⁾ The organic matter which is present in the HCl-extract is inconvenient to the titration with KMnO₄.

³⁾ In order to make the removal of the H₂O₂ more complete.

⁴⁾ I. M. KOLTHOFF, loc. cit., 306.

⁵⁾ Every analysis was corrected with a blank.

⁶⁾ According to VON LORENZ, *Methoden van Onderzoek aan het R. L. P. te Maastricht*, pag. 14.

⁷⁾ See: *Methods*, pag. 26. Silica disturbs the quantitative precipitation of PO₄''' by sulfate-molybdate-solution.

⁸⁾ Cl' disturbs the PO₄'''-determination.

being heated to the boiling-point, 50 cc of a sulfate-molybdate-solution were added.

The precipitate was filtered by means of suction, after standing from 12 to 18 hours, into a glass crucible (Jena G 4), washed successively with 2% NH_4NO_3 and acetone and after being kept for one hour under 100–200 mm pressure, it was weighed.

Determination of Al_2O_3 .

The Al_2O_3 -content of the HCl-extract was found by subtracting the separately determined quantities Fe_2O_3 and P_2O_5 from the total precipitate: „ $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{P}_2\text{O}_5$ ”.¹⁾

c. Treatment of the HCl-residue of the Soil with NaOH.

5 g of the carefully mixed HCl-residue of the soil were treated with 100 cc NaOH sp.gr. 1.04 at 50° C in an erlenmeyer-flask (300 cc).

After putting a thermometer into the flask, the whole was shaken and placed into a steam-bath, which had been heated previously to a temperature of 55° C.

By repeated shaking, the contents of the erlenmeyer-flask were heated up to 50° C. and after that the temperature of the steam-bath was regulated so that during the extraction it remained at 50° C. (49.5–50.5° C).

The duration of the extraction was reckoned from the moment that the extract reached the temperature of 45° C. From this moment, the residue was extracted for 5 minutes with repeated shaking; after that, the extract was cooled (under the tap) to 20° C., the thermometer was washed and the extract filtered by means of suction through a membrane-filter (10–20 sec., diameter 15 cm). The filtrate was caught in an erlenmeyer-flask which was placed in the filter-apparatus. The NaOH-residue was washed with H_2O till the filtrate no longer reacted alkaline towards litmus and after it was transferred quantitatively into a porcelain-dish, it was evaporated on the steam-bath to dryness.

After cooling, the residue was quantitatively taken into an agate mortar by means of a horn spatula and rubbed down under light pressure, dried and weighed.

d. Determination of SiO_2 in the NaOH-extract.

The NaOH-extract was transferred to a 250 cc graduated flask and filled up to the mark.

¹⁾ See: Note 3, pag. 26.

200 cc of the extract were pipetted into a porcelain dish (300 cc) and after neutralization with HCl, evaporated to dryness on the steam-bath. The SiO_2 was separated and determined as indicated in the SiO_2 -determination in the HCl-extract ¹⁾).

C. The Determination of the Adsorption capacity

Because the adsorption capacities of the soil, the HCl-residue and the HCl-NaOH-residue were carried out in the same way, the general description of the method follows below.

The method is based on the fact mentioned before and discovered by WAY, that the adsorbed cations which are present in the adsorption-complex of the soil exchange with those of an electrolyte-solution in an equivalent proportion.

To the cations which occur in the soil in an adsorbed state generally belong: Ca^{++} , Mg^{++} , K^+ , NH_4^+ , Na^+ and H^+ . In comparison with the others, H^+ and Ca^{++} are more difficultly exchanged by another cation from the adsorption-complex; in other words the adsorption-energy of these cations is greater than that of Mg^{++} , K^+ , NH_4^+ and Na^+ . With regard to this quality of the cations, the insights have in recent times become considerably deeper especially on account of the extensive investigations of WIEGNER ²⁾, GEDROIZ ³⁾ and HISSINK ⁴⁾.

Whereas originally objections had been raised to the experiences of WAY, in connection with the statement of a non-equivalent exchange for unsaturated soil, afterwards these objections were removed by the investigations of GEDROIZ ⁵⁾, HISSINK ⁶⁾ and VAN DER SPEK ⁷⁾.

From these investigations it appeared that when the H-ions were included in the equilibrium, the equivalence of exchange was established for all pH-values.

In the adsorption-complex of the Dutch clay-soils, the Ca-ion

¹⁾ See: Methods, pag. 26. The filtrate of the SiO_2 -determination was analysed for Al^{+++} , through which seldom traces had been found.

²⁾ G. WIEGNER, *Ergänz. Bd. Koll. Ztschr.*, **36**, 341. H. JENNY, *Koll. Chem. Beih.*, **23**, 428 (1927).

³⁾ K. K. GEDROIZ, *Die Lehre v. Ads. Verm. d. Böden*, 413 (1931).

⁴⁾ D. HISSINK, *Versl. Ldbk. Onderz. R. L. P.*, **24**, 173, 224 (1920).

⁵⁾ See note 3.

⁶⁾ D. HISSINK, *Intern. Mitt. f. Bod. k.*, **12**, 81 (1922).

⁷⁾ J. VAN DER SPEK, *Versl. Ldbk. Onderz. R. L. P.*, **27**, 162 (1922).

predominates as an adsorbed cation. HISSINK ¹⁾ found, that on an average, per 100 adsorptively-bound cations in the Dutch clay-soils, 79 Ca⁺⁺, 13 Mg⁺⁺, 6 Na⁺ and 2 K⁺ were present ²⁾. As long as the soil possesses a sufficient base-provision to resist the exchange-energy of the H-ion, no H-ions will penetrate into the adsorption-complex; when on the contrary such free salts as CaCO₃ and MgCO₃ have almost been washed away, the displacement of the adsorbed cations by the H-ions of the soil-solution begins: the soil becomes „unsaturated” and therefore in the soils in which these salts are not found, part of the exchange capacity of the complex is taken up by the H-ion.

Because these H-ions possess a great adsorption-energy the replacement of them by other cations is very difficult and this quality of the H-ion is taken advantage of for the determination of the basic cations which are present in the soil. To this purpose, GEDROIZ uses 0.05 n. HCl; the H-ion-concentration of this solution is low enough to leave the adsorption-complex intact, whereas the adsorbed basic cations exchange quantitatively with the H-ion and can be determined in the filtrate ³⁾.

In order to be able to determine the total adsorption capacity of the soil, it is also necessary to exchange, not only the basic cations which are present in the adsorption-complex of the soil, but also the adsorbed H-ions up a certain equilibrium. When therefore the total adsorption capacity of the soil is determined by treatment of the soil with a solution of a neutral salt, e.g. with a NH₄Cl-, KNO₃- or Na₂SO₄-solution, the H-ions, which have been exchanged, will try in their turn to replace the cations which have taken in their places, because they are not inactivated by the anions of the electrolyte-solution i.e. because they are not fixed in the form of an acid, which is weakly dissociated.

It is for this reason, that the total adsorption capacity is determined by treatment of the soil with solutions of salts of weak acids as: (CH₃COO)₂Ca and CH₃COONa ⁴⁾ through which the

¹⁾ D. HISSINK, Die Bodenadsorption. Bericht für die Groninger Sitzung der II Kommission (1926). Proc. of the sec. Comm. of the Intern. Soc. of Soil Sci., Vol. B (1927).

²⁾ From unpublished investigations of the laboratory of agricultural chemistry at Wageningen, it appears that Mg⁺⁺ may occur to a larger percentage in Dutch clay-soils.

³⁾ By other investigators, other electrolyte-solutions are used for the exchange of the basic cations from the complex: NH₄Cl (KNOPP) KCl (DAIKUHARA) NaCl and BaCl₂ (HISSINK) BaCl₂ (GEDROIZ), A. STEBUTT, Lehrb. d. alg. Bod. k. 222 (1930).

⁴⁾ Meth. f. d. Unters. d. Bod. I Beih. z. Ztschr. f. Pfl. Ern. D. u. Bod. k., 61 (1932).

A. BAUMANN und E. GULLY, cited from KAPPEN, Die Bodenazidität, 90 (1929).

A. STEBUTT, Lehrb. d. alg. Bod. k., 246 (1930). H. KAPPEN, Die Bodenazidität, 97 (1929).

H-ions, which have been exchanged out of the adsorption-complex, are buffered by the formation of the weakly dissociated CH_3COOH and so withdrawn from the equilibrium-reaction ¹⁾.

The determination of the adsorption capacity may be carried through in two different ways.

In the first place it is possible, by means of shake-tests, to exchange to a certain extent the cations which are present in the soil against the cations of an electrolyte-solution which has been added. By this method of shaking however, an equilibrium is established influenced by the re-action of the replaced ions. In order to determine what the final-equilibrium will be when the influence of the replaced ions is eliminated, the shake-test is repeated with a solution of the same electrolyte of another concentration. From the quantities of the electrolyte, which were found in both cases in the filtrate of the suspension, the so-called „adsorption-curve” can be calculated ²⁾. The limit of the curve gives a value for the adsorption capacity of the soil where the re-action of the replaced cations is eliminated. This value is a conventional magnitude. Indeed it still remains possible to reach another value by use of an electrolyte-solution of another pH.

The extrapolation, which is connected with this method of determining the adsorption capacity of the soil, and likewise the necessity of at least two experiments to calculate the limit-value, are the reasons why preference was given to another method for the determination of the adsorbed cations in the soil to get comparable adsorption-values: the percolation-method.

By this method the soil is leached by the electrolyte-solution, in a way which will be described hereafter, so that the cations which have been exchanged from the adsorption-complex of the soil are led away.

Through this the re-action of the exchanged ions is made impossible ³⁾. The percolation is continued until the solution, which

¹⁾ The use of these salts of weak acids is especially necessary for the determination of the adsorption capacities of the HCl-residues because the adsorbed cations, which are possibly still present, are necessarily H-ions.

²⁾ P. VAGELER, *Fortschr. d. Landw.*, **3**, 76 (1931). The formula according to VAGELER was criticized by L. WEISZ, *Der Kationenumtausch an Permutiten und seine Formulierung*, Promot. Arb., Zürich (1932).

³⁾ The apparatus for this method are principally described by J. F. BREAZALE, *Univ. of Arizona techn. Bull.*, **26**, 41 (1929); and also by P. S. BURGESS, *Univ. of Arizona techn. Bull.*, **28**, 108 (1929). A reproduction of the apparatus which are used in this research may be found in P. PRILLWITZ, *De invloed van den basentoestand op de ontwikkeling van de Thee-plant*. Diss. Wageningen, 19 (1932).

leaves the percolation-tube in drops, has the same composition as the original percolation-solution. By this method, a comparable value is obtained as to the adsorption capacity of the soil by a single determination, if for all soils a similar electrolyte-solution is used: the equilibrium is then established against electrolyte-solutions of the same composition. ¹⁾

The manipulation was as follows:

The cations, which were present in the adsorption-complex of the soil, were replaced by Ca-ions by means of $(\text{CH}_3\text{COO})_2\text{Ca}$ -percolation and these were in their turn exchanged by NH_4 -ions during NH_4Cl -percolation.

4 g of the soil, of the HCl-residue, or of the HCl-NaOH-residue, were mixed with 30 g of quartz-sand in an agate mortar and the mixture was quantitatively transferred to a percolation-tube, (length 30, interior diameter 2 cm), by means of a filling-funnel, which, to the narrowed lower end, was shut off by a plug of glasswool on which ± 5 g of quartz-sand were put. The mixture was again covered with ± 5 g of quartz-sand and the percolation-tube was shut off with a perforated rubber stopper. Through the perforation of the stopper, a glass tube was led to the upper reservoir, filled with the percolation-solution. The inlet-tube was provided with a pinch cock in order to regulate the speed of percolation. This velocity was so regulated, that the total percolation lasted $\pm 3\frac{1}{2}$ hours. The percolate was caught in a graduated flask of 500 or 200 cc which was placed under the percolation-tube. Through the soil, 500 cc n. $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution of pH ± 8.5 (rose-coloured with phenolphthaleine) ²⁾, 200 cc boiled H_2O ³⁾ and 200 cc n. NH_4Cl -solution ⁴⁾ were suc-

¹⁾ Moreover when the concentration of the electrolyte-solution is chosen in such a way, that an increase of the concentration of the electrolyte-solution cannot increase the adsorption-value, then in a sense, i.e. for the prevailing pH, a final value is obtained which is comparable with the extrapolation-value of the shake-method.

²⁾ $(\text{CH}_3\text{COO})_2\text{Ca}$ was chosen in order to exchange also the H-ions to a certain equilibrium with the Ca-ions. The pH of a n. $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution however is lower than 8.5; to reach this pH, per L.n., about 12 cc saturated $\text{Ca}(\text{OH})_2$ were added. After the percolation of 500 cc n. $(\text{CH}_3\text{COO})_2\text{Ca}$ of pH ± 8.5 , for two samples of high clay-contents and of differing values of the „pH of the suspension“ (soils 2 and 12), only 1 cc 0.1 n. NaOH was wanted for the sixth 100 cc of the percolate for the neutralization towards phenolphthaleine. Subsequent 100 cc all wanted still about 1 cc 0.1 n. NaOH (See: PRILLWITZ, loc. cit., pag. 23), so that it could be concluded that after percolation of the fifth 100 cc, a certain limit to the $\text{Ca}^{++}\text{-H}^+$ -exchange was reached. Because the adsorption-energy of the H-ion in comparison with the other cations was greatest, it may be accepted that for the other cations also this limit was reached.

³⁾ H_2O was percolated until negative Ca^{++} -reaction of the percolate (with $(\text{COONH}_4)_2$). This washing was necessary for the removal of the $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution which has remained in the soil after the $(\text{CH}_3\text{COO})_2\text{Ca}$ -percolation.

⁴⁾ In the third 100 cc of the NH_4Cl -percolate, only a trace of Ca^{++} was found for the soils 2 and 12 (See: Note 3).

cessively percolated. Finally, the Ca^{++} was precipitated in the NH_4Cl -percolate as oxalate, filtered through a perforated crucible, washed, and dissolved in 50% H_2SO_4 .

After dilution with H_2O , the $\text{H}_2\text{C}_2\text{O}_4$ which was formed, was titrated with $\text{KMnO}_4 \pm 0.1 \text{ n.}$ ¹⁾. The results were all corrected with a blank-percolation of 40 g of quartz-sand ²⁾.

In connection with the determination of the adsorption capacities of soils, which contain CaCO_3 , the complication occurs that the CaCO_3 completely or at least partly is dissolved during the NH_4Cl -percolation. This difficulty was eliminated by following the NH_4Cl -percolation of the soil with a percolation of 150 cc of alcohol (70%) ³⁾, followed by a percolation of 200 cc n. KCl -solution ⁴⁾. Through this, the adsorbed NH_4^+ was again exchanged with K^+ in the KCl -percolate and was determined by distillation ⁵⁾.

2. THE INFLUENCE OF HCl -EXTRACTION ON THE ADSORPTION CAPACITY OF THE SOIL

A. Preliminary Investigations

Before telling how the so-called „weathering-complex A, according to VAN BEMMELEN” behaves on extraction with HCl of various concentrations, an investigation was made as to the influence of the period of extraction, the temperature of extraction and the ratio of the quantities soil and HCl during the extraction on the decomposition of the Al-Fe-Si -compounds of the soil ⁶⁾.

The most moderate extraction used by VAN BEMMELEN, was a treatment of the soil with HCl , sp.gr. 1.035, for half an hour, at 55°C , with a ratio soil: HCl of 1 : 20. The reasons why VAN BEMMELEN chose such conditions of extraction are not mentioned by him.

¹⁾ W. TREADWELL, Kurz. Lehrb. d. Anal. Chem., 2, 61, 532 (1921).

²⁾ In order to get a perfect contact of the soil particles with the percolation-liquid, HUDIC introduced the mixing of the soil with quartz-sand.

³⁾ By washing with H_2O the clay-fraction of the soil was washed out of the percolation-tube. After 150 cc alcohol (70%) had been percolated, the reaction with Nessler's reagent for NH_4^+ was very weak.

⁴⁾ In the third 100 cc of the KCl -percolate, only a trace of NH_4^+ was found.

⁵⁾ Meth. v. Onderz. R. L. P. Maastricht, 4 (1923).

⁶⁾ In future by „oxidised” soil is indicated the soil which is freed from oxidisable organic matter, with 6% H_2O_2 .

Experimental Part.

After careful mixing, every time 5 g of the oxidised soil 2 (Ulsda) were weighed in an erlenmeyer flask of 300 cc and extracted with 2 n. HCl (7.3%) at a fixed temperature, for a fixed time and by a fixed ratio soil: HCl. ¹⁾ In the extracts, Fe⁺⁺⁺ was determined titrimetrically according to the method of ZIMMERMANN-REINHARDT. ²⁾ The conditions were varied after the scheme mentioned below. (See: pag. 37).

Considering the values of the table, in which the Fe-content of the extract, expressed in Fe₂O₃, is indicated in the 7-th column, it appears that the Fe-content of the extract is higher as the temperature rises, the period of extraction increases and the ratio soil: HCl decreases.

In the figures II and III, respectively the influence of the prolongation of the period of extraction and that of the reduction of the ratio soil: HCl is expressed with the different temperatures.

From figure II it appears that during the second 30 minutes, at 35° C: 0.18 and 0.20% Fe₂O₃, at 55° C: 0.48 and 0.48% Fe₂O₃ and at 75° C: 0.50 and 0.48% Fe₂O₃ is brought into solution.

By prolongation of the extraction from 30 to 60 minutes, the attack on the weathering-silicate is thus influenced in the same way at 55° C as at 75° C: ± 0.50% Fe₂O₃ is dissolved: i.e. the difference of attack at 55° and 75° C reaches a definite value during the first 30 minutes; during the second 30 minutes, the difference remains constant.

From figure III, it appears that by a ratio soil: HCl = 1 : 40, at 35° C: 0.09 and 0.11% Fe₂O₃, at 55° C: 0.15 and 0.15% Fe₂O₃ and at 75° C: 0.16 and 0.14% Fe₂O₃ more is dissolved than by a ratio soil: HCl = 1 : 20. The second 100 cc thus influences the attack in the same way at 55° as at 75° C.: ± 0.15% Fe₂O₃ is dissolved; i.e. the difference of attack at 55° and 75° C reaches a definite value by a ratio soil: HCl = 1 : 20 (in the first 100 cc); by a ratio 1 : 40, in the second 100 cc the difference remains constant.

Finally it appears from figure IV that at 55° C, the influence of the ratio soil: HCl (1 : 20 and 1 : 40) and of the period of extraction (30 and 60 minutes) becomes constant. At 75° C in all cases ± 1.34% Fe₂O₃ is dissolved more than at 55° C.

¹⁾ See: Methods, pag. 25.

²⁾ I. M. KOLTHOFF, Die Maszanalyse, 305 (1928). See: Methods, pag. 28.

FIGURE II

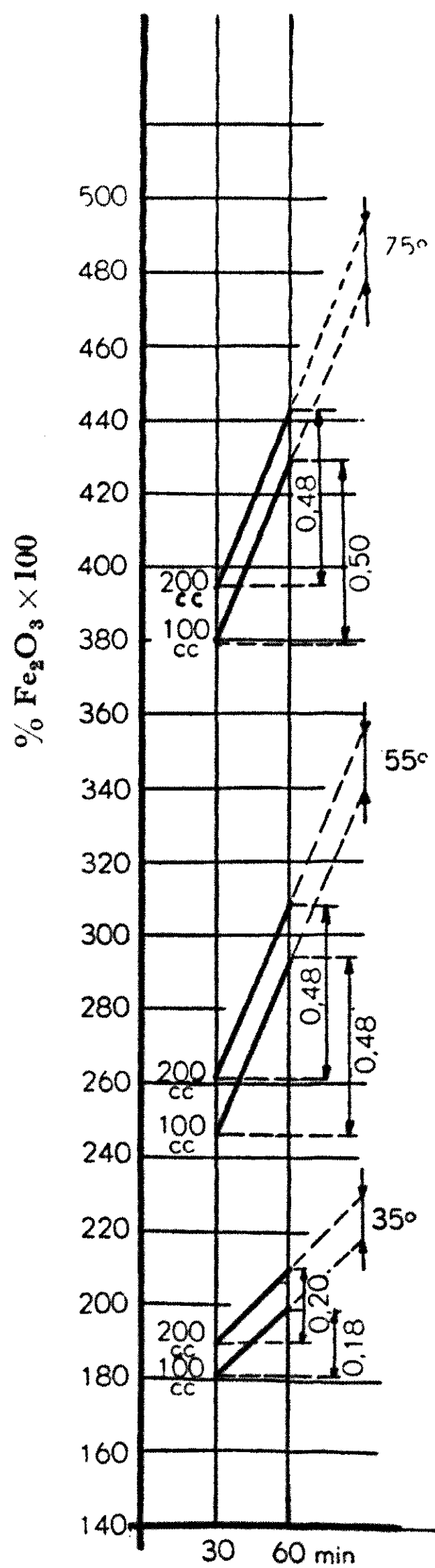


FIGURE III

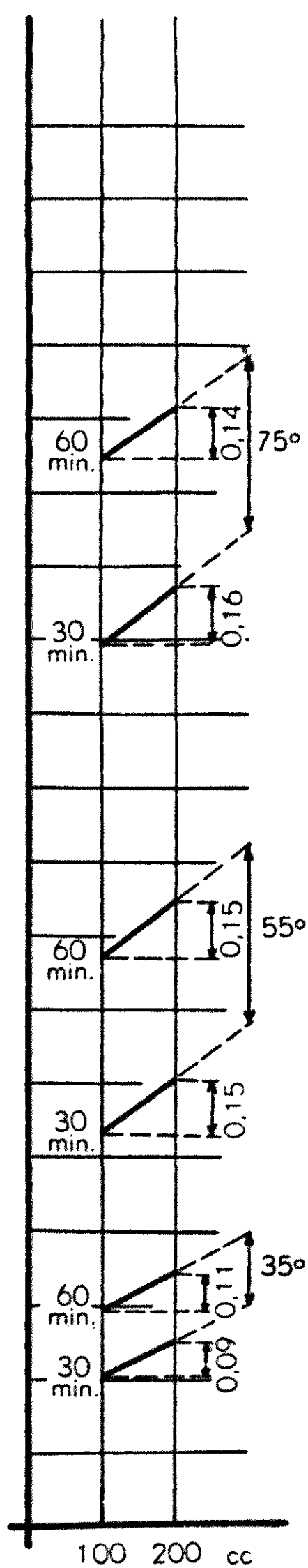
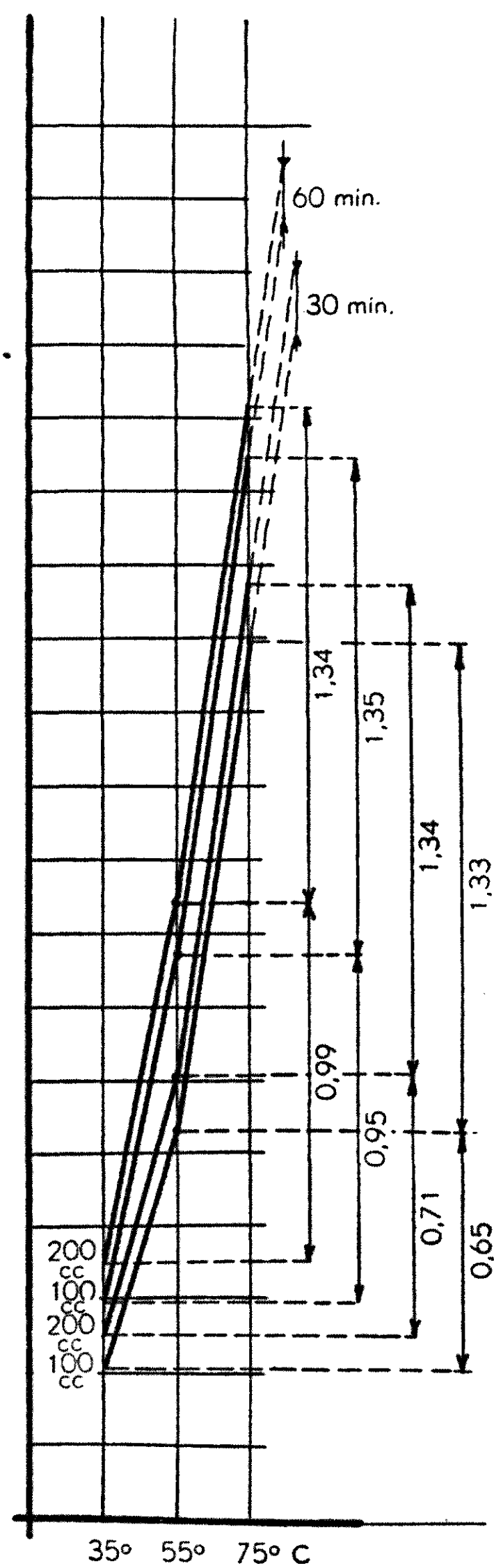


FIGURE IV



Scheme:

Concen- tration HCl.	Soil in g	Tempe- rature in °C	Duration of the extraction (in minutes)	Volume HCl (in cc)	Extraction number	Fe_2O_3 in the extract (in % of the air-dry oxidised soil.)	Fe_2O_3 in 60 min. — — Fe_2O_3 in 30 min. (See: Figure II)	Fe_2O_3 in 200 cc — — Fe_2O_3 in 100 cc (See: Figure III)	Fe_2O_3 at 55° C — — Fe_2O_3 at 35° C and Fe_2O_3 at 75° C — — Fe_2O_3 at 55° C (See: Figure IV)
2 N. (7,3%)	5	35	30	100	1	1,81	—0,18	—0,09	—0,65
			60	200	2	1,90	—0,20	—0,11	—0,71
			30	100	3	1,99	—0,95	—0,99	—1,33
			60	200	4	2,10	—1,34	—1,35	—1,34
	5	55	30	100	5	2,46	—0,48	—0,15	—1,35
			60	200	6	2,61	—0,48	—0,16	—1,34
			30	100	7	2,94	—0,50	—0,14	—1,34
			60	200	8	3,09	—0,48	—0,14	—1,34
	5	75	30	100	9	3,79	—0,50	—0,16	—1,34
			60	200	10	3,95	—0,48	—0,16	—1,34
			30	100	11	4,29	—0,48	—0,16	—1,34
			60	200	12	4,43	—0,48	—0,16	—1,34

Increase of the temperature above 55° C, prolongation of the period of extraction above 30 minutes, and reduction of the ratio soil: HCl below 1 : 20, thus do not alter the nature of the attack: By the extraction of the soil with 2 n. HCl for 30 minutes at 55° C and by a ratio soil: HCl 1 : 20, a limit is reached where a definite part of the soil or a definite mixture of soil-parts is attacked. By the prolongation of the period of extraction, increase of the temperature and reduction of the ratio soil: HCl, apparently no soil-parts of another chemical composition are affected. The decomposition can however well be accelerated by these changes. ¹⁾

Under these conditions it must thus be possible to dissolve, completely or partly, the weathering-silicate which is soluble in HCl.

Based on such a research, VAN BEMMELEN very probably also fixed the extraction of the soil for 30 minutes, at a temperature of 55° C and by a ratio soil: HCl of 1 : 20. ²⁾

This method was chosen for the following experiments, in order to examine the influence of the HCl-concentration on the quantity and composition of that part of the „weathering-complex A according to VAN BEMMELEN”, which is brought into solution during the extraction.

The preliminary investigations were performed with a red clay-soil, nr 12, from Etten (Gld.).

From the mechanical analysis according to OLMSTEAD ³⁾ it appeared that about 50% of the soil consisted of parts < 10 μ (< 10 μ : 53.9% ; < 2 μ : 36.2%). The soil therefore may be classified among the heavier sorts of clay.

The content of organic matter in the soil was 4.6% and for a study of the properties of the inorganic part of the adsorption-complex, it was therefore necessary to remove the organic part of the soil as completely as possible. This was done by a pre-treatment of the soil with 6% H₂O₂. ⁴⁾

The oxidised soil was extracted with various concentrations of HCl so as to dissolve the adsorption-complex. The decomposition was controlled by the determination of the adsorption capacity of the soil before as well as after the extraction.

¹⁾ By the method „VAN BEMMELEN-HISSINK”, 6.37% Fe₂O₃ is dissolved out of this soil. See: pag. 99.

²⁾ Ztschr. f. anorg. Chemie, 42, 288 (1904).

³⁾ See: pag. 77.

⁴⁾ See: Methods, pag. 23.

Scheme.

From the carefully mixed oxidised soil, portions of 10 g were extracted with 200 cc HCl of various concentrations, for 30 minutes, at 55° C. From the HCl (1x)-residue, the adsorption-value was found by mixing 4 g of the residue with 30 g of quartz-sand in an agate-mortar and by treating the mixture in a percolation-tube successively with 500 cc n. (CH₃COO)₂Ca-solution, 200 cc H₂O and 200 cc n. NH₄Cl-solution; finally the Ca⁺⁺ that was exchanged by the NH₄⁺ was determined in the NH₄Cl-percolate ¹⁾.

TABEL 3.

EXTRACTION OF SOIL 12 (ETTEN) WITH VARIOUS CONCENTRATIONS HCl

Concentration HCl in %	Adsorption capacity in M.E. (Ca ⁺⁺) per 100 g residue
1.0	21.5
3.0	19.7
5.0	19.4
7.0	19.7
14.0	19.9
17.0	19.9
21.0	19.7

The adsorption-value of the original oxidised soil amounts to 23.7 M.E. (Ca⁺⁺) per 100 g.

By extraction of the soil with 1%, 3% and 5% HCl, the adsorption capacity of the HCl-residue respectively decreases by 2.2, 4.0 and 4.3 M.E. (Ca⁺⁺) per 100 g residue, whereas after extraction with 7%, 14%, 17% and 21% HCl, the adsorption-value per 100 g residue becomes constant. Therefore by 3% HCl, apparently that part of the soil is dissolved or inactivated through which the adsorption capacity of the original soil becomes higher than 19.8 M.E. ²⁾.

By extraction of the soil with HCl of various concentrations, the adsorption-value of the residue appears to decrease to 83.6 %, at the utmost, of the adsorption capacity of the original soil.

¹⁾ See: Methods, pag. 33.

²⁾ The average adsorption-value of the HCl-residue was calculated from the adsorption-values of the HCl-residues after the extraction with 3%, 7%, 14%, 17% and 21% HCl.

The value, after the extraction with 5% HCl, was left out of account. See: pag. 74, note 5.

