THE EXCHANGEABLE CATIONS IN SOILS FLOODED WITH SEA WATER

W. H. VAN DER MOLEN

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STELLINGEN

I

Bij Nederlandse jonge zeekleigronden is de nadelige invloed van een hoog gehalte aan uitwisselbaar magnesium op de structuur zeer gering.

vgl. **Brooks** c.s., *Proc. Soil Sci. Soc. of Am. 20* (1956), 325—327.

II

De ionenbezettingen van knikkleien wijzen op een uiterst geringe waterpassage door deze gronden.

Veenenbosch, J. S., *Zeitschr. f. Pflanzenern., D. u. Bodenk. 68* (1955), 141—158.

III

De conclusie van **Domby** & **Kohnke** betreffende de geringe invloed van een oppervlakkige korst op de gasuitwisseling tussen atmosfeer en bodemlucht kan niet worden overgedragen op gronden die met zeewater overstroomd zijn geweest.

Domby, C. W. & H. **Kohnke**, *Proc. Soil Sci. Soc. of Am. 20* (1956), 1—5.

IV

Voor klimaten met een geringe neerslagintensiteit gedurende het natte jaargetijde kan het vraagstuk van de niet-stationnaire grondwaterstroming in een gedraineerde grond bij benadering worden opgelost door aan te nemen, dat de vorm van de niet-stationnaire grondwaterspiegel weinig zal afwijken van die bij een reeks opeenvolgende stationnaire toestanden. Deze benadering is voor praktische doeleinden voldoende nauwkeurig.

V

Aan een algemene toepassing van infiltratie in de Nederlandse pleistocene zandgebieden zijn bezwaren verbonden, die een gevolg zijn van het relief en van de zeer grote dikte en doorlatendheid van het pleistocene lagenpakket.

VI

Dwars- en lengteprofiel van getijdekreken in het natuurlijke schorrenlandschap worden bepaald door het tijverschil, de grootte van het stroomgebied, de oeverbegroeiing en de bodemgesteldheid van het schor.

Blench, T., *Regime Behaviour of Canals and Rivers*, 1957.

VII

Bij het opstellen van plannen voor cultuurtechnische werken in semiariede gebieden met uitgesproken relief is een studie omtrent het regime van intermitterende stromen onmisbaar.

VIII

Bij de keuze van grasmengsels voor voetbalvelden dient in de eerste plaats rekening te worden gehouden met de mate, waarin de verschillende soorten en rassen bestand zijn tegen betreding.

IX

Het zou gewenst zijn voor de inzaai van voetbalvelden te beschikken over gekweekte meerjarige variëteiten van *Poa annua* L.

W. H. VAN DER MOLEN, 1958.

Dit proefschrift met stellingen van
WIEBE HENDERIKUS VAN DER MOLEN,
landbouwkundig ingenieur,
geboren te Amsterdam, 15 augustus 1922,
is goedgekeurd door de promotoren
DR. A. J. ZUUR,
hoogleraar in de leer van het in
cultuur brengen van drooggevallen gronden
en
DR. A. C. SCHUFFELEN,
hoogleraar in de landbouwscheikunde.

De Rector Magnificus
der landbouwhogeschool,
W. DE JONG

Wageningen, 7 mei 1958

THE EXCHANGEABLE CATIONS IN SOILS FLOODED WITH SEA WATER

UITWISSELBARE KATIONEN IN GRONDEN NA OVERSTROMING DOOR ZEEWATER

PROEFSCHRIFT
TER VERKRIJGING VAN DE GRAAD
VAN DOCTOR IN DE LANDBOUWKUNDE,
OP GEZAG VAN DE RECTOR MAGNIFICUS IR. W. DE JONG,
HOOGLERAAR IN DE VEETEELTWETENSCHAP,
TE VERDEDIGEN TEGEN DE BEDENKINGEN
VAN EEN COMMISSIE UIT DE SENAAT
VAN DE LANDBOUWHOGESCHOOL TE WAGENINGEN
OP VRIJDAG 4 JULI 1958 TE 16 UUR

DOOR

WIEBE HENDERIKUS VAN DER MOLEN

STAATSDRUKKERIJ 'S-GRAVENHAGE
1958

Aan mijn vader

WOORD VOORAF

Hooggeleerde ZUUR, hooggeachte promotor, Uw belangstelling, Uw raad, Uw grote ervaring en Uw opbouwende kritiek hebben tot dit proefschrift zeer belangrijke bijdragen geleverd. Daarnaast zal ik de jaren, dat ik het voorrecht had onder Uw leiding te mogen werken, niet vergeten; zij hebben veel tot mijn vorming bijgedragen.