Assuming that the Al-Fe-Si-complex, which causes the adsorption-phenomena in the soil is soluble in HCl, as was experimentally stated by WAY, MULDER, VAN BEMMELEN, HISSINK, GANSSEN, etc., — the method „VAN BEMMELEN-HISSINK” and the method of the „Preussische geologische Landesanstalt” base upon this property of the adsorption-complex the determination of the soil-colloids, — it can be imagined that the adsorption in the soil is caused by two components, different from each other according to their relative solubility in HCl ¹⁾, viz. a compound, which is dissolved by dilute HCl, and a compound which appears to be rather resistant.

The difference of resistance between these two compounds towards attack with HCl could be ascribed to a difference in structure between these two. It is however equally possible that this greater resistance is caused by a secondary factor, in other words by a change which the substance has undergone during the HCl-extraction. By the HCl-extraction Al⁺⁺⁺ and Fe⁺⁺⁺, together with small quantities of Si⁺⁺⁺⁺, are dissolved out of the soil-complex while at the same time an important part of the Si⁺⁺⁺⁺ is separated insolubly ²⁾ and it is therefore quite possible that this SiO₂ envelops the soil-particles as a protecting film, with the result that the further disintegration would be impeded. ³⁾

To get an insight into the composition of the adsorptive part of the soil, the latter was repeatedly extracted with 6.6 % HCl, the extracts were analysed, and the adsorption-values of the HCl-residues were determined.

Scheme.

50 g of the original, oxidised soil 12 (Etten) were extracted for 30 minutes at 55° C, with 200 cc 6.6 % HCl per 10 g of soil ⁴⁾ and the extract was analysed. ⁵⁾

¹⁾ By „relative solubility” is meant the quantity of Al-Fe-Si-compounds which is dissolved in the conditions of extraction used.

²⁾ J. M. VAN BEMMELEN, Ztschr. f. anorg. Chemie, 42 (1904).

³⁾ With heterogenous chemical reactions, the velocity of reaction is mainly dependent on the diffusion, (besides the influences of structure and surface of the substance). The diffusion of the Si⁺⁺⁺⁺, dissolved at first instance in the HCl-solution, is impeded however by the HCl so that the proposition of a SiO₂-film round the parts of the soil seems to be very acceptable. The further disintegration of the soil-particles could then be defined by the velocity of diffusion of the HCl through this SiO₂-film. Since the experimental part of this study was finished, it has been shown by WOLF and KÄCHELE that the HCl-extraction of kaolinites causes the formation of a SiO₂-film which impedes the further attack by HCl (Verh. der II ten Komm. d. Int. Bod. k. Ges. A (1933) Kopenhagen).

⁴⁾ See: Methods, pag. 25.

⁵⁾ See: Methods, pag. 26.

From the HCl-residue, again 40 g were extracted in the same way with 6.6 % HCl and the adsorption capacity of 4 g of the HCl (1×)-residue, after mixing with 30 g of quartz-sand, was determined by percolation of the mixture with 500 cc n. $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution, 200 cc n. NH_4Cl -solution and determination of Ca^{++} in the NH_4Cl -percolate. ¹⁾

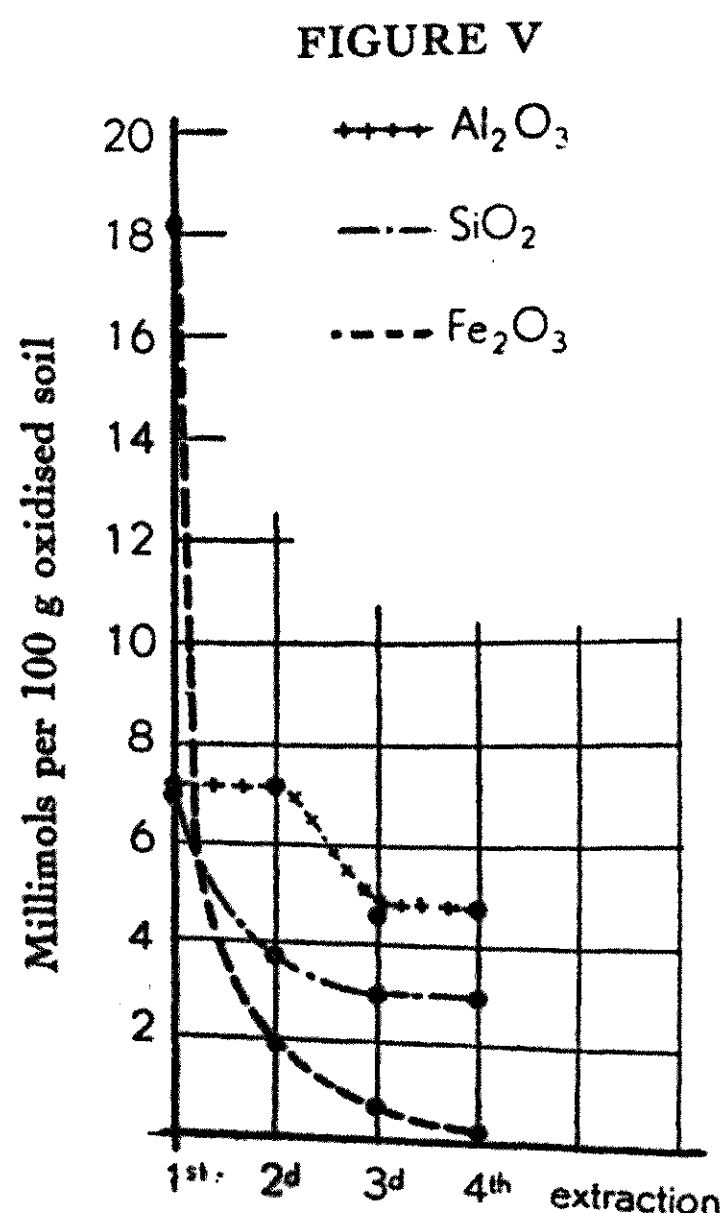
The extraction with HCl was repeated three times and after every extraction the adsorption capacity of the residue was found.

TABLE 4.

REPEATED EXTRACTION OF SOIL 12 (ETTEN) WITH 6.6% HCl

Extraction nr	Totally dissolved in % of air-dry oxidised soil	SiO_2	Al_2O_3	Fe_2O_3	mm per 100 g
1	7.5	7.0	7.3	18.2	oxidised soil
2	2.1	4.0	7.7	1.9	HCl (1×)-residue
3	2.1	3.3	5.2	0.8	HCl (2×)-residue
4	2.0	3.3	5.4	0.3	HCl (3×)-residue

When the quantities of the extracts are calculated on „oxidised soil”, the following values are obtained:



Extraction nr	SiO_2	Al_2O_3	Fe_2O_3	mm per 100 g
1	7.0	7.3	18.2	oxidised soil
2	3.7	7.1	1.8	„ „
3	3.0	4.7	0.7	„ „
4	2.9	4.8	0.3	„ „

From the results of the analyses of the extracts, it appears clearly that by the first and the second extraction a surplus of the three components is dissolved. After that, the attack comes to a limit: the quantities of SiO_2 and Al_2O_3 , which are dissolved by the third and the fourth extraction, are respectively equal and therefore possibly originate from an Al-Fe-Si-complex which is left after the second extraction,

¹⁾ See: Methods, pag. 33.

and obviously possesses a smaller solubility in HCl than that, which was dissolved by the previous HCl-extractions. ¹⁾

Also the determinations of the adsorption-values of the HCl-residues furnish information which justify the supposition that after the second HCl-extraction an Al-(Fe-)Si-complex is left, which is apparently identical with that which results from the third and the fourth extraction: Whereas the adsorption capacity of the soil, which has once been extracted with HCl, still amounts to 20.4 M.E., and this value after the second extraction is reduced to 19.0 M.E., it remains after the third and the fourth extraction 18.6 and 18.4 i.e. practically equal to the adsorption-value after the second extraction.

TABLE 5.

ADSORPTION CAPACITY OF SOIL 12 (ETTEN) AFTER
REPEATED EXTRACTION

Extraction nr	Adsorption capacity in M.E. (Ca'') per 100 g of the residue	Adsorption capacity in M.E. (Ca'') calcu- lated per 100 g oxidised soil
1	20.4 ²⁾	18.9
2	19.0	17.2
3	18.6	16.5
4	18.4	16.0

When the Al-(Fe-)Si-skeleton, which is brought into solution by the quadruple HCl-extraction, — without taking in account the non-determined quantities SiO₂, which are separated insolubly in the residues by the HCl-treatments, — is reconstructed from the fourth extraction, the subsequent representation is obtained of the complex which was present before the extraction. (See: figure VI)

To begin with the quantities Al₂O₃ and SiO₂, which were dissolved by the fourth extraction, in the figure the values from table 4 are respectively added.

So, on line D, the quantities Al₂O₃ and SiO₂ are indicated,

¹⁾ Finally for „the total HCl-soluble Al-Fe-Si-complex”, according to the method of VAN BEMMELEN-HISSINK, is found a complex consisting of 53.1 mm Al₂O₃, 36.6 mm Fe₂O₃, and 151.0 mm SiO₂ per 100 g oxidised soil. See: pag. 99.

²⁾ That the adsorption-value after the first extraction amounts to 20.4 M.E., while in the previous series by an analogous determination 19.7 M.E. was found, is principally caused, apart from experimental errors, by the fact that in this series another quantity of the sample was used.

which were found in the fourth extract and these points therefore give an idea of the soil before the fourth extraction.

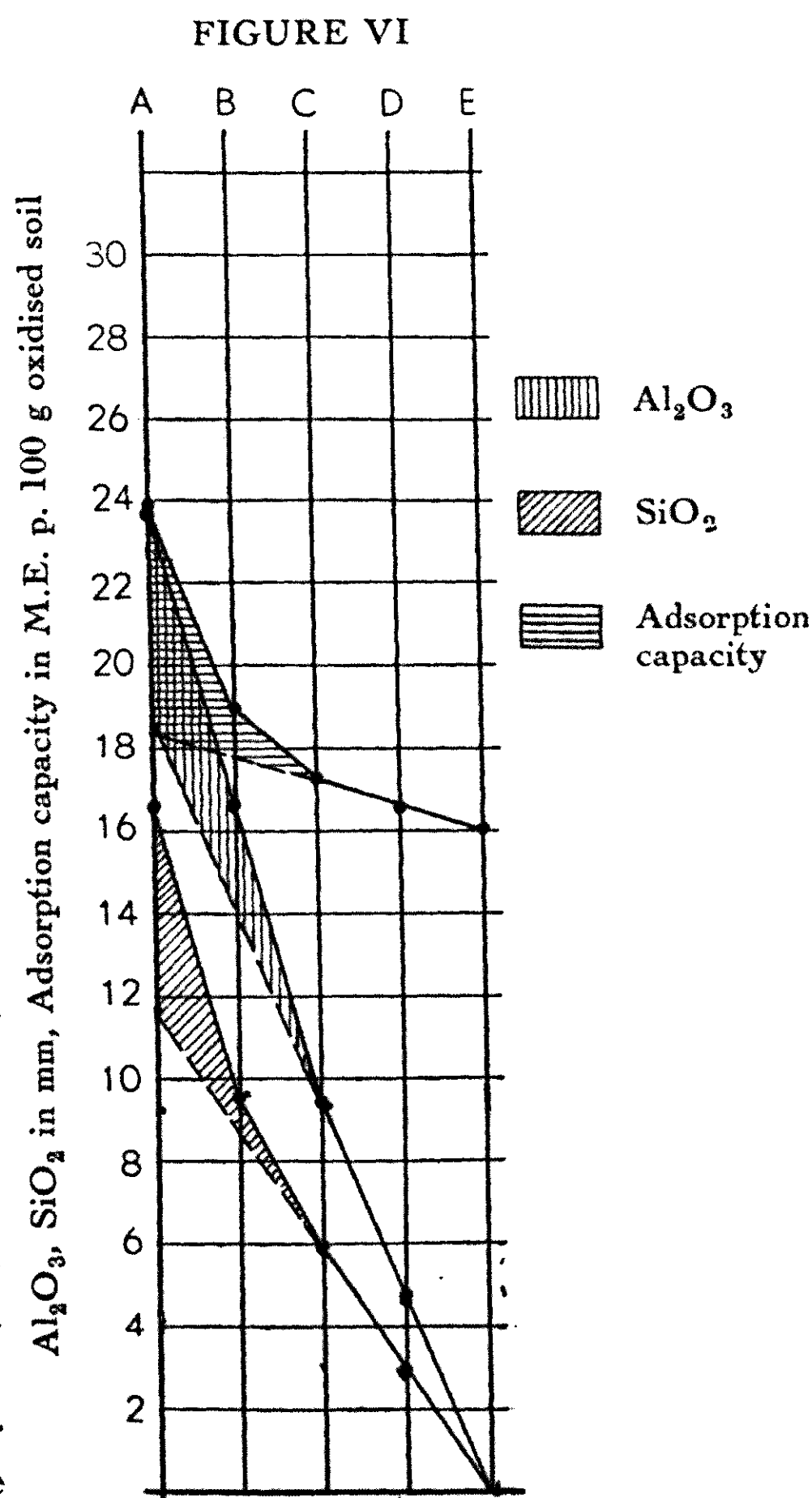
On line C the quantities of Al_2O_3 and SiO_2 , which were found in the fourth extract, plus the respective quantities which were dissolved by the third extraction are given so that the points on this line represent the soil before the third extraction.

Similarly the points on line B interpret the soil before the second extraction, while finally, on line A, the quantities Al_2O_3 and SiO_2 which in total were dissolved out of the soil by the quadruple HCl-extraction are shown.

The Fe_2O_3 -contents of the extracts are not concerned in the reconstruction; firstly, because the Fe-content of the complex after the second extraction is unimportant and secondly, because the small contents of Fe_2O_3 in the last two extracts do not allow one to decide whether a constant limit has been reached.

It is once more mentioned emphatically that in this reconstruction the SiO_2 -gel which has been left insolubly is not concerned, so that the SiO_2 -values are only parts of the quantities which were brought into solution by the HCl-extractions.

Finally the adsorption-values of table 5 can be represented graphically. On line D, on which are indicated the quantities Al_2O_3 and SiO_2 in mm that were dissolved by the fourth HCl-extraction and which gives a representation of the soil after the third extraction, the residual adsorption is indicated in M.E. per 100 g; just as on line E the residual adsorption after the fourth extraction, on line C the residual adsorption after the second extraction, on line B the residual adsorption after the first extraction and on line A the adsorption capacity of the original oxidised soil is indicated.



From the graphical reconstruction of the Al-Fe-Si-complex, which was brought into solution by the repeated HCl-extraction, it appears that by the two repetitions after the second HCl-extraction, the adsorption-values of the HCl-residues are decreased by equivalent very small amounts: 17.2→16.5 and 16.5→→16.0 M.E. per 100 g oxidised soil, whereas the quantities Al-Si-complex which are dissolved by these extractions are also equivalent.

The residues after the second, the third and after the fourth extraction, therefore agree completely in their adsorptive power and their relative solubility in HCl.

On the supposition that by the HCl-extraction no secondary changes have taken place in the residue which could influence the further attack by repeated extraction, the excess of Al_2O_3 and SiO_2 which is dissolved by the first and the second extraction, as compared with the subsequent repeated extractions, could be found by graphical extrapolation.¹⁾ This excess of Al_2O_3 and SiO_2 , plus the non-defined quantity of SiO_2 , which was separated insolubly by the HCl-extraction, and moreover possibly a certain quantity of Fe_2O_3 would then be responsible for the adsorption-excess of the original oxidised soil and the HCl-residue after the second extraction over the adsorption-values of the HCl-residues of the repeated extractions following afterwards. However as will be shown afterwards, on HCl-extraction appears a complication through which the repeated extraction is influenced.

The lower contents of Al^{+++} and Si^{++++} in the second, the third and the fourth extract, need not necessarily be a proof therefore of real decrease of material soluble in HCl under these conditions.

Meanwhile it remains imaginable, that the residual adsorption is caused by the SiO_2 -gel which has been separated insolubly during the HCl-extraction. It seems to be very improbable that this SiO_2 -gel would account for the total adsorption-value after the HCl-extraction, because it may be expected that in the residues, from the first up to the fourth, continually greater amounts of SiO_2 are found. After the first extraction a certain quantity SiO_2 -gel is left insolubly; this residue is now again extracted with HCl, during which a certain quantity of the Al-Fe-Si-compounds which are still present is decomposed, as again Al^{+++} and Si^{++++} are

¹⁾ It is assumed that the ions, which are present in the solution during the extraction, have no influence on the further attack.

present in the extract. During this second extraction, again a certain quantity of SiO_2 -gel will be separated, so that more SiO_2 -gel will be present in the residue after the second extraction than after the first.

This will appear to be so, when the residue of the single HCl-extraction is shaken with NaOH, sp.gr. 1.04, for 5 minutes at 50°C , according to the method of VAN BEMMELEN.¹⁾

If the residual adsorption had only been caused by the SiO_2 -gel, then an increase of the adsorption-values of the residues could be expected with repeated extraction. The opposite was found however. From the fact that the adsorption capacity of the residue after the third and the fourth extraction comes to a constant value, it may rather be deduced that only a very small amount of the adsorption-value of the residue is due to the SiO_2 -gel.

VAN BEMMELEN²⁾ proved by experiments with pure SiO_2 -gel, that this gel, together with alkali, is capable of forming a so-called „absorption-compound”. These compounds, according to him, consist of many molecules of strongly hydrated SiO_2 and a few molecules of alkali. As the ratio SiO_2 : alkali becomes smaller, the compound becomes more soluble and so he found that before one molecule KOH comes in contact with one molecule SiO_2 , the latter has gone into solution.

Provided the residue of the HCl-extraction is treated with lye, the SiO_2 which has been separated by the HCl-extraction is brought into solution and this method is therefore used to determine the SiO_2 , which has been separated insolubly by the HCl-extraction. Before VAN BEMMELEN introduced the NaOH-treatment of the HCl-residue, the analysis of the adsorption-complex of the soil was limited to that of the HCl-extract and it was always omitted to include in the analysis the SiO_2 -gel, which had been separated by the HCl-extraction.³⁾

In order to eliminate the influence of the SiO_2 -gel on the adsorption-value of the HCl-residue, experiments were carried out to show whether the removal of the SiO_2 -gel after the HCl-extraction, by means of the NaOH-treatment according to VAN BEMMELEN, affected the value of the residual adsorption. Moreover, from the Al_2O_3 -, Fe_2O_3 -, and SiO_2 -content of the HCl-

¹⁾ See: Methods, pag. 29.

²⁾ J. M. VAN BEMMELEN, Landw. Versuchsstat., 23, 288 etc. (1879).

³⁾ J. M. VAN BEMMELEN, Ztschr. f. anorg. Chemie, 42, 265 (1904).

extract, together with the SiO_2 -content of the subsequent NaOH-extract, the skeleton of the Al-Fe-Si-complex, which had been brought into solution, could be reconstructed. As it appeared after the NaOH-treatment that the adsorption-value of the HCl-NaOH-residue still amounted to about 75 % of that of the oxidised soil, an attempt was made to dissolve the adsorptive soil-particles, which were relatively less soluble in dilute HCl, by extraction of the residue with 50 % H_2SO_4 . By the NaOH-treatment following on this H_2SO_4 -extraction, it was again possible to remove the SiO_2 -gel which had been separated by this extraction and to reconstruct the Al-Fe-Si-complex which had been dissolved.

Scheme.

50 g of the oxidised soil 12 (Etten) were extracted for 30 minutes at 55°C , with 200 cc 6.6 % HCl per 10 g of soil ¹⁾ and the extract was analysed. ²⁾

From the HCl (1 \times)-residue, 40 g were treated with 200 cc NaOH (sp.gr. 1.04) per 10 g of the HCl (1 \times)-residue, for 5 minutes at 50°C ³⁾ and the extract was analysed. ⁴⁾ As usual, from the HCl (1 \times)-residue and also from the HCl(1 \times)-NaOH-residue, the adsorption-value was determined. ⁵⁾

From the HCl (1 \times)-NaOH-residue, afterwards, 30 g were extracted, for 30 minutes, at 55°C , with 200 cc 50 % H_2SO_4 per 10 g HCl (1 \times)-NaOH-residue and the extract was analysed.

From the H_2SO_4 -residue, 20 g were treated with 200 cc NaOH (sp.gr. 1.04) per 10 g H_2SO_4 -residue as usual and the extract was analysed.

From the H_2SO_4 -residue and also from the H_2SO_4 -NaOH-residue, the adsorption-value was found in the usual way.

The residue of the H_2SO_4 (1 \times)-NaOH-extraction was once more extracted in the same way with H_2SO_4 and the H_2SO_4 (2 \times)-residue treated with NaOH. The extracts were analysed.

From the H_2SO_4 (2 \times)- and from the H_2SO_4 (2 \times)-NaOH-residue, finally the residual adsorption was determined.

1) See: Methods, pag. 25.

2) See: Methods, pag. 26.

3) See: Methods, pag. 29.

4) See: Methods, pag. 29.

5) See: Methods, pag. 33.

TABLE 6.

REPEATED EXTRACTION OF SOIL 12 (ETTEN) WITH 6.6% HCL AND 50% H_2SO_4 , ALTERNATED WITH TREATMENTS WITH NaOH, SP. GR. 1.04

Extraction nr	Totally dissolved in % of the oxidised soil	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Expressed in mm per 100 g	Indication of the residue
1 (HCl)	7.0	7.0	7.3	18.2	oxidised soil	Residue Z ₁
1 (NaOH)	2.1	18.8	1.3	—	residue Z ₁	Residue L ₁
2 (H ₂ SO ₄)	3.6	1.2	12.7	7.8	residue L ₁	Residue Z ₂
2 (NaOH)	3.8	40.3	2.4	—	residue Z ₂	Residue L ₂
3 (H ₂ SO ₄)	2.5	0.0	7.2	1.3	residue L ₂	Residue Z ₃
3 (NaOH)	3.1	26.5	1.9	—	residue Z ₃	Residue L ₃

When the contents of the NaOH-extracts are calculated on the previous HCl- resp. H_2SO_4 -residues, the following values are obtained:

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	
<i>First extract:</i>				
1 (HCl)	7.0	7.3	18.2	mm p. 100 g oxidised soil
1 (NaOH)	17.5	1.2	—	„ „ 100 „ „ „
Total in the first extract:	24.5	8.5	18.2	„ „ 100 „ „ „
Ratio SiO ₂ : Al ₂ O ₃ = 2.9				
<i>Second extract:</i>				
2 (H ₂ SO ₄)	1.2	12.7	7.8	mm p. 100 g residue L ₁
2 (NaOH)	38.8	2.3	—	„ „ 100 „ „ L ₁
Total in the second extr.:	40.0	15.0	7.8	„ „ 100 „ „ L ₁
Ratio SiO ₂ : Al ₂ O ₃ = 2.7				
<i>Third extract:</i>				
3 (H ₂ SO ₄)	0.0	7.2	1.3	mm p. 100 g residue L ₂
3 (NaOH)	25.8	1.9	—	„ „ 100 „ „ L ₂
Total in the third extr.:	25.8	9.1	1.3	„ „ 100 „ „ L ₂
Ratio SiO ₂ : Al ₂ O ₃ = 2.8				

When finally the quantities of the extracts are calculated on „oxidised soil”, the following values are obtained:

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	
1st extr. (6.6% HCl)	24.5	8.5	18.2	mm p. 100 g oxidised soil
2d extr. (50% H ₂ SO ₄)	36.4	13.6	7.1	„ „ 100 „ „ „
3d extr. (50% H ₂ SO ₄)	21.8	7.7	1.1	„ „ 100 „ „ „
Totally dissolved	82.7	29.8	26.4	„ „ 100 „ „ „

Ratio SiO₂ : Al₂O₃ = 2.8

By extraction of the soil with 6.6% HCl, a complex appears to be dissolved in which the ratio SiO₂ : Al₂O₃ = 2.9 : 1. The subsequent extraction of the residue with H₂SO₄ also dissolves a complex of the same composition.

Apparently in this way the same soil-particles are attacked by the 6.6 % HCl-extraction as by the 50 % H₂SO₄-extraction. The strong H₂SO₄ however, dissolves absolutely much more Al-Si-complex than the dilute HCl. ¹⁾ Only the Fe₂O₃ is obviously dissolved in the main by the HCl-extraction.

By the second H₂SO₄-extraction, again a compound of the same SiO₂ : Al₂O₃-ratio is brought into solution. The absolute quantities however are smaller than those of the first H₂SO₄-extract.

Apparently after the previous HCl-NaOH-H₂SO₄-NaOH-extraction, the quantity of Al-Fe-Si-complex, which is soluble in acids under these conditions, has diminished.

The determination of the residual adsorption-values furnished the following results:

TABLE 7.

DETERMINATION OF THE RESIDUAL ADSORPTION-VALUES OF SOIL 12 (ETTEN), AFTER REPEATED EXTRACTION WITH 6.6% HCl AND 50 % H₂SO₄, ALTERNATED WITH TREATMENTS WITH NaOH SP. GR. 1.04

Residue:	Adsorption capacity in M.E. (Ca ⁺⁺) per 100 g of the residue:	Adsorption capacity in M.E. (Ca ⁺⁺) calculated per 100 g oxidised soil
Z ₁	20.2 ²⁾	18.8
L ₁	19.7	17.9
Z ₂	18.6	16.3
L ₂	17.4	14.7
Z ₃	18.1	14.9
L ₃	17.7	14.1

¹⁾ It must however be taken into consideration, that by the first extraction 3.8% and by the second extraction 1.9% of compounds other than Al-Fe-Si-compounds were dissolved out of the soil.

²⁾ See: note 2, pag. 42.

By the removal of the SiO_2 -gel from the HCl-residue, the residual adsorption decreases from 18.8 M.E. to 17.9 M.E.; moreover an Al-Fe-Si-compound which was present in the HCl-residue is attacked, because 1.2 mm Al_2O_3 are found in the extract.

The decrease of the adsorption-value to the amount of 0.9 M.E. therefore will be caused only partly by the SiO_2 -gel which is present in the HCl-residue.

When the residue of the HCl-NaOH-extraction is extracted with 50 % H_2SO_4 , the residual-adsorption decreases from 17.9 to 16.3 M.E.; by this extraction also an important amount of the Al-Fe-Si-complex is brought into solution. Moreover it appears from the subsequent NaOH-treatment, that the adsorption is still decreased by this, by $16.3 - 14.7 = 1.6$ M.E., only part of which is accounted for by the SiO_2 -gel which has been separated by the H_2SO_4 -extraction and is dissolved by the NaOH-treatment, whilst another part can be ascribed to the Al-Si-complex which is brought into solution by the NaOH-treatment: in the NaOH-extract viz. 2.1 mm Al_2O_3 are found. ¹⁾

On the second extraction with 50 % H_2SO_4 , it appears that the residual adsorption increases with regard to the H_2SO_4 -NaOH-residue. This increase must be ascribed to the SiO_2 -gel which has been separated by the repeated H_2SO_4 -extraction, because after the subsequent NaOH-extraction, the adsorption-value of the residue again decreases below the value of the residual adsorption before the repeated H_2SO_4 -extraction: $14.7 \rightarrow 14.1$ M.E.

In order to get an idea of the adsorption-value of SiO_2 -gel, which is separated by dilute HCl, a „Sodium-permutite according to GANSSEN” was treated for 30 minutes at 55°C , with 200 cc 7.3 % HCl per 10 g.

The HCl-residue from the subsequent NaOH-treatment appeared to consist of 73.4 % SiO_2 . ²⁾ The adsorption-value of the HCl-residue, defined in the same way as that of the soil, amounts to 51.5 M.E. per 100 g.

When only the SiO_2 -gel, which is present in the residue, is sup-

¹⁾ In the residue of the first H_2SO_4 -extraction, 40.3 mm SiO_2 per 100 g Z_2 -residue have been found. Calculated on the original soil, $0.93 \times 0.979 \times 0.964 \times 40.3 = 35.3$ mm. SiO_2 are present in the residue; in exactly the same way $0.93 \times 0.979 \times 0.964 \times 2.4 = 2.1$ mm Al_2O_3 are found in the subsequent NaOH-extract.

²⁾ Of the HCl-residue, 97.4% dissolves in lye. The remaining $97.4 - 73.4 = 24.0\%$ of the HCl-residue may have consisted principally of H_2O and a small quantity of Na-salts; only a trace of Al^{+++} was found in the SiO_2 -filtrate.

posed to be responsible for the residual adsorption, then the SiO_2 -gel adsorbs 0.69 M.E. (Ca^{++}) per g.

After the repeated H_2SO_4 -extractions, the H_2SO_4 -residues contain respectively 40.3 and 26.5 mm SiO_2 per 100 g (See table 6). The adsorption-value of this, under these conditions, can amount to: 2.42×0.69 and 1.59×0.69 or: 1.7 and 1.1 M.E. at the utmost.

However, in these cases, the influence of the SiO_2 -gel on the residual adsorption appears to be only $18.6-17.4 = 1.2$ and $18.1-17.7 = 0.4$ M.E. (see table 7). Similarly, by the HCl - NaOH -extraction, which preceded these H_2SO_4 -extractions, 18.8 mm SiO_2 per 100 g are present in the HCl -residue. The adsorption, that may be caused by this, amounts to $1.13 \times 0.69 = 0.8$ M.E., whereas by the NaOH -treatment, the residual adsorption is only decreased by $20.2 - 19.7 = 0.5$ M.E.

Subsequent experiments will show that, during the determination of the adsorption-value, viz. by the percolation with $(\text{CH}_3\text{COO})_2\text{-Ca}$ -solution, an important part of the SiO_2 -gel is dissolved out of the residue. ¹⁾

From these considerations the conclusion is drawn, that by extraction of the soil with dilute HCl , the influence of the SiO_2 -gel, which is present in the HCl -residue, on the residual adsorption is very small and thus can be neglected as regards this research.

Finally, it still could be supposed, that even after the NaOH -extraction a certain quantity of SiO_2 -gel is left in the residue, which then might be the cause of the residual adsorption of the NaOH -residues.

VAN BEMMELEN however, proved that before 1 mol. lye had come in contact with 1 mol. SiO_2 , the latter had completely been dissolved. ²⁾

When e.g. 40.3 mm SiO_2 are dissolved out of a soil-residue after the extraction with an acid, then by the extraction of the residue with 200 cc NaOH (sp.gr. 1.04), the ratio $\text{NaOH} : \text{SiO}_2$ in mols is:

$$\frac{2 \times 3.43}{40} : \frac{0.0403}{10} = 42 : 1,$$

¹⁾ See: table 21, pag. 86.

²⁾ See: pag. 17.

so that it may be accepted, that the SiO_2 -gel has gone quantitatively into solution.

The adsorption capacity of the residue, which remains after the HCl-extraction, is therefore caused by an adsorption-complex that either has remained, or has been formed again after the HCl-extraction.

By the extraction of the soil with 6.6 % HCl only 7 % of the soil dissolves in total ¹⁾, whereas by the subsequent extraction with 50 % H_2SO_4 , further 3.6 % of the residue is brought into solution. ¹⁾

36.2 % of the soil consists of particles $< 2 \mu$, so that it appears that the clay-fraction is rather resistant as regards attack with acids. This fact is in accordance with the results of BRADFIELD. ²⁾

Now the question is, which part of the quantities of Al^{+++} , Fe^{+++} and Si^{+++} , which are brought into solution by extraction with acids, originate from the clay-fraction of the soil. It seems very probable that also the coarser particles, be it to a less degree, contribute to the content of the extract, so far as they do not consist of quartz or of fragments of minerals, which are unattackable to acids. In order to define this influence, the fraction $< 2 \mu$ of soil 12 (Etten), was obtained by decantation, by means of the SIKORSKY-apparatus, so that it might be shown from extractions with HCl and the analyses of the extracts, how far the ratio $\text{SiO}_2 : \text{Al}_2\text{O}_3$ of this fraction agreed with that of the total soil.

From the results may be deduced whether or not the part, which is possibly dissolved out of the coarser fraction by the HCl-extraction, is of the same chemical composition as that of the clay-fraction of the soil.

A second question, which is decided by this experiment, is: by what soil-particles the residual adsorption after the extraction with an acid is caused: Does this adsorption originate from the parts of the clay-fraction which have been left unattacked by the acid-extraction or by a new adsorption-complex, which has been formed out of the coarser fractions during the extraction?

By determining the residual adsorption, after the extraction of the fraction $< 2 \mu$ with HCl, it will be obvious which of the two hypotheses is right.

¹⁾ See: table 6, pag. 47.

²⁾ R. BRADFIELD, Journ. of the Amer. Soc. of Agronomy, 17, 253 (1925), proved that an artificial gel of Al_2O_3 , Fe_2O_3 and SiO_2 completely dissolved in dilute HCl, whereas the clay-fraction of the soil only was dissolved to a relatively small amount by that treatment.

Scheme.

25 g of the fraction $< 2 \mu$ of the oxidised soil 12 (Etten) were extracted for 30 minutes at 55°C with 100 cc 6.6 % HCl per 5 g of the soil ¹⁾ and the extract was analysed ²⁾. From the HCl (1 \times)-residue, 20 g were treated with 100 cc NaOH (sp.gr. 1.04) per 5 g ³⁾ and the extract was analysed. ⁴⁾

The adsorption capacity of the HCl (1 \times)-NaOH-residue was found as usual. ⁵⁾

From the HCl (1 \times)-NaOH-residue, 15 g were extracted for 30 minutes at 55°C with 100 cc 6.6% HCl per 5 g of the residue ¹⁾ and the extract was analysed ²⁾.

From the HCl (2 \times)-residue, 10 g were treated with 100 cc NaOH (sp.gr. 1.04) per 5 g of the residue ³⁾ and the extract was analysed. ⁴⁾ From the HCl (2 \times)-NaOH-residue the adsorption capacity was determined. ⁵⁾

Finally, from the HCl (2 \times)-NaOH-residue, 5 g were extracted for 30 minutes at 55°C with 100 cc 6.6 % HCl ¹⁾ and the extract was analysed. ²⁾ The residue of the HCl (3 \times)-extraction was treated with 100 cc NaOH (sp.gr. 1.04) ³⁾ and the extract was analysed ⁴⁾. The adsorption capacity of the HCl (3 \times)-NaOH-residue afterwards was determined. ⁵⁾

TABLE 8.

REPEATED EXTRACTION OF THE FRACTION $< 2 \mu$ OF SOIL 12 (ETTEN), WITH 6.6% HCl ALTERNATED WITH TREATMENTS WITH NaOH (SP.GR. 1.04)

Extraction nr	Totally dissolved in % of the oxidised fraction $< 2 \mu$	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Expressed in: m.m. per 100 g	Indication of the residue
1 (HCl)	13.1	12.5	13.0	16.8	oxidised fraction $< 2 \mu$	Residue Z ₁
1 (NaOH)	4.2	25.8	1.2	—	Residue Z ₁	„ L ₁
2 (HCl)	5.2	13.8	16.7	5.9	„ L ₁	„ Z ₂
2 (NaOH)	3.0	39.5	2.4	—	„ Z ₂	„ L ₂
3 (HCl)	6.0	12.3	14.8	4.4	„ L ₂	„ Z ₃
3 (NaOH)	1.4	27.5	0.1	—	„ Z ₃	„ L ₃

¹⁾ See: Methods, pag. 25.

²⁾ See: Methods, pag. 26.

³⁾ See: Methods, pag. 29.

⁴⁾ See: Methods, pag. 29.

⁵⁾ See: Methods, pag. 33.

When the contents of the NaOH-extracts are calculated on the previous HCl-residue, the following values are obtained:

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	
<i>First extract:</i>				
1 (HCl)	12.5	13.0	16.8	mm p. 100 g oxid. fract. < 2 μ
1 (NaOH)	22.4	1.0	—	„ „ 100 „ „ „ < 2 μ
Total in the first extract	34.9	14.0	16.8	„ „ 100 „ „ „ < 2 μ
Ratio SiO ₂ : Al ₂ O ₃ = 2.5				

<i>Second extract:</i>				
2 (HCl)	13.8	16.7	5.9	mm p. 100 g residue L ₁
2 (NaOH)	37.4	2.3	—	„ „ 100 „ „ „ L ₁
Total in the sec. extract:	51.2	19.0	5.9	„ „ 100 „ „ „ L ₁
Ratio SiO ₂ : Al ₂ O ₃ = 2.7				

<i>Third extract:</i>				
3 (HCl)	12.3	14.8	4.4	mm p. 100 g residue L ₂
3 (NaOH)	27.1	0.1	—	„ „ 100 „ „ „ L ₂
Total in the third extr.	39.4	14.9	4.4	„ „ 100 „ „ „ L ₂
Ratio SiO ₂ : Al ₂ O ₃ = 2.6				

When finally the quantities of the extracts are calculated on „oxidised fraction < 2 μ”, the following values are obtained:

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	
1st extract	34.9	14.0	16.8	mm p. 100 g oxidised fraction < 2 μ
2d extract	42.6	15.8	4.9	„ „ 100 „ „ „ < 2 μ
3d extract	30.1	11.4	3.4	„ „ 100 „ „ „ < 2 μ
Totally dissolved	107.6	41.2	25.1	„ „ 100 „ „ „ < 2 μ
Ratio SiO ₂ : Al ₂ O ₃ = 2.6				

From the data of table 8, it appears indeed that by the repeated extraction of the fraction < 2 μ of soil 12 (Etten), a certain complex is attacked, in which the ratio SiO₂ : Al₂O₃ on an average is 2.6.

By the repeated extraction of the total soil 12 (Etten), (See: table 6) the average composition of the complex, which had been dissolved, was 2.8, so that apparently in the coarser fractions of

the soil are found Al-Fe-Si-compounds of relatively higher Si-contents, which are brought into solution by the acid-extraction. The composition of this Al-Fe-Si-complex can be calculated from the data of the tables 6 and 8. Because the fraction $< 2 \mu$ amounts to 36.2 % of the total soil, the share of the fraction $< 2 \mu$ in the 6.6 % HCl-extract of the total soil follows from table 8.

In the first extract of the fraction $< 2 \mu$ of soil 12 (Etten) were found: 34.9 mm SiO_2 , 14.0 mm Al_2O_3 and 16.8 mm Fe_2O_3 per 100 g $< 2 \mu$.

100 g of the soil contain 36.2 g $< 2 \mu$, so that the fraction $< 2 \mu$ contributes to the extract of the total soil:

$$\begin{aligned} 0.362 \times 34.9 &= 12.6 \text{ mm SiO}_2 \\ 0.362 \times 14.0 &= 5.1 \text{ mm Al}_2\text{O}_3 \\ 0.362 \times 16.8 &= 6.1 \text{ mm Fe}_2\text{O}_3 \end{aligned}$$

In an analogous extract of the total soil are present: 24.5 mm SiO_2 , 8.5 mm Al_2O_3 and 18.2 mm Fe_2O_3 per 100 g ¹⁾, so that by the extraction of the total soil with 6.6 % HCl is dissolved out of the fraction $> 2 \mu$:

$$\begin{aligned} 24.5 - 12.6 &= 11.9 \text{ mm SiO}_2 \\ 8.5 - 5.1 &= 3.4 \text{ mm Al}_2\text{O}_3 \\ \text{and } 18.2 - 6.1 &= 12.1 \text{ mm Fe}_2\text{O}_3 \end{aligned}$$

Out of the fraction $> 2 \mu$ thus an Al-Fe-Si-complex is brought into solution, in which the ratio $\text{SiO}_2 : \text{Al}_2\text{O}_3 = \frac{11.9}{3.4} = 3.5$. In the coarser fractions of the soil, the ratio $\text{SiO}_2 : \text{Al}_2\text{O}_3$ thus increases.

This result agrees on the information of VAN BEMMELEN ²⁾ that the ratio $\text{SiO}_2 : \text{Al}_2\text{O}_3$ is higher in sandy clay-soils (4–5), than in heavy clay-soils (± 3) and also with the conclusions of PUCHNER ³⁾, in consequence of a research concerning the distribution of the plant-feeding matters in the soil through the different fractions: that, going from the coarser to the finer fractions, the content of SiO_2 decreases whereas that of Al_2O_3 and Fe_2O_3 increases. GIESECKE ⁴⁾ also found on analysis of various fractions of six German clay-soils a continual increase of the ratio $\text{SiO}_2 : \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, going from clay to sand.

¹⁾ See: Table 6, pag. 47.

²⁾ J. M. VAN BEMMELEN, Ztschr. f. anorg. Chemie, 42, 269 (1904).

³⁾ PUCHNER, Landw. Versuchsstat., 66, 463 (1907).

⁴⁾ F. GIESECKE, Chemie d. Erde, 3, 106 (1928).

The determinations of the adsorption-values, after the repeated HCl-extractions, gave the following results:

TABLE 9.

DETERMINATION OF THE ADSORPTION CAPACITIES OF THE HCl-NaOH-RESIDUES OF THE FRACTION $< 2 \mu$ OF SOIL 12 (ETTEN), AFTER REPEATED EXTRACTION WITH 6.6% HCl, ALTERNATED WITH TREATMENTS WITH NaOH, (SP.GR. 1.04)

Residue	Adsorption capacity in M.E. (Ca ⁺⁺) p. 100 g of the residue	Adsorption capacity in M.E. (Ca ⁺⁺) calculated p. 100 g oxidised fraction $< 2 \mu$
L ₁	48.3	40.2
L ₂	50.1	38.3
L ₃	50.4	35.7

The adsorption capacity of the oxidised fraction $< 2 \mu$ of soil 12 (Etten), determined in the usual way ¹⁾, amounts to 41.6 M.E. (Ca⁺⁺) per 100 g $< 2 \mu$, whereas that of the oxidised soil amounts to 23.7 M.E. per 100 g ²⁾. Of these 23.7 M.E., $\frac{36.2}{100} \times 41.6 = 15.1$ M.E. is due to the fraction $< 2 \mu$, because the soil contains 36.2 % $< 2 \mu$, so that $23.7 - 15.1 = 8.6$ M.E. of the adsorption originates from the parts $> 2 \mu$, of which by the single HCl-extraction an Al-Fe-Si-complex was brought into solution having the ratio $\text{SiO}_2 : \text{Al}_2\text{O}_3 = 3.5 : 1$.

As an important quantity of Al_2O_3 , Fe_2O_3 and SiO_2 was found in the first HCl-NaOH-extract, viz. in total: $34.9 \times 0.060 + 14.0 \times 0.102 + 16.8 \times 0.160 = 6.21$ % of the soil (See: table 8), the adsorption capacity of the NaOH-residue only decreases with $41.6 - 40.2 = 1.4$ M.E.

By the second extraction, the adsorption capacity of the NaOH-residue is decreased again by 1.9 M.E., whereas $42.6 \times 0.060 + 15.8 \times 0.102 + 4.9 \times 0.160 = 4.95$ % of „ $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{SiO}_2$ ” of the HCl (1 \times)-residue has gone into solution.

Likewise in the third extraction, $30.1 \times 0.060 + 11.4 \times 0.102 + 3.4 \times 0.160 = 3.51$ % of Al-Fe-Si-complex is dissolved from the HCl (2 \times)-residue, while the adsorption capacity of the NaOH-residue decreases by 2.6 M.E.

The adsorption capacity of the original oxidised fraction $< 2 \mu$ amounts to 41.6 M.E., whereas that after the first HCl-NaOH-

¹⁾ See: Methods, pag. 33.

²⁾ See: pag. 39.

extraction amounts to 48.3 M.E. per 100 g of the residue; on the contrary, after the second extraction, the adsorption-complex appears to be of the same composition as that after the third extraction, because respectively: 50.1 and 50.4 M.E. per 100 g of the NaOH-residue are adsorbed.

This agrees with what had been found by the HCl-extraction of the total soil, viz.: after the second extraction, the adsorption of the subsequent residues reaches practically a constant value of 17.4 and 17.7 M.E. ¹⁾. Besides it is remarkable, that there a relation appears to exist between the adsorption-values after the second acid-extraction of the total soil and that of the fraction $< 2 \mu$ of the original oxidised soil.

When the adsorption-values of the residues of the total soil after the successive NaOH-extractions are multiplied by $\frac{100}{36.2}$ ²⁾, it appears that after the second and the third NaOH-extractions the adsorption-values of the fraction $< 2 \mu$, which have been calculated from those of the total soil, agree with the experimental values. ³⁾

TABLE 10.

Residue:	Total soil	Fraction $< 2 \mu$	
	Adsorption capacity in M.E. (Ca'') p. 100 g of the residue	Adsorption capacity in M.E. (Ca'') p. 100 g of the residue	Adsorption capacity in M.E. (Ca'') p. 100 g. of the residue, calculated from the residues of the extraction of the total soil
L ₁	19.7	48.3	54.4
L ₂	17.4	50.1	48.1
L ₃	17.7	50.4	48.9

Whereas in the original soil, the adsorption capacity of the fraction $< 2 \mu$ only amounts to $\frac{15.1}{23.7} \times 100 = 63.7\%$ of the total adsorption capacity of the soil and 36.3 % is caused by soil-particles $> 2 \mu$, it appears that after the second extraction the residual adsorption is completely defined by the fraction $< 2 \mu$.

Moreover, from the fact that the adsorption-value of the total-

¹⁾ See table 7, pag. 48.

²⁾ The fraction $< 2 \mu$ of soil 12 (Etten) amounts to 36.2%. See: pag. 80.

³⁾ The deviation falls within the experimental error.

soil-residue after the H_2SO_4 -extraction, calculated on 100 % of the fraction $< 2 \mu$, shows the adsorption capacity of the residue of the fraction $< 2 \mu$ after the 6.6 % HCl-extraction, it appears that the attack on the fraction $< 2 \mu$ with 50 % H_2SO_4 does not differ essentially compared with that with 6.6 % HCl.

Through this, it is also proved, that the influence of the fraction $> 2 \mu$ on the adsorption-values, is annulled after the second extraction.

When the Al-Fe-Si-complex, which is relatively easily soluble in HCl and which is present in the particles $<$ as well as $> 2 \mu$, is dissolved out of the soil by means of extraction with HCl and NaOH, then an Al-(Fe-)Si-complex is left which can be brought only very gradually into solution by HCl-extraction.

Conclusions.

By the extraction of a red clay-soil 12 (Etten) (fraction $< 2 \mu$ 36.2 %, fraction $< 10 \mu$ 53.9 %), the composition of the Al-Fe-Si-complex, which was brought into solution by various acid-extractions was determined, likewise the influence which the removal of that complex exerted on the adsorption capacity of the soil. From this research, the following conclusions may be drawn.

After the extraction of the soil with various concentrations of HCl, under the same conditions, the adsorption capacity of the HCl-residues appeared to be lower than the adsorption of the original oxidised soil. The higher the concentration of the HCl used for the extraction, the lower the residual adsorption; after the extraction with 3 % HCl however, a residue appeared to have been left that, as regards the residual adsorption, was identical with the residues after the extractions with higher concentrations HCl. This residual adsorption then still amounted to 83.6 % of the adsorption-value of the original oxidised soil.

It was suggested that the adsorption in the soil was caused by two Al-Fe-Si-compounds, differing as to their „relative solubility” in HCl, one of which being more resistant towards the attack with HCl. The latter then should be responsible for 83.6 % of the adsorption capacity of the original oxidised soil, i.e.: to the residual adsorption.

From this idea it was possible that the difference in resistance towards HCl of these two compounds was caused by an original difference in structure, while in the case of the more resistant

compound could also be thought of as a secondary impediment caused by the SiO_2 -gel, which had been separated insolubly by the HCl-extraction; this SiO_2 -gel then might envelop the soil-particles through which the further attack could possibly be impeded.

By repeated extraction it appeared that after the second extraction, in the third and the fourth extraction, equal amounts of the Al-(Fe-)Si-complex had been brought into solution.

From the determinations of the adsorption-values of the residues of the repeated extraction with HCl of the same concentration, it appeared that by the once repeated HCl-extraction, the residual adsorption was brought to a level, which by an eventual repetition of the extraction could not be exceeded.

In dissolving the SiO_2 -gel, which had been left insolubly in the HCl-residue after the HCl-extraction, by a subsequent NaOH-treatment according to VAN BEMMELEN, it was proved that the adsorption caused by the SiO_2 -gel was very small, as the adsorption capacity of the HCl-residue decreased only very little by this treatment. By means of this NaOH-treatment, it was also possible to define the composition of the Al-Si-complex which had been brought into solution by the HCl-extraction.

By repeated extraction with 50 % H_2SO_4 , under the same conditions, it appeared that the composition of the Al-(Fe-)Si-complex, which had been brought into solution by the repeated extraction, possessed the same $\text{SiO}_2 : \text{Al}_2\text{O}_3$ -ratio as that which had been brought into solution by the single 6.6 % HCl-extraction; obviously by the repeated H_2SO_4 -extraction the same Al-(Fe-)Si-complex is reached as that which had been attacked by the 6.6 % HCl-extraction.

Whereas by the directly repeated extraction of the soil ¹⁾ with 6.6 % HCl, without interpolation of an NaOH-treatment, in the second HCl-extract less Al-(Fe-)Si-complex had been dissolved than in the first, and finally by the third and subsequent extractions an equal amount of the respective components had been brought into solution, corresponding to a constant residual adsorption of the residues, it appeared that by interpolation of an NaOH-treatment between the first and the second HCl-extract of the fraction $< 2 \mu$ of the soil, in the second HCl-extract only

¹⁾ By the first extraction, in total 32.5 mm, by the second extraction, in total 13.6 mm. Al-Fe-Si-complex were dissolved. See: table 4, pag. 41.

a little less Al-(Fe-)Si-complex had been brought into solution than in the first.¹⁾ Finally by the third extraction, much less Al-(Fe-)Si-complex had been brought into solution than in the previous extractions, just as was found by the direct HCl-extraction.

By the repeated 50 % H₂SO₄-extraction of the total soil, alternated with NaOH-treatments, as well as by the use of an analogous scheme of extraction for the fraction $< 2 \mu$ with 6.6 % HCl, it appeared that after the second extraction a residue had been left of which the adsorption capacity, by repeated extraction, had reached a constant value; after the second extraction the adsorption-value decreases no more.

This agrees with the fact established by the directly repeated extraction of the soil: after the second extraction only an Al-(Fe-)Si-complex is left that, on account of the conditions of extraction used, shows a relatively smaller solubility than the Al-(Fe-)Si-complex that had been dissolved by the previous extractions. The residue after the second extraction contains an adsorption-complex that can only very gradually be decomposed by the acid-extraction.

From a repeated extraction of the fraction $< 2 \mu$ with 6.6 % HCl it could be deduced, that whereas before the extraction with acid the adsorption capacity of the soil only for 63.7 % could be ascribed to the fraction $< 2 \mu$, the residual adsorption after the once repeated HCl-extraction, alternated with and followed by an NaOH-treatment, was completely defined by the fraction $< 2 \mu$ of the original oxidised soil.

By this extraction, out of the fraction $< 2 \mu$ an Al-Fe-Si-complex was dissolved in which the SiO₂ : Al₂O₃-ratio was 2.6; for the total soil this ratio was 2.8 and so the Al-Fe-Si-complex that had been brought into solution by this extraction from the particles $> 2 \mu$ of the soil could be reconstructed.

This complex, for which the ratio SiO₂ : Al₂O₃ = 3.5 was calculated, apparently has been completely dissolved out of the soil after the second extraction because thereafter the adsorption

¹⁾ By the first extraction in total 65.7 mm, by the second extraction in total 63.3 mm. Al-Fe-Si-complex were brought into solution. See: table 8, pag. 53. By the first extraction however, 10.6%, by the second extraction 1.7% other than Al-Fe-Si-compounds were dissolved, so that apparently by the first extraction relatively more Al-Fe-Si-complex is dissolved than by the subsequent extraction, for all that. If therefore these other parts had been removed from the soil before, then in the first extract $100 : 89.4 \times 65.7 = 73.5$ mm and in the second extract $100 : 98.3 \times 63.3 = 64.4$ mm Al-Fe-Si-complex would have been dissolved.

capacity of the residue is completely defined by the fraction $< 2 \mu$ of the soil, in other words: the influence of the fraction $> 2 \mu$ on the residual adsorption has disappeared after the once repeated extraction.

When based on the preceding considerations an idea is developed of the structure of the inorganic adsorption-complex of soil 12 (Etten), the conception that the clay-fraction should consist chiefly of a complex-gel of aluminium-hydroxide and silica does not appear able to be maintained because it contradicts the results of the HCl-extractions.

On the contrary with GEDROIZ, one will have to accept still colloidal weathering-residues of a more complicated composition¹⁾ in the clay-fraction, which show a greater resistance towards the attack by HCl than the mutually coagulated Al-Si-gels.

The investigations by CUSHMAN²⁾ create the possibility of giving an interpretation of the facts:

The origin of the inorganic adsorptive soil-complex can be explained by the influence of mechanical, chemical and biological agents on the rock minerals.

CUSHMAN and HUBBARD³⁾, who eliminated the influence of the biological agent by performing their experiments on unweathered minerals, limited the chemical agent to the influence of H_2O and some electrolyte-solutions and imitated the mechanical influence by grinding the minerals.

By bringing a feldspath-powder in contact with H_2O , hydrolytic products, which are microscopically perceptible after colouring with phenolphthaleine, proceed from the surfaces of the feldspath-particles.

The hydrolysis of the mineral-fragments reaches a limit, because the film of hydrolytic products, which has been formed at the surface, protects the interior of the mineral against a further influence. The attack can be continued however, when through the action of electrolytes, by electrolysis or grinding, the film consisting of products of hydrolysis is removed.

According to CUSHMAN and HUBBARD, the hydrolysis occurs spontaneously when the feldspath-powder comes in contact with H_2O . From their investigations it can be concluded, that during

¹⁾ See: pag. 12.

²⁾ A. S. CUSHMAN, U.S. Dept. of Agr. Bur. of Chem. Bull., 92 (1905).

³⁾ A. CUSHMAN and P. HUBBARD, Dept. of Agr. Off. of publ. Roads Bull., 28 (1907).

the weathering of the natural feldspaths, H_2O plays a prominent part, whereas by BISCHOF ¹⁾ the opinion, which had hitherto prevailed, was established that the weathering was defined by the CO_2 -content of H_2O . RAMANN ²⁾ also is of opinion that the principal influence must be ascribed to H_2O though CO_2 and electrolytes also exercise their influences. He goes even further and limits the silicate-weathering to an effect of OH-ions, the hydrolysis as well as the CO_2 -attack resulting in an action of OH-ions. This conception agrees with the fact, discovered already in 1860 by WAY, that impure kaolin is capable of becoming soluble in HCl by the influence of alkali and alkali-carbonates. ³⁾

According to NIKLAS ⁴⁾, weakly dissociated silica arises from the silicates by the hydrolysis of H_2O and is separated insolubly; the reaction becomes alkaline. Insoluble colloidal silicates are formed, which are separated in a thin layer at the surfaces of the mineral particles and moreover bases are set free which are partly adsorbed by the colloidal film. ⁵⁾ This conception of the formation of a colloidal film round the mineral particles is therefore accepted at present by many investigators. ⁶⁾

By this conception, the clay-fraction of the soil can be considered to originate from the rock-building minerals. The influence of the weathering-agents begins at the surfaces of the particles and comes to a standstill because the weathering-products have accumulated on the surfaces of the mineral soil-particles apart from the small quantities which are led away by the soil-solution. From this moment, the weathering can only go on when the hydrolytic products are removed by the soil-solution, an action which will take place very regularly and continually under natural circumstances.

From this point of view, this hydrolytic film is a dynamic system, which is in equilibrium on the one side with the soil-solution and on the other with an unweathered crystalline kernel. ⁷⁾

¹⁾ G. BISCHOF, Lehrb. d. Chem. u. Phys. Geologie, 764 (1847) (Cited from H. NIKLAS, Chem. Verwitterung der Silikate u. Gesteine (1912).

²⁾ E. RAMANN, Centr. blt. f. Miner. Geol. u. Paleont., 233, 266 (1921).

³⁾ G. J. MULDER, De Scheikunde der bouwbare Aarde, 4, 367 (1860).

⁴⁾ H. NIKLAS, Chemische Verwitterung der Silikate und Gesteine, 139 (1912).

⁵⁾ According to CERNESCU. (See: note 5, pag. 14) this film is mono-molecular.

⁶⁾ L. E. JENKS, Journ. Phys. Chem., 33, 1733 (1929).

W. H. PIERRE and G. D. SCARSETH, Soil Sci., 31, 99 (1931).

N. C. CERNESCU, Anuarul Institutului Geologic al Românicilor, 16 (1931).

⁷⁾ MULDER says it in other words: „Het is zeker, dat van het in zoutzuur oplosbare, van het zeolitische deel, ook wordt verbruikt bij de vegetatie en wat verbruikt wordt moet hersteld worden, of de bouwgrond verarmt.” De Scheikunde der bouwbare Aarde, 4, 366 (1860).

With this hypothesis of the structure of the clay-fraction, the nature of the HCl-extraction can be explained completely now.

During the attack with dilute HCl, the hydrolytic products of the minerals will be dissolved and the mineral kernels, lying under it, will be attacked up to their respective solubilities in HCl and whether or not impeded by the SiO_2 -film, which was separated round the soil-particles during the HCl-extraction.

By the extraction with HCl of a higher concentration, besides the hydrolytic film also a greater part of the kernel lying under it will be dissolved. After the HCl-extraction, the residue is washed with H_2O and after drying on the steam-bath, percolated with an alkaline $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution ($\text{pH} \pm 8.5$): the surface of the mineral-fragments is hydrolyzed and apparently, the residue possesses a definite adsorption-capacity. At first, the adsorption of the residue decreases by extraction with an increasing concentration of HCl. However the residual adsorption reaches a definite value, under which it can not decrease by extraction with a higher concentration HCl under the same conditions as the others. Obviously, the total-surface and composition of the soil-particles remains unchanged by the extraction with HCl of higher concentrations, so that after these extractions a hydrolytic film will always be formed of the same quantity and quality.

Moreover it appears that the residual complex of the total soil is formed practically only by the particles $< 2 \mu$, because after the second extraction, there appears to be a clear dependence on the adsorption capacities of the residues of the total soil and those of the fraction $< 2 \mu$ after the corresponding extractions, whereas originally this connection does not exist. The interpretation of this fact is as follows: In the original soil, round the soil-particles $<$ and $> 2 \mu$, a film is found consisting of hydrolytic products originating from the minerals. By the repeated HCl-respectively H_2SO_4 -extraction, this film is brought into solution. The residue is treated with H_2O and a $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution through which treatment a hydrolytic film arises round the soil-particles. The adsorption of this residual complex appears to be completely defined by the fraction $< 2 \mu$ of the original soil.

To confirm this theory about the structure of the inorganic part of the adsorption-complex, which is present in the soil, proof is wanting only that after reaching a constant residual adsorption,

the total-surface of the particles of the residue is no more modified by a subsequent extraction.

Before attempting to establish this theory however, it seemed desirable to extend the analytical data to the soil-samples used in this research.

In the next chapter we shall see therefore if after extraction of these samples with HCl of a certain concentration, also a residual complex, which shows a constant residual adsorption, in comparison with that of a HCl-residue which has remained after extraction with HCl of a higher concentration, is left.

B. *Analogous Investigations with the different Soils*

Experimental Part.

The behaviour of the soils used in this investigation ¹⁾ on HCl-extraction as compared with soil 12 (Etten), which was examined in the preliminary work, is now the object of study.

The soils are all extracted with HCl of concentrations varying from 1 to ± 5 N., for 30 minutes at 55° C.²⁾ The HCl-extract is quantitatively analysed for SiO₂, Al₂O₃ and Fe₂O₃. ³⁾

After washing and drying, one part of the HCl-residue is used for the determination of the residual adsorption ⁴⁾, while another is treated for 5 minutes at 50° C in order to determine the SiO₂-gel which has been separated by the HCl-extraction. ⁵⁾

Moreover the adsorption capacities of the original oxidised soils, 8 ('s Heere Abtskerke), 9 (Hedel), 10 (Susteren) and 12 (Etten) are determined. It is impossible to determine the adsorption-values of the other original oxidised soils in the usual way, ⁶⁾ because they contain CaCO₃. ⁷⁾

¹⁾ See: Origin Description and Sampling of the Soils, pag. 20.

²⁾ See: Methods, pag. 25.

³⁾ See: Methods, pag. 26.

⁴⁾ See: Methods, pag. 33.

⁵⁾ See: Methods, pag. 29.

⁶⁾ See: Methods, pag. 33.

⁷⁾ See: table 2. Comparative adsorption-values of the original oxidised soils are afterwards determined in another way. (See: pag. 90, table 24).

TABLE 11.

Extracted with.....	3.0%	5.0%	7.3%	18.7%	HCl
SOIL 1 (Drieborg):					
Totally dissolved	11.4	12.4	12.9	15.5	% of the air-dry oxidised soil
Fe ₂ O ₃	9.9	11.1	12.5	19.4	mm p. 100 g air-dry oxidised soil
Al ₂ O ₃	6.4	7.7	7.5	11.3	„ „ 100 „ „ „ „
Sesquioxides	16.3	18.8	20.0	30.7	„ „ 100 „ „ „ „
SiO ₂	12.3	11.8	10.7	2.5	„ „ 100 „ „ „ „
SiO ₂ in the subsequent NaOH-extract	38.0	46.3	52.0	102.3	„ „ 100 „ „ HCl-residue
Do	33.5	40.6	45.3	86.4	„ „ 100 „ „ oxidised soil
Total SiO ₂	45.8	52.4	56.0	88.9	„ „ 100 „ „ „ „
Residual adsorption	0.76	0.82	0.80	0.81	M.E. (Ca'') per 4 g HCl-residue
SOIL 2 (Ulsda):					
Totally dissolved	8.5	8.8	9.1	10.7	% of the air-dry oxidised soil
Fe ₂ O ₃	13.4	15.1	15.8	23.8	mm p. 100 g air-dry oxidised soil
Al ₂ O ₃	5.6	6.2	7.0	11.0	„ „ 100 „ „ „ „
Sesquioxides	19.0	21.3	22.8	34.8	„ „ 100 „ „ „ „
SiO ₂	11.0	11.0	9.5	2.5	„ „ 100 „ „ „ „
SiO ₂ in the subsequent NaOH-extract	29.3	34.0	38.3	76.2	„ „ 100 „ „ HCl-residue
Do	26.8	31.0	34.8	68.0	„ „ 100 „ „ oxidised soil
Total SiO ₂	37.8	42.0	44.3	70.5	„ „ 100 „ „ „ „
Residual adsorption	0.98	1.01	1.00	0.98	M.E. (Ca'') per 4 g HCl-residue
SOIL 3 (St. Anna Par.):					
Totally dissolved	7.2	7.4	7.5	8.2	% of the air-dry oxidised soil
Fe ₂ O ₃	4.1	4.8	5.3	9.5	mm p. 100 g air-dry oxidised soil
Al ₂ O ₃	2.9	3.6	4.1	6.3	„ „ 100 „ „ „ „
Sesquioxides	7.0	8.4	9.4	15.8	„ „ 100 „ „ „ „
SiO ₂	6.7	7.0	6.7	2.3	„ „ 100 „ „ „ „
SiO ₂ in the subsequent NaOH-extract	14.0	15.7	17.8	36.7	„ „ 100 „ „ HCl-residue
Do	13.0	14.5	16.5	33.7	„ „ 100 „ „ oxidised soil
Total SiO ₂	19.7	21.5	23.2	36.0	„ „ 100 „ „ „ „
Residual adsorption	—	0.52	0.49	0.52	M.E. (Ca'') per 4 g HCl-residue

Extracted with.....	3.0%	5.0%	7.3%	18.7%	HCl
SOIL 4 (Menaldum):					
Totally dissolved	4.7	4.7	4.8	5.2	% of the air-dry oxidised soil
Fe ₂ O ₃	2.8	3.3	3.8	7.0	mm p. 100 g air-dry oxidised soil
Al ₂ O ₃	3.2	3.6	4.2	6.0	„ „ 100 „ „ „ „
Sesquioxides	6.0	6.9	8.0	13.0	„ „ 100 „ „ „ „
SiO ₂	5.0	5.6	5.6	2.3	„ „ 100 „ „ „ „
SiO ₂ in the subsequent NaOH-extract	14.2	14.0	17.7	28.2	„ „ 100 „ „ HCl-residue
Do	13.5	13.3	16.8	26.7	„ „ 100 „ „ oxidised soil
Total SiO ₂	18.5	18.9	22.4	29.0	„ „ 100 „ „ „ „
<i>Residual adsorption</i>	0.39	0.42	0.43	0.39	M.E. (Ca'') per 4 g HCl-residue
SOIL 5 (Zwaag):					
Totally dissolved	9.9	10.0	10.1	10.5	% of the air-dry oxidised soil
Fe ₂ O ₃	5.7	6.6	6.7	11.9	mm p. 100 g air-dry oxidised soil
Al ₂ O ₃	3.8	4.3	4.4	7.3	„ „ 100 „ „ „ „
Sesquioxides	9.5	10.9	11.1	19.2	„ „ 100 „ „ „ „
SiO ₂	8.0	9.0	8.0	2.3	„ „ 100 „ „ „ „
SiO ₂ in the subsequent NaOH-extract	19.3	20.2	24.0	50.2	„ „ 100 „ „ HCl-residue
Do	17.4	18.2	21.6	44.9	„ „ 100 „ „ oxidised soil
Total SiO ₂	25.4	27.2	29.6	47.2	„ „ 100 „ „ „ „
<i>Residual adsorption</i>	0.76	0.72	0.78	0.73	M.E. (Ca'') per 4 g HCl-residue
SOIL 6 (Wilhelmina-dorp):					
Totally dissolved	18.2	18.3	18.4	19.1	% of the air-dry oxidised soil
Fe ₂ O ₃	7.4	8.9	9.9	15.5	mm p. 100 g air-dry oxidised soil
Al ₂ O ₃	2.6	2.5	3.9	4.7	„ „ 100 „ „ „ „
Sesquioxides	10.0	11.4	13.8	20.2	„ „ 100 „ „ „ „
SiO ₂	9.2	9.2	9.5	2.3	„ „ 100 „ „ „ „
SiO ₂ in the subsequent NaOH-extract	18.0	22.0	24.8	54.1	„ „ 100 „ „ HCl-residue
Do	14.7	18.0	20.2	43.8	„ „ 100 „ „ oxidised soil
Total SiO ₂	23.9	27.2	29.7	46.0	„ „ 100 „ „ „ „
<i>Residual adsorption</i>	0.78	0.79	0.80	0.77	M.E. (Ca'') per 4 g HCl-residue

Extracted with.....	3.0%	5.0%	7.3%	18.7%	HCl
SOIL 7 (Rietveld):					
Totally dissolved	7.1	7.2	7.4	8.1	% of the air-dry oxidised soil
Fe ₂ O ₃	12.6	13.6	15.0	22.0	mm p. 100 g air-dry oxidised soil
Al ₂ O ₃	5.4	6.1	6.1	10.4	„ „ 100 „ „ „ „
Sesquioxides	18.0	19.7	21.1	32.4	„ „ 100 „ „ „ „
SiO ₂	5.0	5.3	6.2	2.8	„ „ 100 „ „ „ „
SiO ₂ in the subsequent NaOH-extract	16.7	18.3	20.4	36.7	„ „ 100 „ „ HCl-residue
Do	15.5	17.0	18.9	33.7	„ „ 100 „ „ oxidised soil
Total SiO ₂	20.5	22.3	25.1	36.5	„ „ 100 „ „ „ „

Residual adsorption 0.90 1.00 0.96 0.99 M.E. (Ca⁺⁺) per 4 g HCl-residue

SOIL ('s Heere Abtskerke):

Totally dissolved	2.8	2.9	3.0	3.5	% of the air-dry oxidised soil
Fe ₂ O ₃	3.8	4.2	4.8	8.5	mm p. 100 g air-dry oxidised soil
Al ₂ O ₃	1.2	2.0	2.7	4.0	„ „ 100 „ „ „ „
Sesquioxides	5.0	6.2	7.5	12.5	„ „ 100 „ „ „ „
SiO ₂	3.2	3.3	4.7	2.2	„ „ 100 „ „ „ „
SiO ₂ in the subsequent NaOH-extract	9.7	10.8	11.3	23.3	„ „ 100 „ „ HCl-residue
Do	9.4	10.4	11.0	22.5	„ „ 100 „ „ oxidised soil
Total SiO ₂	12.6	13.7	15.7	24.7	„ „ 100 „ „ „ „

Residual adsorption 0.35 – 0.36 0.39 M.E. (Ca⁺⁺) per 4 g HCl-residue

Adsorption capacity of the original oxidised soil: 0.44 M.E. (Ca⁺⁺) per 4 g.

SOIL 9 (Hedel):

Totally dissolved	2.2	2.4	2.7	3.9	% of the air-dry oxidised soil
Fe ₂ O ₃	5.2	6.0	6.4	10.4	mm p. 100 g air-dry oxidised soil
Al ₂ O ₃	2.5	3.3	3.6	5.7	„ „ 100 „ „ „ „
Sesquioxides	7.7	9.3	10.0	16.1	„ „ 100 „ „ „ „
SiO ₂	4.5	5.0	4.7	1.8	„ „ 100 „ „ „ „
SiO ₂ in the subsequent NaOH-extract	8.3	8.7	9.7	21.7	„ „ 100 „ „ HCl-residue
Do	8.1	8.5	9.4	20.8	„ „ 100 „ „ oxidised soil
Total SiO ₂	12.6	13.5	14.1	22.6	„ „ 100 „ „ „ „

Residual adsorption – 0.40 0.38 0.33 M.E. (Ca⁺⁺) per 4 g HCl-residue

Adsorption capacity of the original oxidised soil: 0.46 M.E. (Ca⁺⁺) per 4 g.

Extracted with.....	3.0%	5.0%	7.3%	18.7%	HCl
SOIL 10 (Susteren):					
Totally dissolved	4.7	4.9		6.0	% of the air-dry oxidised soil
Fe ₂ O ₃	7.7	8.7		14.7	mm p. 100 g air-dry oxidised soil
Al ₂ O ₃	4.3	5.1		9.7	„ „ 100 „ „ „ „
Sesquioxides	12.0	13.8		24.4	„ „ 100 „ „ „ „
SiO ₂	4.5	5.2		2.3	„ „ 100 „ „ „ „
SiO ₂ in the subsequent NaOH-extract	10.2	11.2		24.2	„ „ 100 „ „ HCl-residue
Do	9.7	10.6		22.7	„ „ 100 „ „ oxidised soil
Total SiO ₂	14.2	15.8		25.0	„ „ 100 „ „ „ „
Residual adsorption	0.49	0.54		0.59	M.E. (Ca'') per 4 g HCl-residue
Adsorption capacity of the original oxidised soil: 0.63 M.E. (Ca'') per 4 g					
SOIL 11 (IJzendoorn):					
Totally dissolved	4.1	4.5	4.9		% of the air-dry oxidised soil
Fe ₂ O ₃	4.3	5.3	6.5		mm p. 100 g air-dry oxidised soil
Al ₂ O ₃	4.8	5.4	6.9		„ „ 100 „ „ „ „
Sesquioxides	9.1	10.7	13.4		„ „ 100 „ „ „ „
SiO ₂	6.2	7.0	7.5		„ „ 100 „ „ „ „
SiO ₂ in the subsequent NaOH-extract	12.3	12.0	12.9		„ „ 100 „ „ HCl-residue
Do	11.8	11.5	12.3		„ „ 100 „ „ oxidised soil
Total SiO ₂	18.0	18.5	19.8		„ „ 100 „ „ „ „
Residual adsorption	0.52	0.53	0.55		M.E. (Ca'') per 4 g HCl-residue
SOIL 12 (Etten):					
Totally dissolved			7.7	8.6	% of the air-dry oxidised soil
Fe ₂ O ₃			18.1	26.6	mm p. 100 g air-dry oxidised soil
Al ₂ O ₃			8.4	12.0	„ „ 100 „ „ „ „
Sesquioxides			26.5	38.6	„ „ 100 „ „ „ „
SiO ₂			6.3	2.8	„ „ 100 „ „ „ „
SiO ₂ in the subsequent NaOH-extract			17.5	32.4	„ „ 100 „ „ HCl-residue
Do			16.2	29.6	„ „ 100 „ „ oxidised soil
Total SiO ₂			22.5	32.4	„ „ 100 „ „ „ „
Residual adsorption			0.77	0.79	M.E. (Ca'') per 4 g HCl-residue
Adsorption-capacity of the original oxidised soil: 0.94 M.E. (Ca'') per 4 g					

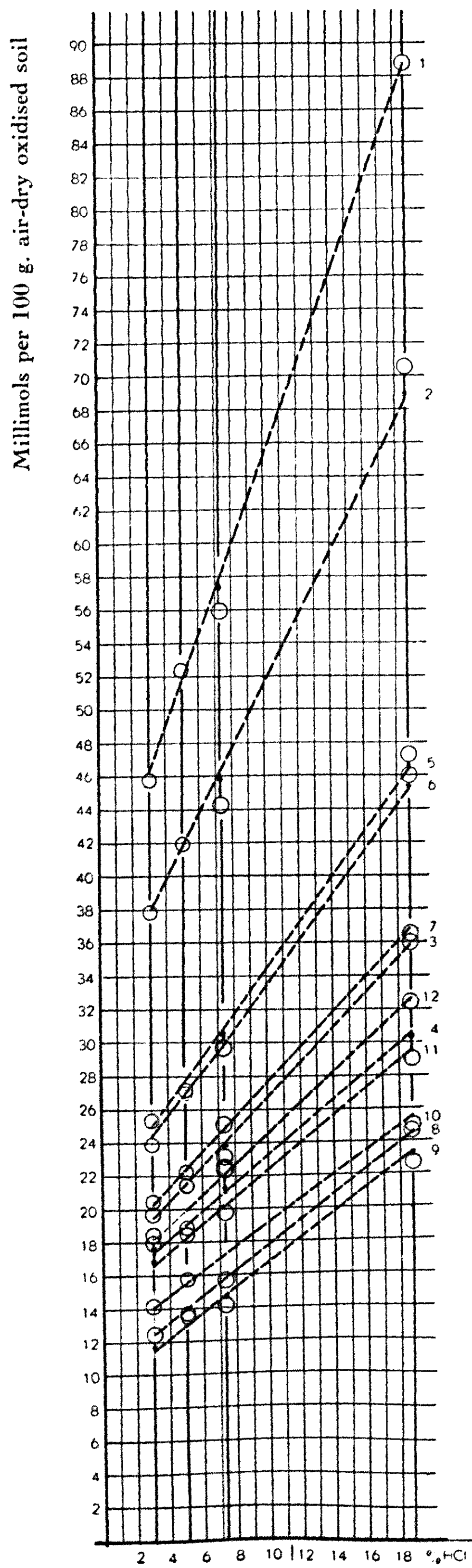
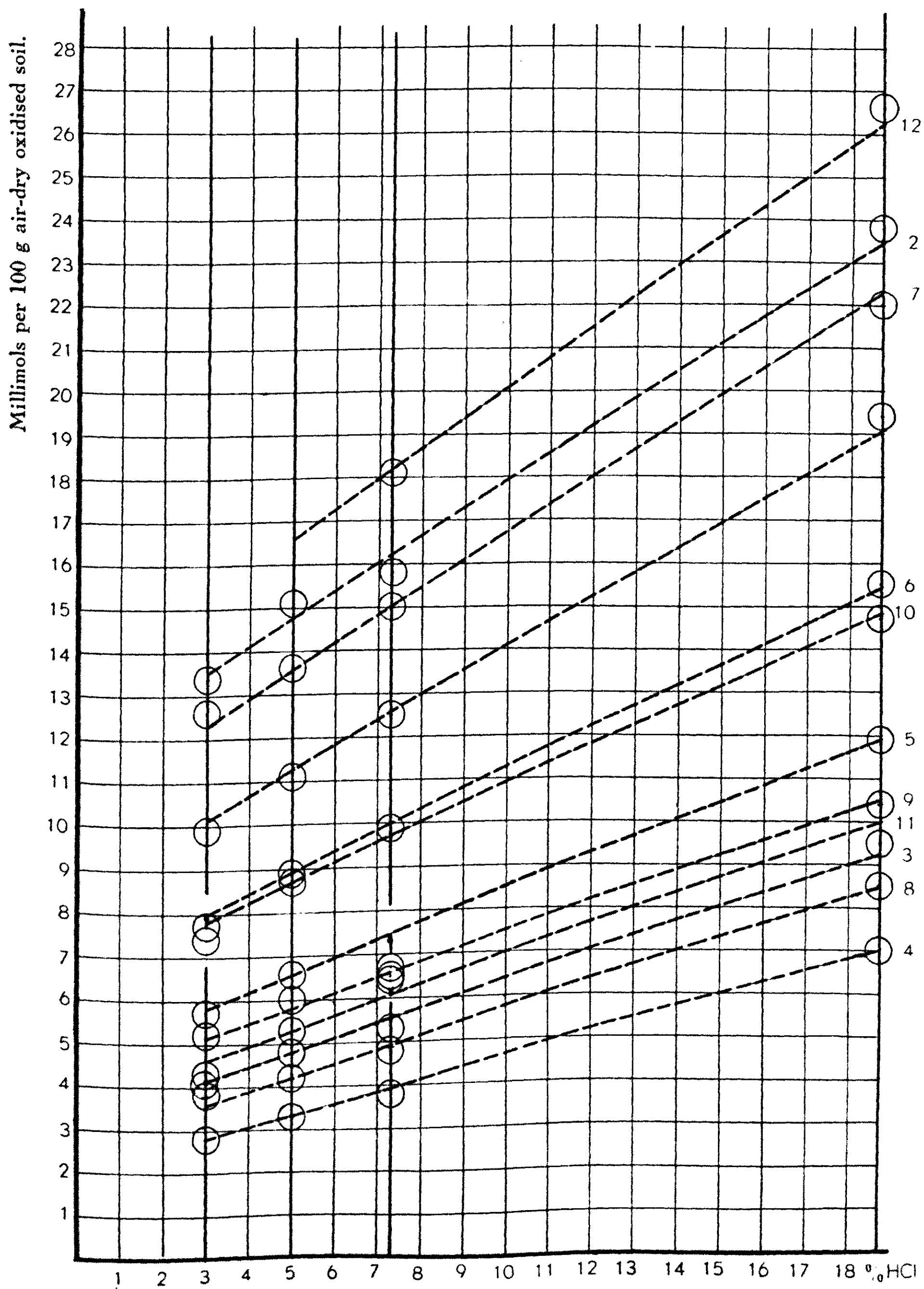


FIGURE VII.
Millimols SiO_2 .

FIGURE VIII. Millimols *Sesquioxides*.



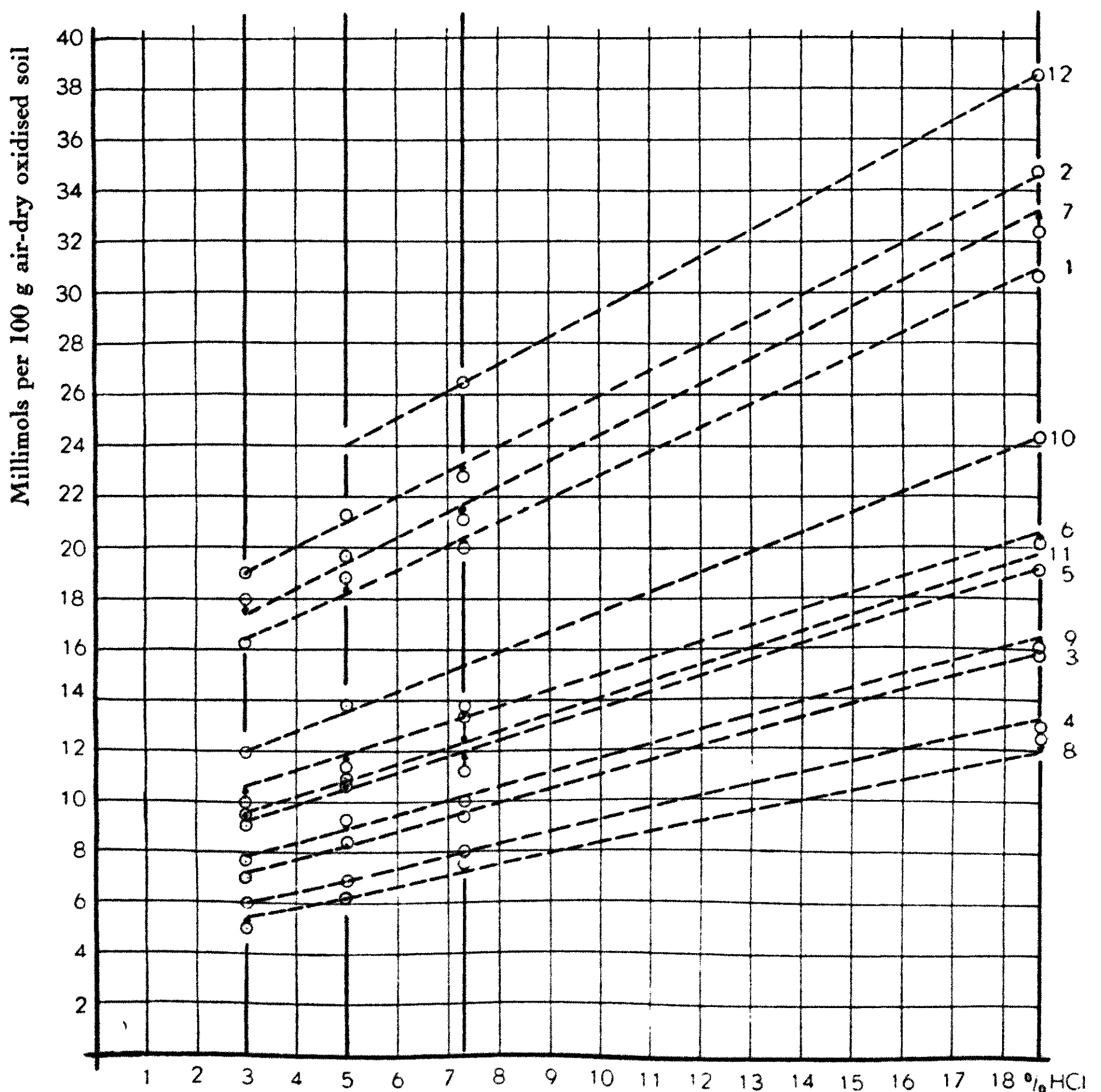
Conclusions

When these data are represented graphically, the following idea is obtained of the attack:

From the figures VII and VIII it appears that the quantities „SiO₂” and „Al₂O₃ + Fe₂O₃”, which are dissolved during the HCl-extraction, increase proportionally with the concentration of the solvent and that this method of HCl-extraction influences all soils in exactly the same way.

Soil 12 (Etten) which had been chosen for the preliminary investigations can therefore be compared with the other soils, in all respects, in its behaviour towards the HCl-extraction under these conditions.

FIGURE IX. Millimols Fe₂O₃.



The ratio $\text{SiO}_2 : \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, characteristic of the Al-Fe-Si-complex, which is brought into solution by the HCl-extraction, is calculated from the graphically corrected values from the figures, together with the ratio $\text{SiO}_2 : \text{Al}_2\text{O}_3$; before calculating the Al_2O_3 -values from the corrected sesquioxide-values however, the Fe_2O_3 -values are corrected graphically.

TABLE 12.

GRAPHICALLY CORRECTED VALUES ¹⁾

Soil Nr	Concentrat- ion HCl.	SiO ²⁾ total.	Sesqui- oxides ²⁾	Fe ₂ O ₃ ²⁾	Al ₂ O ₃ ²⁾	SiO ₂	SiO ₂
						Sesq. ox.	Al ₂ O ₃ .
1	3.0%	46.3	16.4	10.1	6.3	2.8	7.3
	5.0%	51.7	18.2	11.3	6.9	2.8	7.5
	7.3%	57.8	20.4	12.6	7.8	2.8	7.4
	18.7%	88.8	30.9	19.1	11.8	2.9	7.5
2	3.0%	37.9	19.0	13.5	5.5	2.0	6.9
	5.0%	41.9	21.0	14.8	6.2	2.0	6.8
	7.3%	46.3	23.3	16.2	7.1	2.0	6.5
	18.7%	68.7	34.6	23.5	11.1	2.0	6.2
3	3.0%	19.5	7.2	4.1	3.1	2.7	6.3
	5.0%	21.5	8.3	4.8	3.5	2.6	6.1
	7.3%	23.9	9.5	5.5	4.0	2.5	6.0
	18.7%	35.8	15.8	9.3	6.5	2.3	5.5
4	3.0%	17.4	6.0	2.8	3.2	2.9	5.4
	5.0%	19.1	6.9	3.3	3.6	2.8	5.3
	7.3%	21.0	8.0	3.9	4.1	2.6	5.1
	18.7%	30.6	13.3	7.0	6.3	2.3	4.8
5	3.0%	25.0	9.3	5.8	3.5	2.7	7.1
	5.0%	27.7	10.5	6.6	3.9	2.6	7.1
	7.3%	30.9	12.0	7.5	4.5	2.6	6.9
	18.7%	46.4	19.2	11.9	7.3	2.4	6.4
6	3.0%	24.4	10.6	8.0	2.6	2.3	9.4
	5.0%	27.0	11.9	8.9	3.0	2.3	9.0
	7.3%	30.0	13.4	10.0	3.4	2.2	8.8
	18.7%	45.2	20.6	15.4	5.2	2.2	8.7
7	3.0%	20.3	17.4	12.3	5.1	1.2	4.0
	5.0%	22.5	19.4	13.6	5.8	1.2	3.9
	7.3%	24.9	21.7	15.0	6.7	1.2	3.7
	18.7%	36.8	33.1	22.3	10.8	1.1	3.4

Soil Nr	Concentrat- ion HCl	SiO ²) total.	Sesqui- oxides ²)	Fe ₂ O ₃ ²)	Al ₂ O ₃ ²)	SiO ₂	SiO ₂
						Sesq. ox.	Al ₂ O ₃
8	3.0%	12.5	5.4	3.6	1.8	2.3	6.9
	5.0%	14.0	6.3	4.2	2.1	2.2	6.7
	7.3%	15.8	7.3	4.9	2.4	2.2	6.6
	18.7%	24.6	12.1	8.5	3.6	2.0	6.8
9	3.0%	11.6	7.9	5.1	2.8	1.5	4.1
	5.0%	13.1	8.9	5.8	3.1	1.5	4.1
	7.3%	14.8	10.2	6.6	3.6	1.4	4.1
	18.7%	23.4	16.4	10.5	5.9	1.4	4.0
10	3.0%	14.0	12.0	7.8	4.2	1.2	3.3
	5.0%	15.5	13.6	8.7	4.9	1.1	3.2
	7.3%	17.2	15.4	9.7	5.7	1.1	3.0
	18.7%	25.5	24.3	14.8	9.5	1.0	2.7
11	3.0%	16.6	9.6	4.6	5.0	1.7	3.3
	5.0%	18.3	11.0	5.3	5.7	1.7	3.2
	7.3%	20.2	12.4	6.1	6.3	1.6	3.2
	18.7%	29.6	19.8	10.0	9.8	1.5	3.0
12	5.0%	20.0	24.0	16.6	7.4	0,8	2.7
	7.3%	22.1	26.5	18.2	8.3	0,8	2.7
	18.7%	32.6	38.6	26.3	12.3	0.8	2.6

¹) See: Figures VII, VIII and IX.

²) In mm p. 100 g air-dry oxidised soil.

From table 12 it follows that the ratio SiO₂: sesquioxides is constant on extraction with HCl of various concentrations, which means that in these HCl-extractions the same Al-Fe-Si-complex or the same mixture of Al-Fe-Si-compounds is attacked. Only with the soils 3 (St. Anna Parochie), 4 (Menaldum) and 5 (Zwaag), a slight decrease of the values can be stated, possibly pointing to the presence of „free” SiO₂ in the soil and also to the attack of compounds with relatively lower SiO₂-contents by the HCl of higher concentration. It cannot be settled if really „free” SiO₂ is found in the soils, because by the direct treatment of the oxidised soils with NaOH, in order to dissolve this „free” SiO₂, ¹) Al⁺⁺⁺ was always found in the NaOH-extract, so that apparently also the complex is attacked by this treatment. ²) By these extractions only

¹) See: Methods, pag. 29.

²) Soil 2 (Ulsda): 3.8 mm SiO₂ p. 100 g oxidised soil.
Soil 9 (Hedel): 5.1 mm SiO₂ p. 100 g oxidised soil.

very small quantities of SiO_2 are dissolved, notwithstanding the decomposition of the complex.

It seems very improbable that by the higher HCl-concentrations compounds should be attacked with relatively lower SiO_2 -contents, because it has been found by VAN BEMMELEN that the „weathering-silicate” is more easily soluble the more basic it is. ¹⁾

It is obvious therefore, that the deviations are due to experimental error.

Further it follows from the tables that the ratio SiO_2 : sesquioxides differs substantially for the various soils: the extremes are 0.8 and 2.8.

VAN BEMMELEN also stated that in the Dutch alluvial clay-soils, which he examined, only one „weathering-silicate”, which is soluble in HCl, is found and which by extraction under different conditions is brought into solution very regularly. ²⁾ Moreover, the ratio SiO_2 : Al_2O_3 did not appear to be a single constant number, as it varied from 2.5–3.5 for heavy to 3.5–5.0 for sandy clay-soils. ³⁾

From table 12 it can be concluded, that in the extracts with different HCl-concentrations, the ratios SiO_2 : Al_2O_3 only vary a little for any one soil. In general the ratio decreases a little as the attack becomes more intense. As, moreover, the ratios SiO_2 : sesquioxides are constant in the differing HCl-extracts, one might conclude to a replacement of the Fe^{+++} by Al^{+++} in the extract as the attack becomes more intense. The average values of these SiO_2 : Al_2O_3 -ratios however vary for the different soils from about 7.4 to 2.7, so that apparently the variation is greater than was accepted by VAN BEMMELEN.

By many investigators such as HARDY ⁴⁾, ROBINSON and HOLMES ⁵⁾, ANDERSON and MATTSON ⁶⁾, PARKER and PATE ⁷⁾, BAVER and SCARSETH ⁸⁾, BENNETT ⁹⁾, etc., the ratio SiO_2 : $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ is pre-

¹⁾ J. M. VAN BEMMELEN, Ztschr. f. anorg. Chemie, 42, 287 (1904).

²⁾ J. M. VAN BEMMELEN, Ztschr. f. anorg. Chemie, 42, 287 (1904); For soils, which have been formed under other circumstances, VAN BEMMELEN found different ratios SiO_2 : Al_2O_3 for the same soil, by extraction with HCl of various concentrations. These different ratios SiO_2 : Al_2O_3 all represent, according to him, a certain stadium of weathering of a silicate.

³⁾ J. M. VAN BEMMELEN, Ztschr. f. anorg. Chemie, 42, 269 (1904).

⁴⁾ F. HARDY, Journ. of Agr. Sci., 13, 243 (1923).

⁵⁾ W. ROBINSON and R. HOLMES, U. S. Dept. Agr. Bull., 1311 (1924).

⁶⁾ SANTE MATTSON, Journ. of the Amer. Soc. of Agron., 18, 469 (1926).

M. ANDERSON and SANTE MATTSON, U.S. Dept. Agr. Bull., 1452 (1926).

⁷⁾ F. PARKER and W. PATE, Journ. of the Amer. Soc. of Agron., 18, 474 (1926).

W. PATE, Soil Sci., 20, 329 (1925).

⁸⁾ L. BAVER and G. SCARSETH, Soil Sci., 31, 168 (1931).

⁹⁾ H. BENNETT, Soil Sci., 21 (1926).

ferred to the ratio $\text{SiO}_2 : \text{Al}_2\text{O}_3$, founded on the opinion that also the Fe^{+++} would take part in the building of the „weathering-silicate”; others, on the contrary, as JOSEPH and HANCOCK ¹⁾, CROWTHER ²⁾, GANSSEN ³⁾ etc., maintain the $\text{SiO}_2 : \text{Al}_2\text{O}_3$ -ratio thus denying the essential significance of the Fe^{+++} with respect to the construction of the „weathering-silicate”. The constancy of the SiO_2 : sesquioxides-ratios in the different HCl-extracts for the same soil, in connection with the progress of the corresponding $\text{SiO}_2 : \text{Al}_2\text{O}_3$ -ratios however make it probable that the Fe^{+++} does not appear in the soil as a „free” Fe-compound, but is also involved in the construction of the Al-Fe-Si-complex.

The adsorption-values of the HCl-residues also show a corresponding progression for all soils. Notwithstanding the extraction with HCl of a higher concentration, the residue appears to retain a constant residual adsorption.

From figure X ⁴⁾, in which the progression of the adsorption-values of the HCl-residues after the different HCl-extractions is indicated, it appears that after a decline of the adsorption capacity of the original soils by the extraction with 3 % HCl, the adsorption-value of the 3 % HCl-residue does not decrease any more by extraction with HCl of a higher concentration; in some cases even a small increase occurs, caused by the SiO_2 -gel which has been left after the HCl-extraction. ⁵⁾ After extraction of the soil with 3 % HCl, the residual adsorption thus reaches a limit under which it cannot decrease any more by extraction of the soil with a higher concentration of HCl, under these conditions.

All together it can be concluded, that all Dutch clay-soils which are concerned in this research behave in a completely analogous way with respect to HCl-extraction.

¹⁾ A. JOSEPH and J. HANCOCK, Journ. of the Chem. Soc., 125 (1888).

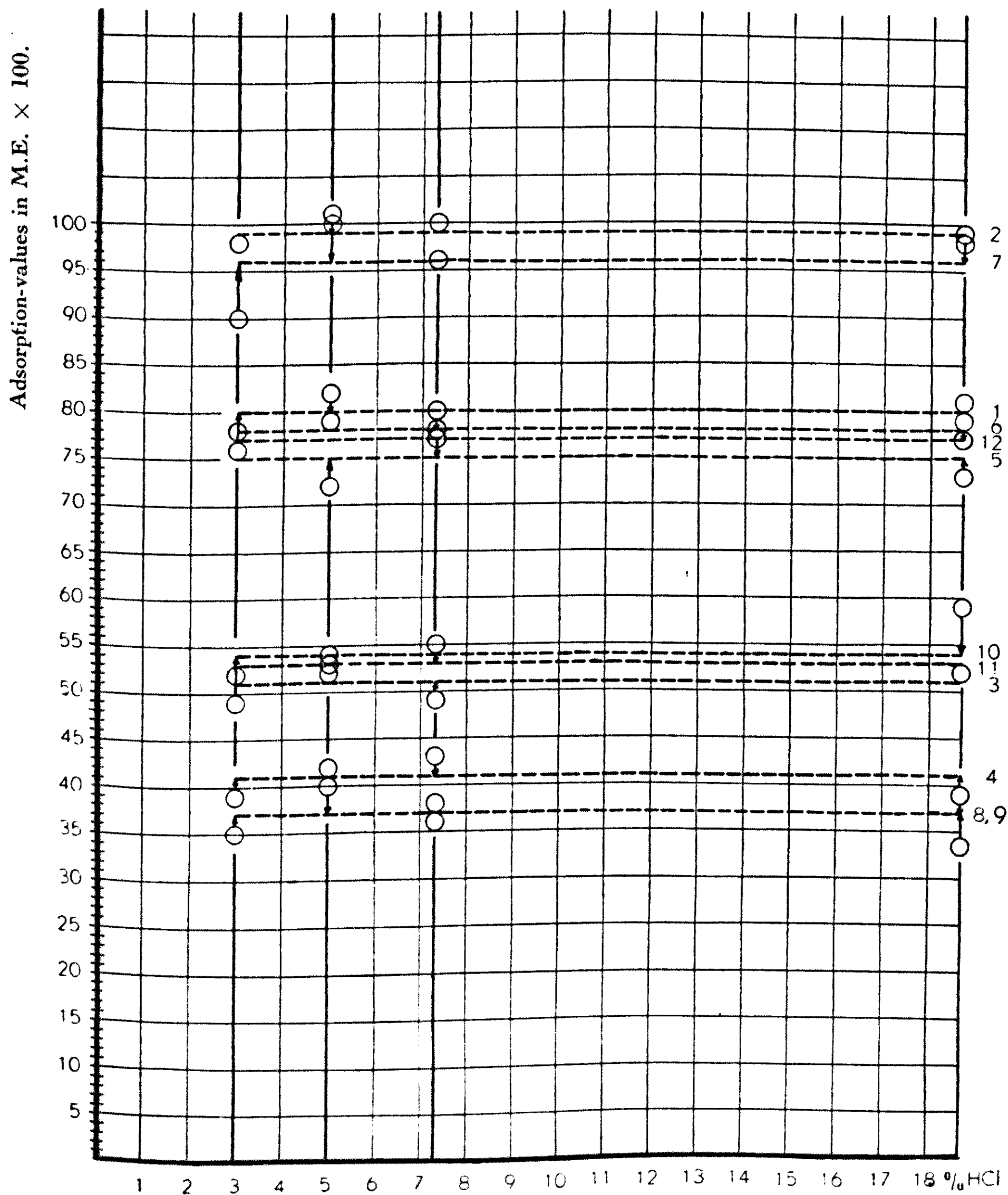
²⁾ E. CROWTHER, Proc. Roy. Soc., 107 (1931).

³⁾ R. GANSSEN, Mitt. d. Preusz. Geol. L.A., 8 (1929).

⁴⁾ See: pag. 75.

⁵⁾ The adsorption-value of the HCl-residue of soil 12 (Etten), which was used in the preliminary investigations, was still lower after the extraction of the soil with 5% HCl than after the extraction with 3% HCl, and finally after the extraction with 7% HCl, the residual adsorption reached again the value of the residue after the extraction with 3% HCl. Apparently the decrease of this value after the extraction with 5% HCl, with regard to that of the HCl-residue after the 3% HCl-extraction, is not essential.

FIGURE X. *Adsorption-values* in M.E. (Ca'') per 4 g HCl-residue, after extraction with 3.0, 5.0, 7.3, and 18.7 % HCl.



C. *Summary and Conclusions*

From the previous investigations it can be concluded (according to the conception of GEDROIZ), that the clay-fractions of Dutch alluvial clay-soils consist of two Al-Fe-Si-compounds, which differ as to their „relative solubility” in HCl, one of which is very easily soluble whereas the other dissolves more difficultly in HCl.

The total soil-complex which dissolves in HCl, possesses the same chemical composition as regards SiO_2 : sesquioxides-ratio. By the removal of the soil-part which is more easily soluble, the adsorption capacity of the HCl-residue decreases with respect to that of the original soil. After the extraction of the soil with a higher concentration of HCl, the residue appears to possess a constant adsorption-value.

The most important part of the adsorption-complex of the different soils, thus appears to be very resistant with regard to extraction with HCl under these different conditions and one cannot consider the Al-(Fe-)Si-compounds, which have been left after the HCl-extraction, as permutoid-compounds because a „Na-permutite according to GANSSEN” is almost completely dissolved by a corresponding HCl-extraction.

The so-called residual complex comes from the hydrolysis of Al-(Fe-)Si-compounds which have been left after the HCl-extraction and can be considered as belonging to the mineral reserve of the clay.

The respectively identical adsorption capacities of the HCl-residues of the different soils, after the extractions with 3.0, 5.0, 7.3 and 18.7 % HCl, must be the consequence of the equal quantities and compositions of the newly formed adsorption-complexes from the remaining Al-(Fe-)Si-compounds.

From the preliminary investigations it has appeared, that whereas in the original soil still an important part of the adsorption is caused by the fraction $> 2 \mu$ of the soil, the residual adsorption of the soil is completely defined by the fraction $< 2 \mu$ of the soil. Therefore it is intended in the next chapter, to examine the connection between the clay-fractions and the adsorption-values for the different soils, together with the influence of the HCl-extraction on the mechanical compositions of the soils.

From the mechanical compositions before and after the HCl-

extraction, an attempt will be made to find an equivalent for the surfaces of the soils, because from this can be decided whether the adsorption capacity of the soil is defined by the surface of the clay-fraction.

From the previous investigations it appears, that the clay-fraction of the soil can consist only for a small part of permutoid Al-Fe-Si-complexes and that after the removal of this more easily soluble part a residue is left, from which, notwithstanding the extraction of the original soil with various concentrations of $\text{HCl} > 3\%$, a residual complex is formed, which shows a constant adsorption capacity.

3. THE INFLUENCE OF HCl-EXTRACTION ON THE SURFACE OF THE SOIL

A. Introduction

In order to examine the influence of HCl-extraction on the mechanical composition of the soil, the soils are analysed according to the method of OLMSTEAD, ALEXANDER and MIDDLETON ¹⁾, after oxidation of the organic matter. Besides the soils are extracted according to VAN BEMMELEN: extraction of 10 g oxidised air-dry soil with 200 cc 7.3 % HCl, for 30 minutes at 55° C and after that the mechanical composition was determined again. From the experiments, the influence of the HCl-extraction on the mechanical composition of the soil will appear. Moreover from the mechanical analysis of the soil can be deduced the eventual connection between the clay-fractions and the adsorption-values before and after the extraction with HCl.

B. Experimental Part

The determination of the mechanical composition of the soils took place according to the method of OLMSTEAD, ALEXANDER and MIDDLETON ²⁾, with a variation supplied by HUDIG and BIEWENGA:

¹⁾ L. OLMSTEAD, L. ALEXANDER and H. MIDDLETON, U.S. Dept. Agr. Bull., 170 (1930).

²⁾ See: note 1.

10 g air-dry oxidised soil are placed on a $50\ \mu$ -sieve ¹⁾ (diameter 8 cm), which has been put in a glass-funnel (greatest diameter 12 cm) with a short shank. This funnel is placed above a cylinder (diameter 6 cm, height 40 cm) by means of a stand with clamp. The particles $< 50\ \mu$ are washed through the sieve with H_2O for which manipulation a short wire haired brush is used.

When the liquid which passes the sieve in drops is no longer cloudy, the sieve and the funnel are washed and the cylinder is filled with H_2O up to the 1 L-mark, after adding 20 cc $\frac{1}{2}$ n. $\text{Na}_2(\text{COO})_2$ -solution.

The residue that is left on the sieve, represents the fraction $> 50\ \mu$. It is washed with H_2O into a porcelain dish, which has been weighed before; and after evaporating to dryness and drying at 105°C it is reweighed.

The upper part of the cylinder was provided with a rubber band by which the glass brim was covered. The cylinder is shut by pressing a porcelain dish with its bottom against the brim of the cylinder and after the soil-residue has been loosened by shaking from the wall of the cylinder, the contents are shaken again 20 times. After that, the cylinder is set down and directly 50 cc of the suspension are pipetted off halfway down the liquid column, evaporated to dryness in a tared porcelain dish, and after being dried at 105°C the residue is weighed. It represents $\frac{1}{20}$ of the fraction $< 50\ \mu$ of the soil. ²⁾

The contents of the cylinder are now once again made homogeneous in the way mentioned and afterwards the cylinder is placed into a celotex case with a loose cover. In the case a thermometer is present. Dependent on the temperature, after 16–20 minutes at 10 cm beneath the surface of the suspension 20 cc are pipetted off, by means of a pipette which can be moved vertically on a support. This quantity of 20 cc is evaporated to dryness in a weighing-flask and after being dried at 105°C the residue is weighed. It represents $\frac{1}{50}$ of the fraction $< 10\ \mu$ of the soil. ²⁾

In the same way, the fraction $< 5\ \mu$ is determined by shaking up

¹⁾ This variation in the method was by HUDIG and BIEWENGA, in order to prevent the dragging along of the finer parts by the coarser-ones $> 50\ \mu$ during the settling, i.e. to prevent the orthokinetic coagulation.

²⁾ H. GESSNER, Die Schlämmanalyse. Kolloidforschung in Einzeldarstellung, 10, 19 (1931). (Formula STOKES).

The correction for the weight of the $\text{Na}_2(\text{COO})_2$ which is present in the residue, is found by evaporating to dryness 20 c.c. $\frac{1}{2}$ n. $\text{Na}_2(\text{COO})_2$ -solution in a weighing-flask and by weighing the residue after drying at 105°C .

and pipetting off 20 cc at 10 cm beneath the surface of the suspension, after standing 66–84 minutes, dependent on the temperature. The residue represents $1/50$ of the fraction $< 5 \mu$ of the soil. ¹⁾

Finally, once more the contents of the cylinder are shaken up and after standing $6\frac{1}{2}$ hours, at a certain depth beneath the surface of the suspension, dependent on the temperature, 20 cc are pipetted off. The weight of the residue, which is obtained in the way mentioned, represents $1/50$ of the clay-fraction $< 2 \mu$ of the soil. ¹⁾

From the weights of the residues, the mechanical composition of the air-dry oxidised soil is calculated by multiplying with 50 or with 20, and after subtracting the correction for the weight of the $\text{Na}_2(\text{COO})_2$, which is present.

When the fractions $< 50 \mu$, from the tables 13 and 14, before and after the HCl-extraction are compared with each other, it appears that the fractions 50–10 μ have increased after the HCl-extraction compared with the corresponding fractions of the original soils. (See: table 15)

The same holds good for the fractions 10–5 μ and 5–2 μ as compared with those before the HCl-extraction.

Exactly the opposite is seen with the fractions $< 2 \mu$. Apparently these have been appreciably reduced by the HCl-extraction compared with the corresponding fractions of the original soils.

One gets the impression that the decrease of the fractions $< 2 \mu$ after the HCl-extractions is caused by coagulation of parts of these fractions to agglomerates which increase coarser fractions.

When therefore the fractions $< 50 \mu$, before and after the HCl-extraction, are compared with each other, they appear to correspond very well taken in account the great analytical errors connected with the determination of this fraction. ²⁾ (See: table 16)

When the adsorption-values of the HCl-residues are compared with the clay-fractions $< 2 \mu$ after the 7.3 % HCl-extractions, there appears to be no relation between the residual adsorption-values and the clay-fractions after the HCl-extraction. (See: table 17)

On the contrary, there appears to exist a clear relation between

¹⁾ See: note 2, pag. 78.

²⁾ The fraction $< 50 \mu$ is found by pipetting off 50 cc half way down the suspension-column, directly after shaking.

TABLE 13.

MECHANICAL COMPOSITIONS OF THE SOILS IN PERCENT BY WEIGHT
OF THE AIR-DRY, OXIDISED SOILS, ACCORDING TO THE PIPETTE-
METHOD OF OLMSTEAD

Soil nr	Fractions				
	$> 50 \mu$	$< 50 \mu$	$< 10 \mu$	$< 5 \mu$	$< 2 \mu$
1	8.8	88.6	58.5	47.1	39.3
2	6.2	91.3	61.5	54.1	48.2
3	36.3	61.9	29.6	26.3	22.8
4	25.2	73.2	26.6	21.1	18.8
5	10.7	86.0	45.7	40.3	33.8
6	10.1	89.3	54.5	45.9	36.7
7	18.8	81.3	61.6	52.1	39.1
8	25.1	72.2	26.2	21.3	16.6
9	59.7	40.6	23.0	19.4	16.2
10	18.2	77.0	34.2	28.3	23.2
11	31.4	66.7	35.0	28.8	23.2
12	30.1	68.9	53.9	46.7	36.2

Soil nr	Fractions					Total
	$> 50 \mu$	$50-10 \mu$	$10-5 \mu$	$5-2 \mu$	$< 2 \mu$	
1	8.8	30.1	11.4	7.8	39.3	97.4
2	6.2	29.8	7.4	5.9	48.2	97.5
3	36.3	32.3	3.3	3.5	22.8	98.2
4	25.2	46.6	5.5	2.3	18.8	98.4
5	10.7	40.3	5.4	6.5	33.8	96.7
6	10.1	34.8	8.6	9.2	36.7	99.4
7	18.8	19.7	9.5	13.0	39.1	100.1
8	25.1	46.0	4.9	4.7	16.6	97.3
9	59.7	17.6	3.6	3.2	16.2	100.3
10	18.2	42.8	5.9	5.1	23.2	95.2
11	31.4	31.7	6.2	5.6	23.2	98.1
12	30.1	15.0	7.2	10.5	36.2	99.0

TABLE 14.

MECHANICAL COMPOSITIONS OF THE HCl-RESIDUES OF THE SOILS,
AFTER EXTRACTION WITH 7.3% HCl, IN PERCENT BY WEIGHT
OF THE AIR-DRY HCl-RESIDUES, ACCORDING TO THE
PIPETTE-METHOD OF OLMSTEAD

Soil nr	Fractions					
	$> 50 \mu$	$< 50 \mu$	$< 10 \mu$	$< 5 \mu$	$< 2 \mu$	
1	6.9	93.3	48.8	35.1	21.4	
2	5.5	92.8	48.4	37.0	20.8	
3	37.1	61.1	22.0	16.2	—	
4	22.1	73.1	18.8	15.6	9.9	
5	10.0	85.7	36.2	23.2	13.8	
6	10.7	88.5	45.6	33.1	19.5	
7	20.0	80.6	62.4	53.1	43.0	
8	26.1	71.1	23.4	17.6	9.4	
9	60.6	38.6	20.7	17.6	10.3	
10	—	—	—	—	—	
11	33.4	65.6	31.9	24.7	17.1	
12	30.7	70.1	53.2	45.4	36.3	

Soil nr	Fractions					Total
	$> 50 \mu$	$50-10\mu$	$10-5 \mu$	$5-2 \mu$	$< 2 \mu$	
1	6.9	44.5	13.7	13.7	21.4	100.2
2	5.5	44.4	11.4	16.2	20.8	98.3
3	37.1	39.1	5.8	—	—	98.2
4	22.1	54.3	3.2	5.7	9.9	95.2
5	10.0	49.5	13.0	9.4	13.8	95.7
6	10.7	42.9	12.5	13.6	19.5	99.2
7	20.0	18.2	9.3	10.1	43.0	100.6
8	26.1	47.7	5.8	8.2	9.4	97.2
9	60.6	17.9	3.1	7.3	10.3	99.2
10	—	—	—	—	—	—
11	33.4	33.7	7.2	7.6	17.1	99.0
12	30.7	16.9	7.8	9.1	36.3	100.8

TABLE 15.

COMPARATIVE TABLE OF THE FRACTIONS BEFORE AND AFTER THE
HCl-EXTRACTION, IN PERCENT BY WEIGHT OF THE RESPECTIVE
SUBSTANCES

Soil nr	Fraction 50-10 μ		Fraction 10-5 μ		Fraction 5-2 μ		Fraction < 2 μ	
	before extraction	after extraction	before extraction	after extraction	before extraction	after extraction	before extraction	after extraction
1	30.1	44.5	11.4	13.7	7.8	13.7	39.3	21.4
2	29.8	44.4	7.4	11.4	5.9	16.2	48.2	20.8
3	32.3	39.1	3.3	5.8	3.5	—	22.8	—
4	46.6	54.3	5.5	3.2	2.3	5.7	18.8	9.9
5	40.3	49.5	5.4	13.0	6.5	9.4	33.8	13.8
6	34.8	42.9	8.6	12.5	9.2	13.6	36.7	19.5
7	19.7	18.2	9.5	9.3	13.0	10.1	39.1	43.0
8	46.0	47.7	4.9	5.8	4.7	8.2	16.6	9.4
9	17.6	17.9	3.6	3.1	3.2	7.3	16.2	10.3
10	42.8	—	5.9	—	5.1	—	23.2	—
11	31.7	33.7	6.2	7.2	5.6	7.6	23.2	17.1
12	15.0	16.9	7.2	7.8	10.5	9.1	36.2	36.3

TABLE 16.

COMPARATIVE TABLE OF THE FRACTIONS
< 50 μ BEFORE AND AFTER THE HCl-EXTRACT-
ION, IN PERCENT BY WEIGHT OF THE
RESPECTIVE SUBSTANCES

Soil nr	Fraction < 2 μ	
	before extraction	after extraction
1	88.6	93.3
2	91.3	92.8
3	61.9	61.1
4	73.2	73.1
5	86.0	85.7
6	89.3	88.5
7	81.3	80.6
8	72.2	71.1
9	40.6	38.6
10	77.0	—
11	66.7	65.6
12	68.9	70.1

TABLE 17.

THE RELATION BETWEEN THE RESIDUAL ADSORPTION AND THE
CLAY-FRACTION $< 2\mu$, AFTER THE HCl-EXTRACTION

Soil nr	Fraction $< 2\mu$ in percent by weight of the 7.3 % HCl-residue	Residual adsorption ¹⁾ in M.E. (Ca ⁺⁺) per 4 g of the 7.3% HCl-residue	Residual adsorption $\times 100$ % $< 2\mu$ of the 7.3 % HCl-residue
1	21,4	0.80	3.7
2	20.8	0.99	4.8
3	—	0.51	—
4	9.9	0.41	4.1
5	13.8	0.75	5.4
6	19.5	0.78	4.0
7	43.0	0.96	2.2
8	9.4	0.37	3.9
9	10.3	0.37	3.6
10	—	0.54	—
11	17.1	0.53	3.1
12	36.3	0.77	2.1

TABLE 18.

THE RELATION BETWEEN THE RESIDUAL ADSORPTION AND THE
CLAY-FRACTION $< 2\mu$ OF THE ORIGINAL OXIDISED SOIL

Soil nr	Fraction $< 2\mu$, in per- cent by weight of the original oxidised soil	Residual Adsorption in M.E. (Ca ⁺⁺) per 4 g of the 7.3% HCl-residue.	Residual Adsorption $\times 100$ % $< 2\mu$ of the soil
1	39.3	0.80	2.0
2	48.2	0.99	2.0
3	22.8	0.51	2.2
4	18.8	0.41	2.2
5	33.8	0.75	2.2
6	36.7	0.78	2.1
7	39.1	0.96	2.4
8	16.6	0.37	2.2
9	16.2	0.37	2.3
10	23.2	0.54	2.3
11	23.2	0.53	2.3
12	36.2	0.77	2.1

the adsorption-values of the HCl-residues and the mechanical compositions of the original soils. (See: table 18)

By the correlation between the residual adsorption and the mechanical composition of the original oxidised soil and also by the fact that the fractions $< 50\mu$ of the soils, before and after the

¹⁾ See: table 11, pag. 64.

TABLE 19.

THE INFLUENCE OF A PREVIOUS PERCOLATION WITH A $(\text{CH}_3\text{COO})_2\text{Ca}$ -SOLUTION ($\text{pH} \pm 8.5$) ON THE MECHANICAL COMPOSITIONS OF THE HCl-RESIDUES, IN PERCENT BY WEIGHT OF THE HCl-RESIDUES

Soil nr	Fractions				
	$> 50 \mu$	$< 50 \mu$	$< 10 \mu$	$< 5 \mu$	$< 2 \mu$
1	7.2	89.4	55.5	46.6	37.4
2	5.4	90.7	60.3	55.0	46.8
3	35.7	—	27.2	24.1	21.0
4	23.1	73.7	24.3	20.5	17.6
5	9.7	86.2	44.2	40.1	34.4
6	9.8	88.0	50.9	44.7	38.0
7	19.4	79.7	61.8	53.9	43.6
8	25.3	73.0	26.3	19.8	16.4
9	59.8	38.5	21.8	—	15.3
10	19.6	76.8	32.4	—	22.7
11	32.6	67.7	33.3	—	23.0
12	31.4	69.4	53.2	—	36.4

Soil nr	Fractions					Total
	$> 50 \mu$	$50-10 \mu$	$10-5 \mu$	$5-2 \mu$	$< 2 \mu$	
1	7.2	33.9	8.9	9.2	37.4	96.6
2	5.4	30.4	5.3	8.2	46.8	96.1
3	35.7	—	3.1	3.1	21.0	—
4	23.1	49.4	3.8	2.9	17.6	96.8
5	9.7	42.0	4.1	5.7	34.4	95.9
6	9.8	37.1	6.2	6.7	38.0	97.8
7	19.4	17.9	7.9	10.3	43.6	99.1
8	25.3	46.7	6.5	3.4	16.4	98.3
9	59.8	16.7	—	—	15.3	98.3
10	19.6	44.4	—	—	22.7	96.4
11	32.6	34.4	—	—	23.0	100.3
12	31.4	16.2	—	—	36.4	100.8

HCl-extraction, practically appear to be identical, it seems probable that the mechanical composition of the original soil, which had been varied importantly by the HCl-extraction, is regenerated during the successive percolations with a $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution, H_2O and an NH_4Cl -solution¹⁾.

Therefore is now investigated, in which way the mechanical

¹⁾ See: Methods, pag. 33.

compositions of the HCl-residues are influenced by previous percolations of these HCl-residues with a $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution ($\text{pH} \pm 8.5$).

The oxidised soils are extracted in the usual way with 7.3 % HCl. ¹⁾ After washing the residues on the membrane-filter, 500 cc $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution ($\text{pH} \pm 8.5$) is percolated in drops by suction. Afterwards the residues are quantitatively washed via the 50μ -sieve into the settling-cylinders and the mechanical compositions are determined in the usual way. ²⁾

When these mechanical compositions are compared with those of the original soils,

TABLE 20.

COMPARATIVE TABLE OF THE FRACTIONS OF THE ORIGINAL SOILS AND THOSE OF THE CORRESPONDING HCl-RESIDUES, AFTER PREVIOUS PERCOLATION WITH A $(\text{CH}_3\text{COO})_2\text{Ca}$ -SOLUTION ($\text{pH} \pm 8.5$), IN PERCENT BY WEIGHT OF THE RESPECTIVE SUBSTANCES

Soil nr	Fraction 50–10 μ		Fraction 10–5 μ		Fraction 5–2 μ		Fraction < 2 μ	
	original oxidised soil	HCl-residue	original oxidised soil	HCl-residue	original oxidised soil	HCl-residue	original oxidised soil	HCl-residue
1	30.1	33.9	11.4	8.9	7.8	9.2	39.3	37.4
2	29.8	30.4	7.4	5.3	5.9	8.2	48.2	46.8
3	32.3	—	3.3	3.1	3.5	3.1	22.8	21.0
4	46.6	49.4	5.5	3.8	2.3	2.9	18.8	17.6
5	40.3	42.0	5.4	4.1	6.5	5.7	33.8	34.4
6	34.8	37.1	8.6	6.2	9.2	6.7	36.7	38.0
7	19.7	17.9	9.5	7.9	13.0	10.3	39.1	43.6
8	46.0	46.7	4.9	6.5	4.7	3.4	16.6	16.4
9	17.6	16.7	3.6	—	3.2	—	16.2	15.3
10	42.8	44.4	5.9	—	5.1	—	23.2	22.7
11	31.7	34.4	6.2	—	5.6	—	23.2	23.0
12	15.0	16.2	7.2	—	10.5	—	36.2	36.4

it appears that the mechanical compositions have been changed only a little by the HCl-extraction. (See: tables 19 and 20)

In general, the clay-fractions of the soils have decreased a little whereas a little increase can be observed with respect to the soils 5, 6 and 7 after the HCl-extraction and the clay-fraction of soil 12 has remained practically unchanged. These increases of the clay-fractions after the HCl-extraction can be explained by the

¹⁾ See: Methods, pag. 25.

²⁾ See: Methods, pag. 77.

supposition, that the original oxidised soils could not be dispersed by the treatment with a $\text{Na}_2(\text{COO})_2$ -solution to the same degree as was the case after the HCl-extraction with the subsequent $(\text{CH}_3\text{COO})_2\text{Ca}$ -percolation. ¹⁾

The clay-fractions of all soils thus appear to be very resistant with regard to HCl-extraction.

Another problem which now appears is to find why the HCl-residues, without a subsequent $(\text{CH}_3\text{COO})_2\text{Ca}$ -percolation, show mechanical compositions which differ significantly from those of the original soils.

Now it is clear that by the HCl-extraction part of the fraction is coagulated to secondary particles, which become one with the coarser fractions, but are dispersed again by an eventual subsequent percolation of the HCl-residue with a $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution. Apparently this part of the clay-fraction is cemented to form larger particles.

In contradistinction to the original soils, the HCl-residues of the soils contain SiO_2 -gel and it is for this reason that in two cases, for which the soils 1 and 6 had been chosen, SiO_2 was determined in the $(\text{CH}_3\text{COO})_2\text{Ca}$ -percolate.

Therefore 200 cc of the percolate were treated, at boiling-point, with an excess of an $(\text{NH}_4)_2\text{CO}_3$ -solution, the CaCO_3 -precipitate was filtered and washed with warm H_2O . The filtrate was evaporated to dryness on the steam-bath and after weak ignition in order to remove the NH_4 -salts, SiO_2 was determined in the residue in the usual way. ²⁾

TABLE 21.

Soil nr	SiO_2 in the $(\text{CH}_3\text{COO})_2\text{Ca}$ -percolate in % of the HCl-residue	SiO_2 in the NaOH-extract in % of the HCl-residue ³⁾
1	1.69	3.12
6	0.64	1.49

As appears from the data of table 21, SiO_2 is dissolved out of the soils by the $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution. However still part of the SiO_2 remains in the residue, as is proved by comparing the SiO_2 -values of the $(\text{CH}_3\text{COO})_2\text{Ca}$ -percolate with those of the NaOH-

¹⁾ For the soils 5 and 6, it is also possible that the coarser fractions of the original soils contain relatively more CaCO_3 . See: table 2, pag. 22.

²⁾ See: Methods, pag. 26.

³⁾ See: Table 11, pag. 64.

extract of the HCl-residue according to the method of VAN BEMMELEN.

This fact is in accordance with the results of VAN BEMMELEN. By treating SiO_2 -gel with a $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution, one part of the SiO_2 is dissolved and another is left as an insoluble Ca-Si-compound. ¹⁾

However the quantity of Ca^{++} , that can be adsorbed by this residual SiO_2 , is very small as was shown already in the preliminary investigations. ²⁾

From these experiments it becomes probable, that by the extraction of the soil with HCl, the SiO_2 which has been separated insolubly, fastens part of the clay-fraction during the extraction or during the evaporation of the residue in such a way, that the $\text{Na}_2(\text{COO})_2$ -solution used by the mechanical analysis is no

TABLE 22.

THE RELATION BETWEEN THE RESIDUAL ADSORPTION-VALUES AND THE CLAY-FRACTIONS OF THE HCl-RESIDUES, AFTER A PREVIOUS PERCOLATION WITH A $(\text{CH}_3\text{COO})_2\text{Ca}$ -SOLUTION

Soil nr	The fractions $< 2 \mu$ in percent by weight of the 7,3% HCl-residues (after a previous $(\text{CH}_3\text{COO})_2\text{Ca}$ -percolation)	Residual adsorption in M.E. (Ca^{++}) per 4 g 7,3%-HCl-residue	Residual Adsorption $\times 100$ % $< 2 \mu$ of the 7,3% HCl- $(\text{CH}_3\text{COO})_2\text{Ca}$ -residue
1	37.4	0.80	2.1
2	46.8	0.99	2.1
3	21.0	0.51	2.4
4	17.6	0.41	2.3
5	34.4	0.75	2.2
6	38.0	0.78	2.0
7	43.6	0.96	2.2
8	16.4	0.37	2.3
9	15.3	0.37	2.4
10	22.7	0.54	2.4
11	23.0	0.53	2.3
12	36.4	0.77	2.1

¹⁾ J. M. VAN BEMMELEN, Landw. Versuchsstat., 23, 297 (1879), proved that by boiling the HCl-residue of a soil with Na_2CO_3 - or K_2CO_3 -solution, the adsorption with respect to neutral salts again shows itself. He ascribes this adsorption to the compounds which are formed, during this treatment, out of the SiO_2 -gel which is present in the HCl-residue and the alkali. These compounds, according to him, consist of many molecules of strongly hydrated SiO_2 and a few molecules of alkali. The chemical equilibrium, which is established between the SiO_2 -gel and the quantity of alkali present in the solution, is unstable. When the quantity of alkali is increased by an equal H_2O -volume, the quantity of undissolved SiO_2 decreases and the quantity of dissolved SiO_2 increases.

²⁾ See: pag. 50.

longer able to disperse these secondary soil-particles. By treating the HCl-residue of the soil with a $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution (pH 8.5) one part of this SiO_2 is brought into solution and another is left as an insoluble Ca-Si-compound; the secondary soil-particles are dispersed and the original mechanical composition is regenerated.

When the residual adsorption-values of the different soils are compared with the corresponding clay-fractions of the HCl-residues, regenerated by the $(\text{CH}_3\text{COO})_2\text{Ca}$ -percolation, the relation between these values and the clay-fractions after the HCl- $(\text{CH}_3\text{COO})_2\text{Ca}$ -treatment is shown. (See: table 22)

From the constant quotients of the residual adsorption-values and the fractions $< 2 \mu$ of the different soils, there is indicated a uniformity in the different clays, which show equal adsorption-values per unit-weight.

The respective totals of the quantities of Al_2O_3 , Fe_2O_3 and SiO_2 , which are brought into solution by the HCl-extraction, appear to

TABLE 23.

QUANTITIES OF „ $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{SiO}_2$ ”, IN mm PER 100 g AIR-DRY, OXIDISED SOIL, DISSOLVED BY THE EXTRACTION WITH 18.7% HCl, ACCORDING TO THE METHOD OF VAN BEMMELEN ¹⁾ AND THE DEPENDENCE OF THE QUANTITIES DISSOLVED Al-Fe-Si-COMPLEX ON THE CLAY-FRACTIONS OF THE SOILS ²⁾

Soil nr	Sesqui-oxides.	Total SiO_2	Total SiO_2 + Sesq. oxides	% CaCO_3 ³⁾	Total SiO_2 + Sesq. oxides calculated on CaCO_3 -free soil	% $< 2 \mu$ ³⁾	Tot. SiO_2 + Sesq. ox. % $< 2 \mu$
1	30.9	88.8	119.7	4.4	125.2	39.3	3.2
2	34.6	68.7	103.3	0.1	103.4	48.2	2.1
3	15.8	35.8	51.6	2.5	52.9	22.8	2.3
4	13.3	30.6	43.9	1.5	44.6	18.8	2.4
5	19.2	46.4	65.6	4.6	68.8	33.8	2.0
6	20.6	45.2	65.8	11.2	74.1	36.7	2.0
7	33.1	36.8	69.9	0.1	70.0	39.1	1.8
8	12.1	24.6	36.7	—	36.7	16.6	2.2
9	16.4	23.4	39.8	—	39.8	16.2	2.4
10	24.3	25.5	49.8	—	49.8	23.2	2.1
11	19.8	29.6	49.4	0.6	49.7	23.2	2.1
12	38.6	32.6	71.2	—	71.2	36.2	2.0

¹⁾ See: Methods, pag. 24.

²⁾ See: Tables 11 and 13, pag. 64 en 80.

³⁾ In % of the air-dry oxidised soil.

be dependent on the respective clay-fractions of the different soils also. (See: table 23)

From this table it can be concluded, that about as much Al-Fe-Si-complex has been dissolved out of the different soils, per unit-weight of the clay, by the 18.7 % HCl-extraction. Only soil 1 (Drieborg) deviates importantly, a fact, which will be reverted to afterwards. After this extraction the mechanical compositions of the HCl-residues are still about equal to those of the original soils. ¹⁾

These results therefore prove, that only a very thin surface-layer of the particles $< 2 \mu$ is brought into solution by the HCl-extraction, because after the extraction the clay-fractions generally have decreased only very little as compared with those of the original soils. Moreover it can be accepted, that the surfaces of all soil-particles $< 2 \mu$ are attacked during the HCl-extraction, because it seems improbable that only a proportional part of the respective clay-fractions of all soils would be attacked by the extraction.

From the fact that the quantities of Al-Fe-Si-complex, which have been brought into solution by the HCl-extraction, appear to be dependent on the clay-fractions $< 2 \mu$, the conclusion can be drawn that this Al-Fe-Si-complex or only the surface-layer of it is the cause of the adsorption-reaction.

The chemical composition of the Al-Fe-Si-complex which has been dissolved by the HCl-extraction differs markedly in the different soils and therefore it can be expected, that the adsorption-complexes of the different HCl-residues also possess various compositions. However the adsorption-value per unit-weight is equal in spite of these differences, and from this it could be concluded, that the chemical composition of the Al-Fe-Si-complex, which is dissolved by the HCl-extraction, is no criterion of the adsorption capacity of the soil.

Therefore whether the adsorption capacities of the original oxidised soils are also defined by the clay-fractions $< 2 \mu$ of these soils is now the object of investigation, and at the same time it will appear how far the chemical composition of the Al-Fe-Si-

¹⁾ The mechanical compositions of the original soils were only little changed by the 7.3% HCl-extraction (See pag. 85). The residual adsorption-values after the 7.3% HCl-extraction, respectively being equal to those after the 18.7%-HCl-extraction, it can be concluded, that also the mechanical compositions of the HCl-residues correspond after the 7.3% and the 18.7%-HCl-extraction respectively.

complex, as determined from the results of the HCl-extraction, influences the adsorption-values of the original oxidised soils.

The adsorption capacity-values of the original soils cannot be determined in the usual way, ¹⁾ because some of them contain CaCO_3 which will be wholly or partly dissolved by the NH_4Cl -percolation, following on the $(\text{CH}_3\text{COO})_2\text{Ca}$ -percolation, for which reason the Ca-determination in the NH_4Cl -percolate cannot yield the exact adsorption capacity of the soil.

Therefore the NH_4Cl -percolation was followed by a percolation with 150 cc 70 % alcohol, in order to remove the NH_4^+ , which had not been adsorbed ²⁾ and thereafter 200 cc n. KCl were percolated. ³⁾

In the KCl-percolate NH_4^+ was determined by distillation. ⁴⁾

TABLE 24.

THE RELATION BETWEEN THE ADSORPTION CAPACITY-VALUES AND THE CLAY-FRACTIONS OF THE ORIGINAL OXIDISED SOILS

Soil nr	Adsorption capacity in M.E. (NH_4^+), p. 4 g air-dry oxidised soil	CaCO_3 in % of the air-dry oxidised soil	Adsorption capacity in M.E. (NH_4^+), p. 4 g air-dry oxidised CaCO_3 -free soil	Fraction $< 2 \mu$ in % by weight of the original oxidised soil	Ads. cap. $\times 100$ ⁵⁾ % $< 2 \mu$ of the or. oxid. soil
1	0.85	4.4	0.89	39.3	2.3
2	1.02	0.1	1.02	48.2	2.1
3	0.49	2.5	0.50	22.8	2.2
4	0.37	1.5	0.38	18.8	2.0
5	0.65	4.6	0.68	33.8	2.0
6	0.74	11.2	0.83	36.7	2.3
7	0.86	0.1	0.86	39.1	2.2
8	0.34	—	0.34	16.6	2.0
9	0.34	—	0.34	16.2	2.1
10	0.48	—	0.48	23.2	2.1
11	0.49	0.6	0.49	23.2	2.1
12	0.71	—	0.71	36.2	2.0

¹⁾ See: Methods, pag. 33.

²⁾ 150 cc 70% alcohol appeared to be sufficient in all cases, because after percolation with this quantity the percolate no longer showed any reaction with NESSLERS-reagent.

³⁾ 200 cc n. KCl appeared to be sufficient to replace the NH_4^+ quantitatively. See note 2.

⁴⁾ See: „Methoden van Onderzoek aan het R.L.P. te Maastricht”, 4 (1923).

⁵⁾ These quotients almost correspond to those of the HCl-residues (See: table 18, pag. 83), whereas it has appeared from previous experiments, that the adsorption capacity of the residue decreases by the HCl-extraction. A probable cause for these corresponding values is the fact, that the adsorption-values of HCl-residues were defined as the quantities of Ca^{++} , which were fixed from a $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution, (pH 8,5), whereas for the original oxidised soils, the NH_4^+ that was fixed from an NH_4Cl -solution (pH 4,6) was determined. Apparently the decrease, which the adsorption capacity has to endure by the HCl-extraction, is compensated by the determination of the adsorption-value at a higher pH.

That the adsorption capacity in this pH-change is largely dependent on the pH, can be deduced a.o. from the investigations of A. DEMOLON, Annal. Agron. 1, 73 (1933).

The adsorption-value per unit-weight of clay $< 2 \mu$ being equal for all soils, it appears that the chemical composition of the Al-Fe-Si-complex, as determined by the HCl-extraction, has no influence on the adsorption capacity of the soil.

From the equal adsorption-values per unit-weight of clay it must follow that the surface per unit-weight is equal for the different clays, as is also required by the equal quantities of Al-Fe-Si-complex that are dissolved per unit-weight of clay.

To prove this, the clay-fractions were fractionated further in parts $< 1\frac{1}{2} \mu$, $< 1 \mu$ and $< \frac{1}{2} \mu$. The settling cylinders with the soils prepared in the usual way ¹⁾, were placed therefore in a constant temperature room ²⁾ and after fixed times, calculated according to the formula of STOKES ³⁾, 20 cc of the suspension were pipetted off. From the weights of the residues, the fractions $< 1\frac{1}{2} \mu$, $< 1 \mu$, and $< \frac{1}{2} \mu$ were calculated by multiplication with

TABLE 25.

MECHANICAL COMPOSITIONS OF THE CLAY-FRACTIONS OF THE DIFFERENT SOILS, IN PERCENT BY WEIGHT OF THE ORIGINAL OXIDISED SOILS

Soil nr	Fractions			
	$< 2 \mu$	$< 1\frac{1}{2} \mu$	$< 1 \mu$	$< \frac{1}{2} \mu$
1	39.3	36.1	32.2	25.6
2	48.2	43.7	41.4	35.8
3	22.8	19.9	18.8	15.7
4	18.8	16.9	15.9	12.9
5	33.8	31.4	28.8	24.6
6	36.7	33.8	29.6	24.1
7	39.1	36.9	34.3	28.8
8	16.6	15.8	14.8	12.4
9	16.2	14.0	13.2	11.3
10	23.2	20.2	19.4	16.4
11	23.2	20.8	19.2	15.7
12	36.2	32.2	28.8	25.5

¹⁾ See: pag. 77.

²⁾ During the experiments, the temperature varied from 12²–12⁸° C.

³⁾ H. GESSNER, Die Schlämmanalyse, 19 (1931). When the suspension was pipetted off at 10 cm beneath its surface, for the different fractions at 12⁵° C, the following settling times were calculated:

Diameter:	$< 2 \mu$	$< 1\frac{1}{2} \mu$	$< 1 \mu$	$< \frac{1}{2} \mu$
	9 h. 28 m. 48 s.	16 h. 51 m. 14 s.	37 h. 55 m. 20 s.	151 h. 41 m. 0 s.

50 and an allowance for the correction with regard to the $\text{Na}_2\text{-(COO)}_2$, which is present in it. ¹⁾ (See: table 25)

When the fractions $< 1\frac{1}{2} \mu$, $< 1 \mu$ and $< \frac{1}{2} \mu$ are expressed in percents of the clay-fractions $< 2 \mu$ it appears that the mechanical compositions of the various clay-fractions are relatively the same.

TABLE 26.

FRACTIONS $< 1\frac{1}{2} \mu$, $< 1 \mu$ and $< \frac{1}{2} \mu$, IN PERCENT BY WEIGHT OF THE CLAY-FRACTIONS $< 2 \mu$

Soil nr	Fractions		
	$< 1\frac{1}{2} \mu$	$< 1 \mu$	$< \frac{1}{2} \mu$
1	92	82	65
2	91	86	74
3	87	82	69
4	90	85	69
5	93	85	73
6	92	81	66
7	94	88	74
8	95	89	75
9	88	81	70
10	87	84	71
11	90	83	68
12	89	80	70
On an average	91	84	70

From these data the surface O of 100 g of clay can be calculated approximately. Supposing the number of the particles between r and $r + dr$ amounts to $\varphi(r) dr$, whereby $\varphi(r)$ is a function of the *diameter* r , then the weight of these particles is the weight of one particle, (also: the volume $\frac{1}{6} \pi r^3$ multiplied with the sp.gr. ρ), multiplied with the number $\varphi(r) dr$, i.o.w.

$$\frac{1}{6} \pi \rho r^3 \varphi(r) dr$$

When the diameter of the particles with the smallest radius is supposed to be r_0 , the weight of all particles smaller than r_k becomes:

$$G(r_k) = \frac{1}{6} \pi \rho \int_{r_0}^{r_k} r^3 \varphi(r) dr \dots\dots\dots (1)$$

G and r being indicated graphically, the line which is obtained shows a curve which makes one think of a logarithmic relation between the two magnitudes. In reality it appears, that the points almost lie on a straight line when G and $^{10}\log r$ are indicated as ordinate and abscissa respectively. The relation between G and r can be found by equalization:

¹⁾ See: pag. 78.

From table 25 the average mechanical compositions of the 12 soils can be calculated:

$< 2 \mu$	$< 1\frac{1}{2} \mu$	$< 1 \mu$	$< \frac{1}{2} \mu$
29.5 %	26.8 %	24.7 %	20.7 %

By equalization the line is found:

r in cm	$^{10}\log r$	G	$u = \frac{G}{^{10}\log r - \overline{^{10}\log r}}$	$v = G - \overline{G}$	$u \times v$	u^2	v^2
2×10^{-4}	- 3.70	29.5	+0.26	+4.1	1.07	0.0676	16.81
1.5×10^{-4}	- 3.82	26.8	+0.14	+1.4	0.20	0.0196	1.96
1×10^{-4}	- 4.00	24.7	- 0.04	- 0,7	0.03	0.0016	0.49
5×10^{-5}	- 4.30	20.7	- 0.34	- 4.7	1.60	0.1156	22.09
	-15.82	101.7			2.90	0.2044	41.35

$$\frac{\Sigma ^{10}\log r}{N} = \overline{^{10}\log r} = - 3,96 \qquad \frac{\Sigma G}{N} = \overline{G} = 25,4.$$

$$\epsilon^2 = (\Sigma v^2 - \frac{(\Sigma uv)^2}{\Sigma u^2}) : N = (41,35 - \frac{(2,9)^2}{0,2044}) : 4 = 0,23$$

From the small value of ϵ it appears that at least for these 4 points, the relation between G and $^{10}\log r$ can be looked upon as linear.

The general formula for the line is: $G = m ^{10}\log r + q$.

$$m = \frac{\Sigma(u \times v)}{\Sigma u^2} = \frac{2,90}{0,2044} = 14.2, \text{ and thus } q \text{ can be calculated by}$$

introduction of the average values for G and $^{10}\log r$:

$$\begin{aligned} \overline{G} &= 14,2 \overline{^{10}\log r} + q \\ 25,4 &= 14,2 \times - 3,96 + q \\ q &= 81,6 \qquad G = 14,2 ^{10}\log r + 81,6 \dots\dots\dots (2) \end{aligned}$$

The point of intersection of the line with the abscissà is found by putting $G = 0$, from which the r_0 of the smallest particle is known:

$$\begin{aligned} 0 &= 14,2 ^{10}\log r_0 + 81,6 \\ ^{10}\log r_0 &= \frac{- 81,6}{14,2} = - 5,75 = 0,25 - 6 \\ r_0 &= 1,78 \times 10^{-6} \text{ cm } (= 17,8 \mu \mu) \end{aligned}$$

The total surface of the particles between 2μ (r_k) and 17.8μ (r_0) is calculated as follows:

$$\text{From 1 follows: } \frac{dG}{dr} = \frac{1}{6} \pi \rho r^3 \varphi(r)$$

$$\text{From 2 follows: } \frac{dG}{dr} = \frac{14,2 \times 0,4343}{r}$$

$$\text{Or by equating 1 to 2: } \varphi(r) = \frac{6,17 \times 6}{\pi \rho r^4}$$

$$O = \pi \int_{r_0}^{r_k} r^2 \varphi(r) dr = \int_{r_0}^{r_k} \frac{37,02}{\rho} \times \frac{1}{r^2} dr \quad \rho = 2,65$$

$$O = \int_r^{r_k} \frac{14,0}{r^2} dr = 14,0 \left[-\frac{1}{r} \right]_{r_0}^{r_k} = 14,0 \left[-\frac{1}{r} \right]_{1,78 \times 10^{-6}}^{2 \times 10^{-4}}$$

$$O = 14,0 \left[-\frac{1}{2 \times 10^{-4}} + \frac{1}{1,78 \times 10^{-6}} \right] = 7,8 \times 10^6 \text{ cm}^2 = 780 \text{ m}^2$$

$$\text{Then the surface of 100 g of clay becomes: } \frac{100}{29,5} \times 780 = \mathbf{2644 \text{ m}^2}.$$

This can only be a rough estimate. The greatest contribution to the surface of the soil is yielded by the particles $< \frac{1}{2} \mu$ and the whole of this share has been found by extrapolation. It is supposed, that the line which has been found from the 4 values of G and r also indicates the state in the sphere of the smaller soil-particles. The value which has been found for the surface of the soil must therefore be considered as an approximate value of the real surface. ¹⁾

When after the extraction with 7.3 % HCl, in the clay-fraction $< 2 \mu$, the percent by weight of the particles $< \frac{1}{2} \mu$ is determined, the resistance of this fraction towards the attack with HCl also appears. (See: table 27)

Moreover the equality of the surfaces will have to be deduced from the hygroscopicity-values per unit-weight of the various clays.

1) When the fraction of $5-2 \mu$ is eventually taken in account, it appears that the total surface of the soil has only increased very little. Based on this calculation, the surface of the particles of $5-2 \mu$ amounts to:

$$O = 14,0 \int_{2 \times 10^{-4}}^{5 \times 10^{-4}} \frac{1}{r^2} dr = 14,0 \left[\frac{1}{2 \times 10^{-4}} - \frac{1}{5 \times 10^{-4}} \right] =$$

$$= 4,2 \times 10^4 \text{ cm}^2 = 4,2 \text{ m}^2$$

Therefore the particles of the soil $> 2 \mu$ practically do not contribute to the total surface of the soil.

TABLE 27.

THE FRACTION $< \frac{1}{2} \mu$, AFTER EXTRACTION OF THE DIFFERENT SOILS WITH 7.3% HCl, FOLLOWED BY THE $(\text{CH}_3\text{COO})_2\text{Ca}$ -PERCOLATION

Soil nr	Fractions in percent by weight of the HCl-residues:		Fraction $< \frac{1}{2} \mu$ in percent by weight of the clay-fraction $< 2 \mu$
	$< 2 \mu$	$< \frac{1}{2} \mu$	
1	37.4	28.0	75
2	46.8	37.1	79
3	21.0	16.5	79
4	17.6	12.6	72
5	34.4	26.0	76
6	38.0	27.9	73
7	43.6	31.0	71
8	16.4	12.4	76
9	15.3	11.0	72
10	22.7	16.6	73
11	23.0	16.0	70
12	36.4	24.6	68

Average value 74¹⁾

1) As appears from these mechanical analyses that the mechanical compositions of the clay-fractions can have been changed only unimportantly by the HCl-extraction, it can roughly be calculated, by means of the surface-value of 100 g original clay $< 2 \mu$ and its adsorption-value, (See: resp. pag. 92 and pag. 87) which are identical for all soils, whether the Ca-ions, round the particles, are present in a mono-ionic film or in a poly-ionic film.

The radius of the Ca-ion is $\pm 1.0 \text{ \AA}$ (PAULING), and the surface, covered by one Ca-ion, in „widest situation”, is therefore:

$$(2\text{ \AA})^2 = 4 \times 10^{-16} \text{ cm}^2$$

The adsorption-value of 100 g clay $< 2 \mu$ amounts to 55.0 M.E. (Ca^{++}) (See: table 23, pag. 88) and as the surface per 100 g clay was 2644 m² (See: pag. 94) the adsorption capacity per 100 m² of the clay amounts to $55.0 : 26.44 = 2.08 \text{ M.E.}$ or 1.04 mm Ca^{++} .

1.04 mm contain $1.04 \times 6 \times 10^{20}$ -ions and these therefore want a surface of:

$$(1.04 \times 6 \times 10^{20}) (4 \times 10^{-16}) = 2.5 \times 10^5 \text{ cm}^2 = 25 \text{ m}^2.$$

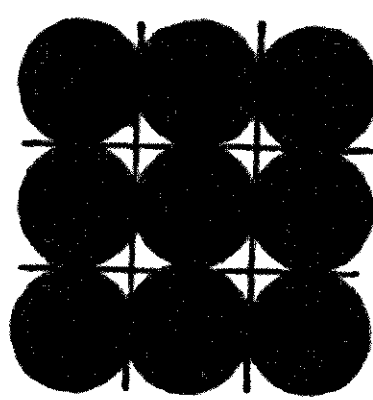
If the Ca-ions are present in a mono-ionic film, in „widest situation”, they cover 25% of the surface of the clay-fraction. When the Ca-ions are present in „narrowest situation”, one Ca-ion needs a surface of:

$$6 \times \frac{1}{3} (\text{ \AA})^2 \sqrt{3} = 2\sqrt{3} (\text{ \AA})^2 = 2\sqrt{3} \times 10^{-16} \text{ cm}^2$$

1.04 mm Ca^{++} , which are found per 100 m² of the clay-fraction, then want a surface of:

$$(1.04 \times 6 \times 10^{20}) (2\sqrt{3} \times 10^{-16}) = 1.25\sqrt{3} \times 10^5 \text{ cm}^2 = 21.6 \text{ m}^2 \text{ narrowest situation}$$

If the Ca-ions are present in a mono-ionic film, in „narrowest situation”, they cover only 21.6% of the surface of the clay-fraction. The results make it very probable, that the adsorbed Ca-ions in the clay-fractions of soils are present in a mono-ionic film. (Hydratation of the ions was left out of account).



widest situation

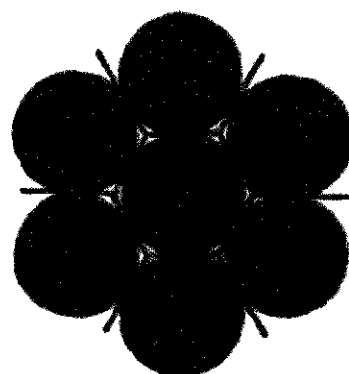


TABLE 28.

THE HYGROSCOPICITY OF THE OXIDISED SOILS, ACCORDING TO THE METHOD OF RODEWALD-MITSCHERLICH AND THE SURFACES OF THESE SOILS, CALCULATED THEREFROM BY MEANS OF THE FORMULA:

$$F = \frac{W_H}{\sqrt[3]{8,3 \times 18 \times 10^{-22}}} \text{ mm}^2$$

Soil nr	Hygros- copicity	% < 2 μ of the original oxidised soil	Hygroscopticity \times 100		The surface of 1 g soil ¹⁾ according to MITSCHER- LICH, in m ²
			% < 2 μ of the original oxidised soil		
1	9.97	39.3	25.4		405
2	9.83	48.2	20.4		399
3	4.80	22.8	21.1		195
4	4.12	18.8	21.9		167
5	7.46	33.8	22.1		303
6	7.78	36.7	21.2		316
7	8.15	39.1	20.8		331
8	3.76	16.6	22.7		153
9	3.16	16.2	19.5		128
10	4.54	23.2	19.6		184
11	4.57	23.2	19.7		186
12	6.80	36.2	18.8		276

The determination of the hygroscopicity was performed on the oxidised soils, according to the method of RODEWALD-MITSCHERLICH. ²⁾ (See: table 28)

Apart from the deviating behaviour of soil 1 (Drieborg) the hygroscopicity-values, per unit-weight of clay < 2 μ , are practically equal for the different soils. In table 23, in which the quantities of Al-Fe-Si-complex were compared, that had been dissolved from the different soils by the 18.7 % HCl-extraction, per unit-weight of the fraction < 2 μ , soil 1 also showed a deviating behaviour.

This soil contains a great quantity of non-oxidisable humus, as appeared from the evaporation of the HCl-residue in order to separate the SiO₂. During this treatment, dark-brown flakes are

¹⁾ According to MITSCHERLICH, per 100 g clay < 2 μ , on an average 20.7 g H₂O are bound (apart from soil 1). The surface of these 100 g, according to him, amounts to 84042 m². However, the surface-values according to MITSCHERLICH are supposed to be too high (P. EHRENBURG, Fühl. Ldwsch. Ztg, 63, 725 (1914) and 64, 233 (1915). According to VAGELER (P. VAGELER, Fühl. Ldwsch. Ztg., 61, 73 (1912) the surface therefrom only amounts to 84042 : 200 = 420 m². From the calculation on pag. 92, the surface of 100 g clay < 2 μ appeared to be 2644 m².

²⁾ E. MITSCHERLICH, Bodenkunde für Land- und Forstwirte, (1913), 12, 66.

formed, which disappear on ignition. The divergent behaviour of this soil with respect to the hygroscopicity-value is possibly caused by this humus. Another reason which places this soil in a special position is its age. In comparison with the other soils which are included in this research, soil 1 is youngest. Compared with the other soils an excess of Al-Fe-Si-complex is present.

According to their hygroscopicity-values the other 11 soils possess almost equal surfaces per unit-weight of the clay-fraction $< 2 \mu$.

It is striking, that for the soils: 2 (Ulsda), 7 (Rietveld), 9 (Hedel), 10 (Susteren), 11 (IJzendoorn) and especially for soil 12 (Etten) the hygroscopicity-values are somewhat lower than for the others and that accordingly the ratios SiO_2 : Sesquioxides of the HCl-extracts are also lower than those of the other soils. ¹⁾

Apparently, the composition of that part of the clay-fraction which is soluble in HCl, influences its hygroscopicity in such a way that as relatively more sesquioxides are present, the fixation of H_2O is relatively smaller.

This conclusion is opposite to that of GIESECKE ²⁾ in a research in which the fractions of 6 German soils, of very different origin and composition, were examined for chemical composition and hygroscopicity. From this he drew the conclusion: that the hygroscopicity of the soil was very dependent on the content of sesquioxides as had been found by BLANCK. ³⁾ According to him, however, the kinds of compounds in which the Fe^{+++} and Al^{+++} are present in the soil must be differentiated. Therefore the greater the ratio SiO_2 : Sesquioxides, the smaller the hygroscopicity. Exactly the reverse can be stated here.

By previous experiments it was proved, that the clay-fractions $< 2 \mu$, of the 12 soils, which are included in this research, show corresponding adsorption-values per unit-weight of the soils before the HCl-extraction; while also after the HCl-extraction the fractions $< 2 \mu$ of the HCl-residues, per unit-weight, possess equal adsorption capacities. Moreover about equal quantities of Al-Fe-Si-complex per unit-weight of clay appear to be dissolved during the HCl-extraction, while the mechanical compositions of the HCl-residues are practically equal to those of the original oxidised

¹⁾ See table 12, pag. 71.

²⁾ F. GIESECKE, *Chemie der Erde*, 3, 136 (1928).

³⁾ E. BLANCK, *Landw. Versuchsstat.*, 84, 439 (1914); *Journ. f. Ldw. sch.*, 60, 59 (1912); *Landw. Versuchsstat.*, 103, 66 (1924).

soils. Out of the clay-particles therefore only a surface-layer of a very small thickness can be dissolved by the HCl-extraction. This surface-layer, or only part of it, must therefore be the cause of the adsorption-reaction. In reality, the surfaces per unit-weight of clay appeared to be the same for all soils.

As appeared from the preliminary investigations, it is typical that also an Al-Fe-Si-complex, which causes part of the adsorption of the original soil, is dissolved out of the soil-particles $> 2 \mu$. As is obvious from other experiments, the adsorption capacity of the original oxidised soil also is defined by the clay-fraction $< 2 \mu$ and therefore the conclusion can be drawn that quantity and quality of the complex in the fraction $> 2 \mu$ is defined by the fraction $< 2 \mu$ of the soil.

Now that it has appeared, that the equal adsorption-values per unit-weight of the clays are the consequence of equal surfaces per unit-weight, will finally be investigated whether the chemical compositions of these surfaces correspond also.

Very different Al-Fe-Si-complexes appeared to be dissolved out of the various soils by the attack with 3.0, 5.0, 7.3 and 18.7 % HCl at 55°C ¹⁾, according to the method of VAN BEMMELEN and therefore it seems very improbable that by another method of extraction equal compositions of the adsorption-complexes, for the various soils, could be arrived at. On the contrary it seems probable that the surface-layer of these soil-particles must be similarly composed, as, besides the structure and surface of the adsorbent, also chemical composition must have an influence on the adsorption capacity.

The method for determining the colloidal soil-part chemically, as was accepted by the Second Commission of Soil Science at Budapest in the year 1929, makes it possible to dissolve the adsorptive soil-part by means of boiling the soil for 1 hour with HCl (sp.gr. 1.10).

For a great number of years this method has been objected to ²⁾ in spite of which it was accepted as an „international method”.

According to this method, the soils were treated and after the HCl-extraction, the usual NaOH-treatment was applied to dis-

¹⁾ See: table 12 pag. 71.

²⁾ D. J. HISSINK, Verh. der IIten Agroeol. Konf. Stockholm, 43 (1910). H. STREMMER u. B. AARNIO, Ztschr. f. Prakt. Geol., 19, 329 (1911).
R. GANSSSEN u. K. UTSCHER, I. Intern. Congr. of Soil Sci., Washington 1927.
R. GANSSSEN, Verh. der IIten Komm. Intern. Bod. k. Ges., Budapest 1929.

TABLE 29.

THE QUANTITIES OF Al_2O_3 , Fe_2O_3 AND SiO_2 IN mm PER 100 g AIR-DRY OXIDISED SOIL, BY EXTRACTION ACCORDING TO THE METHOD OF VAN BEMMELEN-HISSINK

Soil nr	Totally dissolved in % of the air-dry oxid. soil	SiO_2 in % of the air-dry oxidised soil	Fe_2O_3 in mm	Al_2O_3 in mm	SiO_2 in % of the air-dry HCl-residue	Total SiO_2 in mm	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$
1	23.5	0.06	33.2	41.8	15.13	194	4.6	2.6
2	20.3	0.03	39.8	67.4	20.00	266	3.9	2.5
3	13.5	0.10	17.6	21.1	8.31	122	5.8	3.2
4	10.7	0.07	15.8	9.7	6.79	102	10.5	4.0
5	19.4	0.04	25.4	23.7	13.01	176	7.4	3.6
6	26.6	0.09	27.1	25.5	14.55	180	7.1	3.4
7	18.0	0.12	33.2	39.4	14.36	198	5.0	2.7
8	7.7	0.08	15.8	10.7	6.54	102	9.5	3.8
9	7.4	0.07	17.4	10.2	5.42	85	8.3	3.1
10	11.5	0.10	22.5	28.2	7.88	118	4.2	2.3
11	13.1	0.02	21.9	24.7	8.20	119	4.8	2.6
12	14.7	0.02	36.6	53.1	10.59	151	2.8	1.7

solve the SiO_2 , which had been separated insolubly. ¹⁾ (See: table 29)

From these data it follows, that Al-Fe-Si-complexes of totally different compositions are dissolved out of the various soils by the HCl-extractions, whereas the colloidal parts of these soils behave uniformly towards the exchange-reaction. So the method of VAN BEMMELEN-HISSINK fails completely to give an insight into the composition of the adsorption-complex of the soil, i.e. into that part of the clay-fraction to which the exchange-reaction is restricted. ²⁾

¹⁾ O. LEMMERMANN, Methoden für die Untersuchung des Bodens, Beih. z. Ztschr. f. Pfl. Ernähr. D. u. Bod.k., 1 (1932).

²⁾ The adsorption-values of the HCl-NaOH-residues per 100 g, amounts to:

Soil nr	Adsorption-values in M.E. (Ca^{++}) p. 100 g HCl-NaOH-residue	Fraction $< 2 \mu$ in % by weight of the original oxidised soil
2	7.1	48.2
1	8.9	39.3
7	9.3	39.1
6	—	36.7
12	6.0	36.2
5	5.7	33.8
10	5.2	23.2
11	2.6	23.2
3	2.6	22.8
4	—	18.8
8	1.2	16.6
9	1.7	16.2

The soils have been arranged in decreasing clay-contents. Generally, the adsorption-value

When the total Al-Fe-Si-complexes, which have been dissolved by the extraction, are compared with the clay-fractions of the soils, a correlation can again be stated.

TABLE 30.

THE RELATION BETWEEN THE QUANTITY OF THE Al-Fe-Si-COMPLEX, DISSOLVED BY THE METHOD OF VAN BEMMELEN-HISSINK, AND THE CLAY-FRACTION OF THE SOIL

Soil nr	Sesquioxides in mm p.100g air-dry oxidised soil.	SiO ₂ in mm p.100g air-dry oxidised soil.	Al ₂ O ₃ +Fe ₂ O ₃ +SiO ₂ in mm p.100g air-dry oxidised soil.	CaCO ₃ in % by weight of the air-dry oxidised soil.	Sesq. ox. + SiO ₂ in mm p.100g air-dry oxidised CaCO ₃ -free soil.	Fraction < 2 μ in % by weight of the air-dry oxidised soil.	Al ₂ O ₃ +Fe ₂ O ₃ +SiO ₂ % < 2 μ of the air-dry oxid. soil
1	75.0	194	269.0	4.4	281	39.3	7.2
2	107.2	266	373.2	0.1	374	48.2	7.8
3	38.7	122	160.7	2.5	165	22.8	7.2
4	25.5	102	127.5	1.5	129	18.8	6.9
5	49.1	176	225.1	4.6	236	33.8	7.0
6	52.6	180	232.6	11.2	262	36.7	7.1
7	72.6	198	270.6	0.1	271	39.1	6.9
8	26.5	102	128.5	—	128	16.6	7.7
9	27.6	85	112.6	—	113	16.2	7.0
10	50.7	118	168.7	—	169	23.2	7.3
11	46.6	119	165.6	0.6	167	23.2	7.2
12	89.7	151	240.7	—	241	36.2	6.7

From this table it is obvious, that per unit-weight of the clay-fractions < 2 μ about 7.2 mm Al-Fe-Si-complex is dissolved out of the different soils.

Now that it has appeared, that the quantities of Al-Fe-Si-complex, which are brought into solution by the method „VAN BEMMELEN-HISSINK”, are dependent on the respective clay-fractions < 2 μ of the different soils, the question is raised whether the respective clay-fractions are wholly or only partly brought into solution by this method.

To control this, the clay-fractions < 2 μ of some soils were separated. If the residue is lower, the lower the clay-content of the original soil. Apparently by the method of VAN BEMMELEN-HISSINK, all the adsorptive soil-particles are not dissolved. In accordance with the results of VAN BEMMELEN and others, the adsorptions of these residues with respect to a neutral salt have disappeared; in analogy with the phenomena shown with the more moderate extraction, it seems very probable, that by the determination of the adsorption capacity of these residues with a neutral salt, the adsorption capacities would appear to have decreased markedly by coagulation of the particles. When however the HCl-residue is again dispersed by means of a subsequent NaOH-treatment and the SiO₂, which has been separated by the HCl-extraction is dissolved, the adsorption capacity of the residue still appears to have been retained to an important extent.

rated in the usual way, after treating the soils with 6 % H_2O_2 . ¹⁾ The total analyses were performed by fusing the clay-fractions with $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$. The extracts were analysed for Al^{+++} , Fe^{+++} , Si^{++++} and Ti^{++} ²⁾.

TABLE 31.

TOTAL ANALYSES OF THE CLAY-FRACTIONS $< 2\mu$ OF THE SOILS, IN PERCENTS BY WEIGHT OF THE AIR-DRY OXIDISED FRACTIONS $< 2\mu$

Soil nr	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$
1	50.41	10.31	17.03	0.64	3.62	5.02
2	51.28	11.13	22.30	0.53	2.95	3.90
3	50.78	10.26	16.68	0.62	3.70	5.16
4	51.62	12.62	13.74	0.54	4.01	6.37
5	51.29	8.86	15.67	0.53	4.07	5.55
6	47.80	9.00	16.06	0.32	3.71	5.04
7	50.89	6.70	21.71	0.42	3.32	3.97
8	53.51	10.96	19.62	0.62	3.41	4.62
9	45.24	11.09	18.54	0.40	2.99	4.14

Assuming that the CaCO_3 of the soils is principally present in the clay-fractions, the composition of the clay-fractions $< 2\mu$ of the soils, calculated on CaCO_3 -free clay-fractions, can be seen approximately from the following table:

TABLE 32.

TOTAL Al-Fe-Si-COMPLEX OF THE CLAY-FRACTIONS OF THE SOILS, IN PERCENT BY WEIGHT OF THE AIR-DRY, OXIDISED, CaCO_3 -FREE CLAY-FRACTIONS $< 2\mu$

Soil nr	SiO_2	Fe_2O_3	Al_2O_3
1	52.24	10.68	17.65
2	53.67	11.65	23.34
3	61.58	12.44	20.23
4	58.20	14.23	15.49
5	52.28	9.03	15.97
6	51.26	9.65	17.22
7	54.89	7.23	23.41
8	54.97	11.26	20.16
9	47.22	11.58	19.35

¹⁾ See: pag. 23.

²⁾ See: Methods, pag. 27. The determination of Ti^{++} was done colorimetrically.

If the total clay-fraction had been dissolved by the method „VAN BEMMELEN-HISSINK”, then in the v. B.-H.-extract of soil 1 should have been found:

$$0.393 \times 52.24 = 20.53 \% \text{ SiO}_2$$

$$0.393 \times 10.68 = 4.20 \% \text{ Fe}_2\text{O}_3$$

$$\text{and } 0.393 \times 17.65 = 6.94 \% \text{ Al}_2\text{O}_3$$

as 39.3 % of the soil consists of particles $< 2 \mu$.

In the following table, the contents of the v. B.-H.-extracts are compared with the contents, which should have been found if the clay-fractions $< 2 \mu$ had been completely dissolved, and the soil-particles $> 2 \mu$ had been completely retained on extraction according to „VAN BEMMELEN-HISSINK”.

TABLE 33.

Soil nr	SiO ₂ in % of the fraction < 2 μ		Fe ₂ O ₃ in % of the fraction < 2 μ		Al ₂ O ₃ in % of the fraction < 2 μ	
	Total.	v.BEMMELEN-HISSINK ¹⁾	Total.	v.BEMMELEN-HISSINK ¹⁾	Total.	v.BEMMELEN-HISSINK ¹⁾
1	20.53	12.17	4.20	5.56	6.94	4.46
2	25.87	15.99	5.62	6.38	11.25	6.88
3	14.04	7.48	2.84	2.89	4.61	2.21
4	10.94	6.22	2.68	2.57	2.91	0.81
5	17.66	11.04	3.05	4.27	5.40	2.54
6	18.81	12.13	3.54	4.88	6.32	2.93
7	21.46	11.91	2.83	5.33	9.15	4.02
8	9.13	6.12	1.87	2.53	3.35	1.09
9	7.65	5.09	1.88	2.78	3.13	1.04

From these data it appears, that the Al-Si-compounds of the clay-fractions only partly have been brought into solution by the method „VAN BEMMELEN-HISSINK”: after the extraction, an important part of the Al-Si-compounds is still left.²⁾ Moreover Fe⁺⁺⁺ is also dissolved from the soil-particles $> 2 \mu$ during the extraction.

In comparing the ratios SiO₂: Sesquioxides of the Al-Fe-Si-complexes, which are attacked by the method of VAN BEMMELEN-HISSINK, with those which are dissolved by the method of VAN BEMMELEN, with 18.7 % HCl at 55° C, it appears that in the first case an Al-Fe-Si-complex is brought into solution which contains relatively more SiO₂.³⁾ (See: table 34) From the ratios SiO₂:

¹⁾ These values also were calculated on CaCO₃-free soil.

²⁾ This follows also from the adsorption-values of the residues after the extraction. See: pag. 99, note 2.

³⁾ Soil 1 (Drieborg) excepted.

TABLE 34.

COMPARISON OF THE COMPOSITION OF THE Al-Fe-Si-COMPLEX,
DISSOLVED BY EXTRACTION ACCORDING TO THE METHOD OF
VAN BEMMELEN, FOR 30 MINUTES WITH 18.7% HCl, AT 55° C AND
THAT OF THE Al-Fe-Si-COMPLEX BROUGHT INTO SOLUTION
BY EXTRACTION ACCORDING TO THE METHOD
VAN BEMMELEN-HISSINK

Soil nr	Ratio: $\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$		Ratio: $\frac{\text{SiO}_2}{\text{Sesquioxides}}$		Ratio: $\frac{\text{SiO}_2}{\text{Fe}_2\text{O}_3}$	
	Method v. B. ¹⁾	Method v. B.-H. ²⁾	Method v. B. ¹⁾	Method v. B.-H. ²⁾	Method v. B. ¹⁾	Method v. B.-H. ²⁾
1	7.5	4.6	2.9	2.6	4.6	5.8
2	6.2	3.9	2.0	2.5	2.9	6.7
3	5.5	5.8	2.3	3.2	3.8	6.9
4	4.8	10.5	2.3	4.0	4.4	6.4
5	6.4	7.4	2.4	3.6	3.9	6.9
6	8.7	7.1	2.2	3.4	2.9	6.6
7	3.4	5.0	1.1	2.7	1.6	6.0
8	6.8	9.5	2.0	3.8	2.9	6.4
9	4.0	8.3	1.4	3.1	2.2	4.9
10	2.7	4.2	1.0	2.3	1.7	5.2
11	3.0	4.8	1.5	2.6	3.0	5.4
12	2.6	2.8	0.8	1.7	1.2	4.1

:Fe₂O₃ this may be seen still more clearly, whereas the contrary can be observed only as regards the ratios SiO₂ : Al₂O₃ for the soils: 1 (Drieborg), 2 (Ulsda) and 6 (Wilhelminadorp).³⁾ It is striking, that the soils 1, 6 and also 2 are the youngest of all those used in this research. However in two of these soils the ratio SiO₂ : Sesquioxides also increase as the attack becomes more intensive, in other words, as the attack penetrates deeper into the soil-particles.⁴⁾ So the layers of the clay-particles, which are nearer the surface, contain relatively more sesquioxides than the interior layers. In the soils 2 and 6 however, the surface-layers relatively contain less Al⁺⁺⁺ and that they contain relatively more sesquioxides must therefore be ascribed to the Fe⁺⁺⁺.⁴⁾ Of the other soils, the surface-layers contain relatively more sesquioxides and besides they contain relatively more Al⁺⁺⁺ and more Fe⁺⁺⁺.

¹⁾ See: table 12, pag. 71.

²⁾ See: table 29, pag. 99.

³⁾ This agrees with the results of VAN BEMMELEN: that the weathering-silicate is more soluble the more basic it is. J. M. VAN BEMMELEN, Ztschr. f. anorg. Chem., 42, 287 (1904).

⁴⁾ By the extractions of soil 1 (Drieborg) the v. B.-value is even a little higher than the v. B.-H.-value with respect to the SiO₂ : sesq. ox.-ratio. Obviously with this youngest soil, the Fe⁺⁺⁺ has not yet been accumulated sufficiently, so that the Al⁺⁺⁺-loss could not be exceeded.

In accordance with these experiments a theory can be evolved regarding the weathering-process.

On the surfaces of the Al-Fe-Si-compounds, out of which the soil has been produced, Si^{++++} and Al^{+++} are led away by the weathering-agents. Through this the surfaces of the Al-Fe-Si-compounds contain relatively more Fe^{+++} and less Al^{+++} and Si^{++++} than is the case with the interior parts. This progress can be seen with the younger soils.

With the older soils a product is found, on the surfaces of the Al-Fe-Si-compounds, which contains relatively less Si^{++++} and besides these outer layers not only contain relatively more Fe^{+++} , but also more Al^{+++} .

At first Fe^{+++} is therefore accumulated in the soil: when the soils grow older, Al^{+++} also stays behind, so that finally a product is left which contains relatively less Si^{++++} and more sesquioxides than the inner parts of the soil-particles.

Possibly this change of the weathering coincides with the loss of lime in the soil, as in an alkaline milieu Al^{+++} and Si^{++++} are soluble and Fe^{+++} is insoluble, whereas in a neutral milieu also Al^{+++} becomes less soluble.

C. Summary and Conclusions

The determination of the mechanical compositions of the different soils, by means of the Pipette-method of OLMSTEAD before and after the extraction with 7.3 % HCl, shows an important decrease of the clay-fractions $< 2 \mu$ of the soils after the HCl-extraction.

The adsorption-values of the HCl-residues showed no relation to the clay-fractions $> 2 \mu$ of these residues, on the contrary, they were defined by the clay-fractions $< 2 \mu$ of the original oxidised soils.

As it appeared that the fractions $< 50 \mu$ before and after the HCl-extraction almost agreed, it was supposed that the original mechanical compositions had not varied on account of important parts of the clay-fractions, being dissolved by the HCl-extraction, but because these fractions possibly had coagulated.

The determinations of the adsorption-values, which showed the correlation with the clay-fractions $< 2 \mu$ of the original oxidised soils, were performed by means of percolations of the HCl-residues with a $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution. The supposition that

during these percolations the mechanical compositions of the soils, which had been varied by the HCl-extraction, were regenerated, was therefore justified. Indeed it appeared, that by percolating the HCl-residues with a $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution, the original mechanical compositions were almost entirely regenerated.

The coagulation of the HCl-residues, which apparently without previous $(\text{CH}_3\text{COO})_2\text{Ca}$ -percolations cannot be completely dispersed by the $\text{Na}_2(\text{COO})_2$ -peptisations in the mechanical analyses, is caused by the SiO_2 which has been separated during the HCl-extractions. Viz.: part of this SiO_2 had been found again in the $(\text{CH}_3\text{COO})_2\text{Ca}$ -percolates.

Therefore the clay-fractions of the HCl-residues, which have been previously treated with a $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution, define the adsorption-values of the HCl-residues.

The quantities of Al-Fe-Si-complex, which are dissolved out of the different soils by the HCl-extraction, also appear to be dependent on the clay-fractions $< 2 \mu$ of the soils. From this dependence of the quantities of Al-Fe-Si-complex, dissolved by the HCl-extractions, on the clay-fractions of the soils, together with the fact that after the HCl-extractions the mechanical compositions of the original soils have been retained, the conclusion can be drawn that during the HCl-extraction only a surface-film of the soil-particles is dissolved. This film, or only the surface of it, must therefore be the cause of the adsorption phenomena.

The adsorption capacities of the original soils proved to be defined only by the clay-fractions of the soils and no correlation was found between the chemical compositions of the soil-colloids, determined by the method „VAN BEMMELEN-HISSINK”, and the adsorption-values of the original oxidised soils, in other words: the chemical compositions of the soil-colloids, which were determined in that way differed strongly for the different soils, whereas the adsorption-values per unit-weight of the clay-fractions $< 2 \mu$ were equal.

As the adsorption capacities of the clay-fractions and, in general, also the quantities of Al-Fe-Si-complex which were dissolved out of the clay-fractions per unit-weight of clay, by the method „VAN BEMMELEN” and „VAN BEMMELEN-HISSINK” respectively agreed, the surfaces of the clays were supposed to be the same.

When the clay-fractions $< 2 \mu$ of the different soils are fractionated further, the fractions $< 2 \mu$, $< 1\frac{1}{2} \mu$, $< 1 \mu$, and $< \frac{1}{2} \mu$,

indeed appeared to bear the same relation of 100 : 91 : 84 : 70. Based on these equal distributions of the fraction-weights of the clay-fractions $< 2 \mu$, the surface of clay was calculated somewhat speculatively because of the necessary extrapolation.

The equality of the surfaces of the different clays was confirmed by determining the hygroscopicity-values.

By comparing the Al-Fe-Si-complexes, which were brought into solution from the different soils, by the method „VAN BEMMELEN” and „VAN BEMMELEN-HISSINK”, it appeared that the ratios $\text{SiO}_2 : \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ of the HCl-extracts according to the first method, for all soils were lower than the corresponding ratios of the HCl-extracts according to the second method. Apparently the surface-layers of the soil-particles therefore contain relatively less Si than the layers of the soil-particles which are situated under them. In 9 out of 12 cases this conclusion also held good for the $\text{SiO}_2 : \text{Al}_2\text{O}_3$ -ratios. As to the other cases, the proportions in the extracts according to the method „VAN BEMMELEN” were higher than in the extract according to the method „VAN BEMMELEN-HISSINK”. These 3 cases concerned the 3 soils of more recent deposition and in accordance with this difference as against the older soils, a theory was formulated as to the weathering-process.

The fact, that the clay-fractions of the different soils behave uniformly as to their adsorption-values, the quantities of Al-Fe-Si-complex, which are dissolved by the HCl-extraction according to the different methods, and the hygroscopicity-values, must be caused by the corresponding climatologic circumstances during which they have been formed.

It is rather surprising however that when these surface-layers have been removed by the HCl-extraction, the adsorption-values of the HCl-residues, per unit-weight, are still equal. Therefore the composition of the residual complex of the different clays must again be uniform, a fact which however cannot be concluded from the chemical analyses. It can be expected that the standardised treatments of the different HCl-residues for the determination of the adsorption capacity will be responsible for this uniformity.

From the data of the HCl-extractions one gets the impression, that the adsorption-values of the soils are defined rather by the total Al-Fe-Si-complex, which is soluble in HCl under similar conditions, than by the mutual proportion of Al_2O_3 , Fe_2O_3 and SiO_2 in the HCl-extract.

IV. ANALOGOUS INVESTIGATIONS ON MINERALS

A. INTRODUCTION

As the impression was obtained, that part of the Al-Fe-Si compounds, which are present in clays, — judging from its relative solubility in HCl — could consist of minerals, corresponding experiments were performed with a few minerals which are present in Dutch clay-soils.

THIÉBAUT ¹⁾ determined the quantities of mineral components, which were dissolved by treating different minerals with HCl and H₂SO₄, under certain conditions. He came to the following conclusion:

„L'acide chlorhydrique est absolument sans action sur le zircon, le rutile, le quartz et la pyrite. Il agit fort peu sur le feldspath orthose, un peu plus sur les argiles du type de la kaolinite et ne détruit la muscovite dans une assez forte proportion que si les éléments de celle-ci ont une dimension inférieure à μ . Il attaque au contraire facilement la montmorillonite et détruit complètement la biotite et la magnétite. La plupart de ces minéraux (argiles, mica et magnétite) sont entièrement attaqués par l'acide sulfurique. Cependant la pyrite et l'iléménite ne sont pas totalement détruites: le rutile résiste mieux encore à l'action de cet acide; l'orthose est fort peu altéré par lui, le zircon et le quartz ne le sont pas du tout.”

From the investigations of ROSS, HENDRICKS and FRY, KELLEY, DORE and BROWN ²⁾, which have been mentioned in the introduction, it appears that in some American clays so-called „clay-minerals” are supposed to be present and besides it is improbable that, when the fractions from 1 μ onward consist principally of the

¹⁾ J. LUCIEN THIÉBAUT, Contribution à l'étude des Sédiments Argilo-calcaires du Bassin de Paris, (1925).

²⁾ See: Introduction, pag. 12.

minerals: muscovite, quartz and feldspath, as was shown by SCHLUNZ for 2 German clay-soils, these would suddenly disappear in the smaller fractions.

From the research of THIÉBAUT, biotite, kaolinite, orthoclase and muscovite appear to be attacked by HCl. Therefore the experiments were performed with these minerals. Besides these, the minerals: chlorite and basaltic hornblende, which are also found in the sand-fractions of clay-soils, and finally also a so-called „clay-mineral”: halloysite, were included in the investigation.

The behaviour of these minerals with regard to the attack with HCl was compared with that of a zeolite: natrolite and an artificial Na-permutite according to GANSSEN.

B. EXPERIMENTAL PART

The minerals, the zeolite and the permutite were ground in an agate mortar, after being rotated for some days in a ball-mill with porcelain marbles. The finer fraction was obtained by passing through a $250\ \mu$ -sieve. With these fractions $< 250\ \mu$ of the substances the experiments were performed, after grinding them in small portions in an agate mortar.

Scheme.

10 g of the air-dry fraction $< 250\ \mu$ were extracted for 30 minutes, at 55°C , with 200 cc 7.3 % HCl ¹⁾ and the extract was quantitatively analysed for Al^{+++} , Fe^{+++} and Si^{++++} ²⁾

From the HCl-residue, 5 g were treated with 100 cc NaOH, sp.gr. 1.04, for 5 minutes, at 50°C ³⁾ and in the extract Si^{++++} was determined. ⁴⁾

The adsorption-values of the original substance, the HCl-residue and the HCl-NaOH-residue were determined in the usual way. ⁵⁾

After the extraction of the zeolite and the permutite with HCl, respectively 7.9 % and 1.8 % were left after the NaOH-treatment. The clay-fractions of the soils therefore could only have been built up from these substances to a very small extent at the utmost. ⁶⁾

¹⁾ See: Methods, pag. 25.

²⁾ See: Methods, pag. 26.

³⁾ See: Methods, pag. 29.

⁴⁾ See: Methods, pag. 29.

⁵⁾ See: Methods, pag. 33.

⁶⁾ By extraction of the clay-fraction $< 2\ \mu$ of soil 12 (Etten), under the same conditions, only 16,7% of the fraction was brought into solution. (See: table 8, pag. 52).

TABLE 35.

EXTRACTIONS OF SOME MINERALS, A ZEOLITE AND A PERMUTITE WITH 7.3% HCl

	Natro- lite	Permu- tite	Halloy- site	Biotite	Chlorite	Basaltic Horn- blende	Musco- vite	Ortho- clase	Kaoli- nite	Expressed in:
Totally dissolved in HCl...	45.9	30.5	44.1	14.4	12.1	3.1	4.1	1.3	1.5	% of the air-dry substance
Fe_2O_3	—	0.23	2.07	4.31	2.64	0.50	0.21	0.17	—	" " "
Al_2O_3	25.65	15.42	24.49	4.23	2.96	0.55	1.61	0.34	0.12	" " "
SiO_2	10.12	2.45	7.57	2.02	2.40	0.50	0.92	0.11	0.07	" " "
SiO_2 in the subsequent NaOH-extract	57.04	73.44	2.74	7.80	1.00	1.03	1.05	1.15	0.27	% of the HCl-residue
SiO_2 in the subsequent NaOH-extract	30.86	51.04	1.53	6.68	0.88	1.00	1.01	1.14	0.27	% of the air-dry substance
Total SiO_2	40.98	53.49	9.10	8.70	3.28	1.50	1.93	1.25	0.34	" " "
SiO_2 : $Al_2O_3 + Fe_2O_3$	—	5.8	0.6	2.1	1.2	2.9	1.9	4.7	—	" " "
SiO_2 : Al_2O_3	2.7	5.9	0.6	3.5	1.9	4.6	2.0	6.3	4.8	" " "
Original adsorption capacity	12.3	281.4	43.2	11.5	25.3	4.4	10.7	5.5	16.9	M. E. (Ca'') per 100 g air-dry substance
Residual adsorption	61.4	51.5	11.5	16.3	5.9	1.8	6.2	3.1	10.7	M. E. (Ca'') per 100 g air-dry HCl-residue
Adsorption-value of the HCl-NaOH-residue	—	—	5.9	7.6	6.6	2.9	7.8	3.2	15.0	M. E. (Ca'') per 100 g HCl-NaOH-residue

As to the minerals: halloysite appears to be dissolved to an appreciable extent by HCl, whereas biotite and chlorite are less attacked by the HCl-extraction and the other minerals only to a relatively small degree.

The adsorption-value of the permutite amounts to 281.4 M.E. per 100 g. In comparison with that of the clay-fraction of the soil, therefore the former is very high. The clay-fraction adsorbs viz. per 100 g: $25 \times 2.2 = 55$ M.E. (Ca⁺⁺), on an average.

Generally the adsorption-values of the minerals are much lower than those of the clay-fractions of the soils per unit-weight.

The adsorption capacities of the HCl-residues generally are lower than those of the original substances; only natrolite and biotite form exceptions. Apparently in these latter cases the decreases of the adsorption-values, caused by the HCl-extraction, have been surpassed by the adsorption capacity of the SiO₂-gel, which is present in the HCl-residues to a considerable percentage. Therefore the adsorption capacity of the HCl-NaOH-residue of biotite is again lower than that of the original mineral-powder, whereas the HCl-residue of natrolite has been almost entirely dissolved by the NaOH-treatment. ¹⁾

The adsorption-values of the HCl-NaOH-residues of the minerals, generally are higher than those of the HCl-residues. Biotite forms an exception for the above-mentioned reason. Apparently the pre-treatment with NaOH thus causes a higher dispersion of the substance than the direct (CH₃COO)₂Ca-percolation of the HCl-residue. ²⁾

Now it is again of importance to calculate the surfaces of the mineral-powders approximately, as the quantities of Al-Fe-Si-complex, which are dissolved by HCl-extraction, as is also the case with the adsorption-values of the minerals, are defined by their surfaces per unit-weight and it is for this reason that the mechanical compositions of the mineral-powders were determined by means of the pipette-analysis of OLMSTEAD ³⁾.

The fractions $< 1 \mu$ and $< \frac{1}{2} \mu$ also were analysed in order to see if these corresponded to the different substances in percents of the fractions $< 2 \mu$, as had been found for the clay-fractions of the various soils. ⁴⁾

¹⁾ After the NaOH-treatment, 7.9% HCl-NaOH-residue was left.

²⁾ See: table 35, pag. 109. ³⁾ See: Methods, pag. 77.

⁴⁾ According to this method, only the exterior-surface is determined, so that for substances which possess an interior-surface, e.g. natrolite and permutite, an equivalent value for

TABLE 36.

MECHANICAL COMPOSITIONS, IN PERCENT BY WEIGHT, OF THE
AIR-DRY SUBSTANCES, ACCORDING TO THE PIPETTE-METHOD
OF OLMSTEAD

Substance	Fractions						
	$< 250 \mu$	$< 50 \mu$	$< 10 \mu$	$< 5 \mu$	$< 2 \mu$	$< 1 \mu$	$< \frac{1}{2} \mu$
Natrolite	95.5	95.0	90.8	47.0	26.0	4.9	0.5
Permutite	98.6	95.6	58.1	42.6	26.1	13.0	5.1
Halloysite	97.8	93.2	35.5	25.0	13.0	6.5	1.3
Biotite	99.0	67.5	37.1	22.7	12.3	6.9	3.4
Chlorite	101.0	99.8	56.8	35.2	18.4	10.4	3.5
Basaltic-Hornblende	96.5	93.7	39.1	24.0	11.3	4.3	1.3
Muscovite	99.9	69.9	34.6	23.2	14.0	9.2	4.5
Orthoclase	99.4	89.1	39.5	25.4	14.0	7.1	2.8
Kaolinite	100.2	100.2	98.8	92.0	70.0	49.9	32.4

Substance	Fractions						
	250-50 μ	50-10 μ	10-5 μ	5-2 μ	2-1 μ	1- $\frac{1}{2}$ μ	$< \frac{1}{2} \mu$
Natrolite	0.5	4.2	43.8	21.0	21.1	4.4	0.5
Permutite	3.0	37.5	15.5	16.5	13.1	7.9	5.1
Halloysite	4.6	57.7	10.5	12.0	6.5	5.2	1.3
Biotite	31.5	30.4	14.4	10.4	5.4	3.5	3.4
Chlorite	1.2	43.0	21.6	16.8	8.0	6.9	3.5
Basaltic-Hornblende	2.8	54.6	15.1	12.7	7.0	3.0	1.3
Muscovite	30.0	35.3	11.4	9.2	4.8	4.7	4.5
Orthoclase	10.3	49.6	14.1	11.4	6.9	4.3	2.8
Kaolinite	—	1.4	6.8	22.0	20.1	17.5	32.4

When the fractions $< 1 \mu$ and $< \frac{1}{2} \mu$ are expressed in percent of the fractions $< 2 \mu$, it appears that these values disagree very much for the corresponding fractions of the different substances. (See: table 37)

In comparison with the variable mechanical compositions of the „clay-fractions” of these substances, the uniformity of the clays of the respective soils appears very clearly. ¹⁾

It appears impossible to carry out here a calculation of the sur-

the total adsorptive surface cannot be obtained. A second factor makes the equivalent-values for the surfaces of the micaceous minerals: biotite, chlorite, muscovite and kaolinite deviate from the real values. The formula of STOKES viz. can only be applied to spherical particles, whereas the particles of these minerals are platy.

¹⁾ See: table 26, pag. 92.

TABLE 37.

FRACTIONS $< 1 \mu$ AND $< \frac{1}{2} \mu$ OF THE DIFFERENT SUBSTANCES IN PERCENT BY WEIGHT OF THE FRACTIONS $< 2 \mu$

Substance:	Fractions:	
	$< 1 \mu$	$< \frac{1}{2} \mu$
Natrolite	19	2
Permutite	50	20
Halloysite	50	10
Biotite	56	28
Chlorite	57	19
Basaltic-Hornblende.....	38	12
Muscovite	66	32
Orthoclase	51	20
Kaolinite	71	46

face in analogy with the determinations of the surfaces of the various clay-soils. When therefore the adsorption-values of the original materials, together with those of the HCl-residues and of the HCl-NaOH-residues, are compared with the „clay-fractions” $< 2 \mu$ of the original materials, no relation appears to exist. (See: table 38)

TABLE 38.

THE RELATIONS BETWEEN THE ORIGINAL ADSORPTION-VALUES, THE ADSORPTION-VALUES OF THE HCl-RESIDUES AND THE ADSORPTION-VALUES OF THE HCl-NaOH-RESIDUES AND THE FRACTIONS $< 2 \mu$ OF THE ORIGINAL SUBSTANCES ¹⁾

Substance	Fraction $< 2 \mu$ in % by weight of the air-dry substance	Adsorpt.-value in M. E. (Ca ⁺⁺) $\times 100$ per 100 g of the subst.	Adsorpt.-value in M. E. (Ca ⁺⁺) $\times 100$ per 100 g of the HCl-resid.	Adsorpt.-value in M. E. (Ca ⁺⁺) $\times 100$ per 100 g of the HCl- NaOH-residue
		% $< 2 \mu$ of the substance	% $< 2 \mu$ of the substance	% $< 2 \mu$ of the substance
Natrolite	26.0	47.3	—	—
Permutite	26.1	1078.1	—	—
Halloysite	13.0	332.3	88.5	45.4
Biotite	12.3	93.5	—	61.8
Chlorite	18.4	137.5	32.1	35.9
Basaltic-Hornblende ...	11.3	38.9	15.9	25.7
Muscovite	14.0	76.4	44.3	55.7
Orthoclase	14.0	39.3	22.1	22.9
Kaolinite	70.0	24.1	15.3	21.4

¹⁾ The different specific weights of the minerals are not taken in account in this calculation, as the error caused by this, is unimportant in comparison with the diverging mechanical compositions of the fractions $< 2 \mu$.

The values of the fourth and the fifth column were not calculated for natrolite, permutite and biotite. As to the first two, this was omitted because the HCl-residues consisted to a very great part of SiO_2 and were dissolved by the NaOH-treatment up to 85.4 % and 97.4 % respectively. The adsorption-value of the HCl-residue of biotite is higher than that of the original mineral, whereas the adsorption-value of the HCl-NaOH-residue is lower. Apparently in this case, the adsorption-value of the HCl-residue is perceptibly influenced by the SiO_2 -gel which has been separated by the HCl-extraction, so that the comparison of this value with the fraction $< 2 \mu$ has little meaning.

As the surface-equivalent could not be estimated approximately in this way, because the mechanical compositions of the fractions $< 2 \mu$ varied considerably for the various minerals and hence differed essentially from the uniform mechanical compositions of the fractions $< 2 \mu$ of the different soils, an attempt was made to find an equivalent for the mineral surfaces by determining the hygroscopicity-values according to the method of RODEWALD-MITSCHERLICH.¹⁾ (See: table 39)

Between the hygroscopicity-values on the one side, and the fractions $< 2 \mu$ and the adsorption-values in M.E. (Ca^{++}) on the other side, no relation appears to exist. It is by no means surprising

TABLE 39.

DETERMINATIONS OF THE HYGROSCOPICITY-VALUES OF THE SUBSTANCES, ACCORDING TO THE METHOD OF RODEWALD-MITSCHERLICH

Substance	Hygroscopicity in % of the air-dry substance	Fraction $< 2 \mu$ in % by weight of the original air-dry substance	Adsorption-value in M.E. (Ca^{++}) per 100 g of the air-dry substance
Natrolite	0.88	26.0	12.3
Permutite	32.80	26.1	281.4
Halloysite	10.06	13.0	43.2
Biotite	1.85	12.3	11.5
Chlorite	1.36	18.4	25.3
Basaltic-Hornblende . . .	0.41	11.3	4.4
Muscovite	1.46	14.0	10.7
Orthoclase	0.22	14.0	5.5
Kaolinite	3.62	70.0	16.9

1) See: pag. 96, note 2.

that this correlation is not found for the substances with great interior surfaces, such as natrolite and permutite, because for these substances a longer time is required to reach the adsorption-equilibrium than for the percolation connected with the determination of the adsorption-value, ¹⁾ and moreover because the mechanical analysis only gives an equivalent for the exterior surfaces of the substances. Probably the apparent independence of the adsorption-values of the minerals and their hygroscopicity-values is caused by the different cations which are adsorbed by the different substances.

According to VAGELER and ALTEN ²⁾, the hygroscopic water appears to be almost identical with the hydration-water of the adsorbed ions. As soon as the complexes which are compared are not provided with the same ions or the same mixture of ions, the hygroscopicity-values are no longer mutually comparable.

C. SUMMARY AND CONCLUSIONS

By the extraction of different minerals, a zeolite and a „permutite according to GANSSEN“, with HCl, under similar conditions, in the same way as was done with clay-soils, the zeolite and the permutite appeared to be dissolved to 92.1 % and 98.2 % respectively by the HCl-NaOH-extraction. The clay-fractions of Dutch clay-soils are therefore for the greater part not built up from these substances, as during a corresponding extraction of the fraction $< 2 \mu$ of soil 12 (Etten), only 16.7 % had been brought into solution.

Generally the adsorption-values of the minerals are much lower than those of the clay-fractions of soils per unit-weight. However, the fractions $< 2 \mu$ of the minerals were much coarser than the clay-fractions $< 2 \mu$ of the soils as appeared from mechanical analyses.

¹⁾ N. CERNESCU, Kationenumtausch und Struktur, 31 (1931). „Es gibt zwischen Ton, Permutit und Chabasit wesentliche Unterschiede bezüglich ihrer Umtauschgeschwindigkeit bei einer bestimmten Temperatur: Bei Zimmertemperatur (18–20° C) ist das Gleichgewicht beim Ton schon nach 5 Minuten erreicht, beim Permutit erst nach 10 Tagen, während beim Chabasit die Reaktion noch nach 92 Tagen weiterläuft.“

²⁾ P. VAGELER und F. ALTEN, Ztschr. f. Pfl. Ernähr. D. u. Bod. k., A 21, 333 (1931). „Das sogenannte hygroskopische Wasser nach MITSCHERLICH, besteht bei polar sorbierender Substanzen wesentlich wenn auch natürlich durchaus nicht ganz, aus dem Hydrationswasser der Schwarmionen, neben den die eigentliche Oberflächenwirkung der Festen Teilchen und die Hydratisierung löslicher Salze in die zweite Reihe rückt.“

In comparing the adsorption-values of the HCl-residues of the minerals, with those of the HCl-residues of the soils, it appears that these adsorption-values show a similar decline with respect to the original substances. Only biotite behaved differently in consequence of the quantity of SiO_2 -gel, which was present in the HCl-residue. This mineral therefore cannot dominate in the clay-fractions of Dutch clay-soils.

The attempt to find an equivalent-value for the surfaces of the mineral-powders, by continuing the mechanical analyses to the fractions $< \frac{1}{2} \mu$, as well as by determining the hygroscopicity-values, failed, so that the dependence of the adsorption-values on the surfaces and compositions of the minerals, could not be examined.

The fact that the influence of the HCl-extraction on the adsorption-values of the original minerals, corresponds to that on the adsorption capacity of the soil, gave rise to the possibility that these minerals occur in the clay-fractions of the soils.

V. POSTSCRIPT

As has appeared from this investigation, the adsorption-values of the different Dutch clay-soils, per unit-weight, agree completely and therefore it is not improbable that these have been built up from the same mineral or the same mixture of minerals. However, the method „VAN BEMMELEN-HISSINK” and the total-analysis of the clay-fraction, showed very diverging compositions of the different clay-soils. So it seemed important to check the clay-fractions by mineralogical analyses.

For the present, however, the mineralogical analyses of the parts $< 2 \mu$ are still too speculative and the mineralogical research is therefore limited to the sand-fractions of the soils. However, an important difference in the constitution of these would make the

TABLE 40.

MINERALOGICAL ANALYSES OF THE SOILS, ACCORDING TO THE
METHOD OF EDELMAN

Soil nr	Opaque	Tourmaline	Zircon	Garnet	Rutile	Anatase	Brookite	Titanite	Staurolite	Kyanite	Andalusite	Sillimanite	Chloritoid	Epidote	Saussurite	Hornblende	Augite	Hypersthene	Chloropite
1	10	1	4	32	1	—	—	—	4	2	—	—	—	9	6	28	13	—	—
2	25	1	12	26	5	—	—	—	3	3	—	1	—	26	2	15	6	—	—
3	13	2	10	25	5	—	—	—	—	2	—	2	—	23	4	12	15	—	—
4	17	2	7	19	8	1	1	—	5	1	—	—	—	27	3	21	5	—	—
5	15	—	11	26	5	—	—	—	2	2	—	—	—	16	7	21	5	5	—
6	18	—	14	33	5	—	—	—	—	4	—	—	—	19	7	11	5	2	—
7	15	2	7	39	2	—	1	—	2	—	—	—	—	19	12	7	9	—	—
8	25	3	22	28	9	—	1	—	1	—	—	—	—	12	2	19	3	—	—
9	20	2	13	34	3	—	1	—	2	1	—	—	—	17	10	9	8	—	—
10	45	6	27	9	22	—	2	—	3	7	1	—	—	12	3	6	2	—	—
11	11	1	6	35	3	—	—	—	1	—	1	—	—	26	10	9	8	—	—
12	17	4	7	29	3	2	—	1	6	1	1	—	—	11	14	10	8	2	1

similar mineralogical composition of the various clays improbable, whereas on the contrary, the conformity of the sand-fractions would make the mineralogical uniformity of the clay-fractions probable.

At my request, heavy residues of the sand-fractions of the samples were analysed mineralogically by EDELMAN and VAN BAREN.¹⁾ (See: table 40)

From the data they concluded, that the clay-soils which were analysed, all consisted of mixtures of sediments, which generally characterize quarternary deposits of the Netherlands.

From a sedimentary-petrological point of view, not one of the clays represents one of the typical mineral-associations, determined by EDELMAN²⁾, as the standard-compositions of these so-called „sedimentary-petrographical provinces” are as follows:³⁾

TABLE 41.

Group	Opaque	Tourmaline	Zircon	Garnet	Rutile	Anatase	Brookite	Titanite	Staurolite	Kyanite	Andalusite	Sillimanite	Chloritoid	Epidote	Saussurite	Hornblende	Augite	Hypersthene	Chloropite
A-Group	25	2	8	31	2	—	—	1	2	1	—	—	—	27	1	24	1	—	—
X-Group	35	3	15	4	12	—	—	1	1	4	2	—	—	54	1	3	—	—	—
B-Scheemda-group	55	25	8	1	12	1	1	—	16	20	6	9	1	—	—	—	—	—	—
B-Saussurite-group	10	2	4	3	—	—	—	1	1	1	—	—	—	20	40	7	20	—	1
B-Limburg-group	50	30	20	—	15	1	1	1	15	9	6	1	1	—	—	—	—	—	—
B-Elsloo-Group	80	10	17	10	—	—	—	—	—	—	—	—	2	3	8	50	—	—	—

That the mineralogical compounds of the sand-fractions of the soils, mentioned in table 40, are mixtures of these typical provincial deposits, will now be easily understood. Indeed, in all of them can be recognised an evident influence of the A-association, which was found to be typical for the Northern mineral-supply, in which: garnet, epidote and hornblende are abundant. Soil 2 (Ulsda) seems to be rather a pure example of this mineral-supply.

¹⁾ Prof. Dr C. H. EDELMAN, Director of the Mineralogical-Geological Laboratory of the Agricultural University at Wageningen.

The method of analysis can be found in: C. H. EDELMAN and D. J. DOEGLAS, Verh. v. h. Geol. Mijnb.k. Gen., Geol. Ser., 10, 1 (1933).

²⁾ C. H. EDELMAN, Petrologische Provincies in het Nederlandsche Kwartair, Diss. Amsterdam (1933).

³⁾ Further investigation showed there had to be distinguished still a B-Lobith- and a B-Eysden-group. F. A. VAN BAREN, Het voorkomen en de betekenis van kali-houdende mineralen in Nederlandse gronden. Diss. Wageningen, (1934).

The epidote, saussurite and augite combination represents the B-Saussurite-(Rhine-)association. The rutile and metamorphic minerals which are present, be it in rather low percentages, show the influences of the B-Limburg and B-Scheemda associations, in the latter of which, sillimanite especially must be considered as typical. (Soils: 2 (Ulsda) and 3 (St. Anna Parochie)).

The most southern of the soils is soil 10 (Susteren), which indeed is characterized by a greater influence of the B-Limburg association, as is shown by the abundance of rutile and the metamorphic group.

So the soils all contain components belonging to the various provinces, in a higher or lower degree, and therefore must be considered accordingly as mixtures of the standard-associations.

From these results it could be expected that the clay-fractions of the different soils also consisted of the same mixture of minerals; however, the total-analyses of these fractions showed, that their chemical compositions differed substantially.

VI. GENERAL CONCLUSIONS

The clay-fractions of 12 alluvial clay-soils, which have been cultivated for different times, appear to behave uniformly towards extraction with HCl, according to the method of VAN BEMMELEN: extraction with HCl of various concentrations, for half an hour, at 55° C and a ratio of soil: solvent 1 : 20.

The quantities of Al-Fe-Si-complex which are dissolved during this extraction appear to be defined by the clay-fractions $< 2 \mu$ of the soils. ¹⁾

In the soils a more easily and a more difficultly soluble Al-Fe-Si-complex occur, the compositions of which appear to be equal as to the ratio $\text{SiO}_2 : \text{Al}_2\text{O}_3$, by extraction of the residue under similar conditions with HCl of various concentrations.

The difference in relative solubility can be caused by an original difference in structure between these two Al-Fe-Si-complexes, however it is also possible that it is caused by a secondary factor, viz. the SiO_2 , which is separated insolubly during the HCl-extraction. This SiO_2 -gel could envelop the soil-particles and impede a further attack.

As to the different soils, the compositions of the Al-Fe-Si-complexes, which were soluble in HCl, varied importantly.

By a more intensive extraction of the soil, according to the method „VAN BEMMELEN-HISSINK”, for all soils a complex appears to be dissolved; containing relatively more Si^{++++} . The quantities of Al-Fe-Si-complex, which are brought into solution by this method of extraction, are again dependent on the clay-fractions $< 2 \mu$ of the soils.

The adsorption capacities of the original oxidised soils appeared to be defined by the fractions $< 2 \mu$ of these soils.

After the extraction with HCl of varying concentration, the adsorption-values of the HCl-residues appeared to be lower than

¹⁾ The youngest soil 1 (Drieborg), excepted.

those of the original oxidised soils; however they appeared to be equal for the different HCl-concentrations, which were used.

The residual adsorption was not caused by the SiO_2 -gel, which had been separated insolubly during the HCl-extraction, but by an adsorption-complex, which had been left or newly-formed after the HCl-extraction.

The residual adsorption appeared to be defined by the mechanical composition of the original oxidised soil, which was almost unaltered after the HCl-extraction, as followed from the mechanical analyses of the HCl-residues after a previous percolation with a $(\text{CH}_3\text{COO})_2\text{Ca}$ -solution, ($\text{pH} \pm 8.5$).

The soil-particles therefore appeared to be very resistant with regard to the HCl-extraction. From this the conclusion was drawn, that during the HCl-extraction only a very thin surface-film was brought into solution. The thickness of this layer appeared to be defined by the HCl-concentration.

From the fact that the adsorption-values of the HCl-residues of the same soil were equal after extractions with HCl of various concentrations, it was concluded that the surfaces of these HCl-residues must be equal.

As the adsorption-capacities of the original soils and those of the HCl-residues of the different soils were defined by the clay-fractions $< 2 \mu$ of these soils, and at the same time about as much Al-Fe-Si-complex was brought into solution per unit-weight of clay $< 2 \mu$ of the different soils, their surfaces per unit-weight must be equal.

By further fractionation of the clay-fractions this fact was indeed confirmed. Moreover, the equality of the surfaces of the different clays was confirmed by determining the hygroscopicity-values, according to the method of RODEWALD-MITSCHERLICH.

The HCl-extraction of the soils gives no idea of the composition of the adsorption-complex, as the analyses of the HCl-extracts showed very different values for the compositions of the Al-Fe-Si-complexes of the different soils, which were brought into solution, whereas from the identity of the adsorption- and residual adsorption-values it must be deduced that the chemical compositions of the adsorptive parts of the clay-fractions $< 2 \mu$ of the different soils were uniform.

By the method „VAN BEMMELEN-HISSINK” a complex is brought into solution, which contains more Si^{+++} than the complex which

is dissolved by the method „VAN BEMMELEN”, while in both cases the total quantities of Al-Fe-Si-complex, which are brought into solution, appear to be dependent on the clay-fractions $< 2 \mu$. From this it was deduced, that the exterior layers of the clay-particles contained relatively more sesquioxides than their kernels. By weathering the soil therefore becomes relatively rich in sesquioxides.

The idea, that the clay-fraction of the soil should have been built up principally from permutite-like Al-Fe-Si-gels, is contrary to the results of the HCl-extraction. A „permutite according to GANSSEN” appears to be completely dissolved by extraction according to the method „VAN BEMMELEN”, whereas by a similar treatment of the clay-fraction of soil 12 (Etten) only 16.7 % of the clay-fraction $< 2 \mu$ was brought into solution.

According to the opinion of GEDROIZ and of some American investigators, the clay-fractions could have been built up from minerals, in a colloidal state. Experiments on the minerals: Halloysite, chlorite, basaltic-hornblende, muscovite, orthoclase and kaolinite showed, that the HCl-extraction, under the same conditions as those by which the soils were extracted, influenced the adsorption-values of the original minerals in the same way as with the original soils; however, the permutite, the zeolite: natrolite and the mineral: biotite, behaved otherwise.

In consequence of the variations in the fractions $< 2 \mu$ of the minerals, it appeared impossible to determine a surface-equivalent by means of mechanical analysis. Also the determinations of the hygroscopicity-values could not furnish an equivalent value. Neither the quantities of Al-Fe-Si-complex, which were dissolved by the extraction, nor the adsorption-values of the original minerals and of the HCl-residues, were therefore comparable with the corresponding values for the soils.

It seems probable, that a very important part of the clay-fractions of the Dutch clay-soils has been built up from a mixture of minerals. According to the investigations of CUSHMAN, the surfaces of minerals, when brought in contact with H_2O , hydrolyze instantly. This film, consisting of hydrolytic products, would then cause the adsorption.

The uniformity of the clay-fractions of 12 different Dutch clay-soils as to their adsorption capacity, their behaviour towards the HCl-extraction, together with the influence of this extraction on

the adsorption-values, gave rise to the supposition, that these soils could be of the same mineralogical origin. However, the method „VAN BEMMELEN-HISSINK” and the total analyses of the clay-fractions, furnished very diverging $\text{SiO}_2 : \text{Al}_2\text{O}_3$ - and SiO_2 : Sesquioxides-ratios for the different soils.

From the mineralogical analyses of the sand-fractions, all soils appeared to be mixtures of the six sedimentary-petrographical provinces, stated by EDELMAN. However, the chemical analyses of the different clays showed extremes, diverging so widely, that it appeared impossible to conclude to their mineralogical uniformity; so that it must be supposed, that only the films of the hydrolytic products of the minerals which are present in clay, are identical.

VII. BESLUIT

De kleifracties van 12, gedurende verschillende tijden in cultuur zijnde Nederlandsche kleigronden, blijken zich uniform te gedragen ten opzichte van de extractie met HCl van diverse concentratie, gedurende een half uur bij 55° C, verhouding grond : oplosmiddel 1 : 20.

De hoeveelheden Al-Fe-Si-complex, die bij die extractie worden opgelost, blijken namelijk bepaald te worden door de kleifracties $< 2 \mu$ van den grond. ¹⁾

In de gronden komt een onder deze omstandigheden gemakkelijker en een moeilijker-oplosbaar Al-Fe-Si-complex voor, waarvan de samenstelling bij extractie met diverse concentraties HCl, onder overigens dezelfde omstandigheden, gelijk blijkt te zijn wat betreft de verhouding $\text{SiO}_2 : \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$.

Dit verschil in relatieve oplosbaarheid kan worden veroorzaakt door een oorspronkelijk aanwezig verschil in structuur tusschen beide Al-Fe-Si-complexen; het is echter ook mogelijk, dat het wordt veroorzaakt door een secundaire factor, namelijk: het bij de HCl-extractie onoplosbaar afgescheiden SiO_2 -gel, dat de bodemdeeltjes zou kunnen omhullen en daardoor de verdere aantasting bemoeilijken.

Voor verschillende gronden varieerde de samenstelling van het in HCl-oplosbare Al-Fe-Si-complex sterk.

Bij intensievere extractie van den grond volgens de methode „VAN BEMMELEN-HISSINK”, blijkt bij alle gronden een Si-rijker complex in oplossing te worden gebracht. De hoeveelheden Al-Fe-Si-complex, die bij deze extractie-methode in oplossing worden gebracht, zijn wederom afhankelijk van de kleifracties $< 2 \mu$ van de gronden.

De adsorptie-capaciteit van de origineele geoxideerde gronden bleek te worden bepaald door de kleifractie $< 2 \mu$.

¹⁾ Uitgezonderd de jongste grond 1 (Drieborg).

Na de extractie met HCl van diverse concentratie was de rest-adsorptie van de HCl-residuen lager dan die van de origineele geoxideerde gronden, doch voor de gebezigde HCl-concentraties waren de adsorptie-waarden der HCl-residuen onderling gelijk.

De rest-adsorptie werd niet veroorzaakt door het bij de HCl-extractie onoplosbaar afgescheiden SiO_2 -gel, maar door een na de HCl-extractie resteerend of nieuw-gevormd adsorptie-complex.

De rest-adsorptie bleek bepaald te worden door de fractie-verdeeling van de origineele geoxideerde grond, die na de HCl-extractie vrijwel ongewijzigd was gebleven, zooals volgde uit de slib-analyse van de HCl-residuen na voorafgaande percolatie met $(\text{CH}_3\text{COO})_2\text{Ca}$ -oplossing, ($\text{pH} \pm 8.5$). De bodemdeelen bleken dus zeer resistent te zijn, t.o.v. de HCl-extractie. Hieruit volgde, dat bij deze extractie dus slechts een zeer dunne oppervlakte-film van de bodemdeelen in oplossing werd gebracht. De dikte van deze film bleek te worden bepaald door de HCl-concentratie.

Uit het feit, dat de rest-adsorptie van de HCl-residuen van eenzelfde grond, na extractie met HCl van verschillende concentratie, onderling gelijk was, werd geconcludeerd dat de oppervlakten dezer HCl-residuen gelijk moesten zijn.

Daar de adsorpties der origineele gronden en de rest-adsorpties van de HCl-residuen der verschillende gronden bepaald werden door de klei-fracties $< 2 \mu$ van die gronden, terwijl ook per gewichtseenheid klei $< 2 \mu$ ongeveer evenveel Al-Fe-Si-complex in oplossing werd gebracht, moest de oppervlakte per gewichtseenheid klei $< 2 \mu$ voor de verschillende gronden gelijk zijn.

Door de kleifractie verder te fractionneeren werd dit inderdaad geconstateerd. Bovendien werd dit feit bevestigd door de hygroscopiciteits-bepaling volgens RODEWALD-MITSCHERLICH.

De HCl-extractie van de gronden geeft geen inzicht in de samenstelling van het adsorptie-complex, daar de analyse der HCl-extracten voor de verschillende gronden zéér uiteenlopende waarden voor de samenstelling van de in oplossing gebrachte Al-Fe-Si-complexen opleverde, terwijl uit de identiciteit van de adsorptie- en rest-adsorptie-waarden zou moeten volgen, dat de chemische samenstelling van het adsorptieve deel van de klei-fracties $< 2 \mu$ der verschillende gronden uniform is.

Bij de methode „VAN BEMMELEN-HISSINK”, wordt een Si-rijker complex in oplossing gebracht dan bij de methode „VAN BEMME-

LEN'', terwijl in beide gevallen de totale hoeveelheden in oplossing gebracht Al-Fe-Si-complex afhankelijk blijken van de kleifractie $< 2 \mu$. Hieruit werd afgeleid, dat de meer periphere lagen van de kleideeltjes rijker waren aan sesquioxiden dan de kernen der deeltjes. De verweering verloopt dus in de richting van relatieve sesquioxidenverrijking van den grond.

De opvatting, dat de kleifractie van den grond voornamelijk zou zijn opgebouwd uit permutietachtige Al-Fe-Si-gelen druischt in tegen de resultaten van de HCl-extractie. Een „permutiet volgens GANSSEN'' blijkt volledig in oplossing te worden gebracht bij extractie volgens de methode VAN BEMMELEN, terwijl van de kleifractie van een in dit onderzoek betrokken grond 12 (Etten), bij een overeenkomstige behandeling slechts 16.7 % van de kleifractie $< 2 \mu$ wordt opgelost.

Gezien de meening van GEDROIZ en eenige Amerikaansche onderzoekers zou de kleifractie voor een deel kunnen zijn opgebouwd uit mineralen in colloidalen toestand. Onderzoekingen aan de mineralen: halloysiet, chloriet, basaltische hoornblende, muscoviet, orthoklaas en kaolien leerden dat de HCl-extractie, onder overeenkomstige omstandigheden als waarbij de gronden werden geëxtraheerd, op dezelfde wijze de adsorptie-waarde van het oorspronkelijke mineraal beïnvloedde als dit voor de origineele gronden was geconstateerd; de permutiet, de zeoliet: natroliet en het mineraal: biotiet gedroegen zich echter anders.

Gezien de variaties in de fracties $< 2 \mu$ der mineralen was het onmogelijk een oppervlakte-equivalent door middel van de slib-analyse te bepalen. Ook de hygroscopiciteit-bepaling bleek geen equivalent-waarde te kunnen geven. De hoeveelheden Al-Fe-Si-complex, die bij de extractie in oplossing werden gebracht, waren dus evenmin als de adsorptie-waarden der origineele mineralen en HCl-residuen met de overeenkomstige waarden der gronden te vergelijken.

Het lijkt waarschijnlijk, dat een zeer belangrijk gedeelte van de kleifractie der Nederlandsche kleien opgebouwd is uit een mengsel van mineralen. De oppervlakte der mineralen wordt naar de onderzoekingen van CUSHMAN bij in-contact-brenging met H_2O spontaan gehydroliseerd. De hydrolyse-film zou dan de adsorptie veroorzaken.

De uniformiteit der kleifracties van 12 verschillende Nederlandsche kleigronden betreffende de adsorptiecapaciteit, het ge-

drag t.o.v. de HCl-extractie en de invloed daarvan op de adsorptie-waarden, gaf aanleiding tot de veronderstelling dat deze gronden van dezelfde mineralogische origine zouden kunnen zijn.

De methode VAN BEMMELEN-HISSINK en de totaal-analyse van de kleifracties gaven echter voor de verschillende gronden zéér uiteenlopende $\text{SiO}_2 : \text{Al}_2\text{O}_3$ - en $\text{SiO}_2 : \text{Sesquioxiden}$ verhoudingen.

Uit de mineraal-analyse van de zandfracties bleken de gronden alle mengselen te zijn van de zes, door EDELMAN gefundeerde, Nederlandsche petrologische provincies. De chemische analyse van de diverse gronden vertoonde echter te groote extremen om de mineralogische uniformiteit der kleiën te aanvaarden, zoodat verondersteld wordt, dat slechts de hydrolyse-filmen der verschillende, in de klei voorkomende mineralen, identiek moeten zijn.

INDEX

I. Introduction and Purpose.....	9
II. Origin, Description and Sampling of the Soils.....	20
III. Experiments	23
1. Methods	23
2. The Influence of HCl-extraction on the Adsorp- tion Capacity of the Soil.....	34
A. Preliminary Investigations.....	34
Experimental Part	35
Conclusions	57
B. Analogous Investigations with the different Soils	63
C. Summary and Conclusions.....	76
3. The Influence of HCl-extraction on the Surface of the Soil	77
A. Introduction	77
B. Experimental Part	77
C. Summary and Conclusions.....	104
IV. Analogous Investigations on Minerals	107
A. Introduction.....	107
B. Experimental Part	108
C. Summary and Conclusions.....	114
V. Postscript.	116
VI. General Conclusions.....	119
VII. Besluit	123