Hooggeleerde SCHUFFELEN, hooggeachte promotor, U ben ik veel dank verschuldigd voor de belangrijke steun, die ik bij het vervaardigen van dit proefschrift van U mocht ondervinden en vooral voor de bereidwilligheid, waarmede gij mij steeds ter zijde hebt gestaan.

Hooggeleerde REINDERS, Uw voortreffelijke methodiek van onderwijs zal ik niet vergeten.

Hooggeleerde EDELMAN, het is Uw geestdrift geweest, die mij de fundamentele betekenis van de bodemkunde voor de landbouw heeft doen beseffen.

U allen, Hoogleraren en Assistenten, die op enigerlei wijze aan mijn studie leiding hebt gegeven en in het bijzonder U, Hooggeleerde DEWEZ, HELLINGA, HUDIG en TENDELOO, die mij bij mijn ingenieursstudie van dienst zijt geweest, wens ik op deze plaats mijn erkentelijkheid daarvoor te betuigen.

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Het is mij niet mogelijk alle medewerkers aan dit proefschrift afzonderlijk te noemen; er zij daarom hier volstaan met U allen en vooral U, analysten en tekenaars, mijn dank te betuigen.

De Directie van de Wieringermeer ben ik erkentelijk voor de toestemming de verzamelde gegevens in deze vorm te publiceren, de redactie van de Verslagen van Landbouwkundige Onderzoekingen voor haar bereidwilligheid deze studie in haar Verslagen op te nemen.

CONTENTS

Dit proefschrift verschijnt tevens als No. 63.17 in de reeks Verslagen van Landbouwkundige Onderzoekingen.

1. INTRODUCTION

1.1. THE PROBLEMS OF INUNDATED SOILS AND THEIR INVESTIGATION BEFORE 1939

Ever since man occupied the low-lying areas in the Netherlands disasters caused by stormfloods have occurred. Such floods did not only inflict losses on people, cattle and property, but they also made the soil unsuitable for agriculture for many years.

So the 13th-century chronicle of Bloemhof Abbey records that the floods of 1221 and 1249 were followed by years of failing crops, poverty and famine (KRONIEKEN van de Abdij Bloemhof). In the 16th century ANDRIES VIERLINGH, who wrote an excellent treatise on the art of embanking, described how after an inundation of the polder Nieuw Gastel in 1552 the soil remained barren for 8 or 9 years.

But the first elaborate descriptions of the behaviour of soils flooded with sea water and the first recommendations for their treatment were given about 1800 by the farmer HENDRIK PONSE (1808, 1825). Although he did not yet make a clear-cut distinction between the direct harm to the crops caused by the salinity and the indirect damage caused by unfavourable soil structure, he gave excellent descriptions of both phenomena. Moreover he gave sound advice for the management of these soils, based upon his own experiences gathered after the stormflood of 1775. In his publications PONSE emphatically warned against deep tillage and emphasized the importance of shallow ploughing and especially of all measures that make soil tillage unnecessary, such as growing grass or clover for a couple of years.

During the second half of the 19th and the beginning of the 20th century an extensive Dutch literature on these subjects originated, stimulated by several floods (especially those of 1877, 1906 and 1916) and since 1927 also by the reclamation-works in the Zuiderzee area. As this literature has already been reviewed by SEVENSTER (1937), RUSSCHEN (1945), ROWAAN (1951) and HISSINK (1954), only its main features will be mentioned here.

From these investigations it soon became clear that two factors are responsible for the bad results obtained on soils which have been flooded by sea water (VAN BEMMELEN, 1872). The first of these is the high concentration of soluble salts in the soil moisture which directly hampers crop growth. But soon it became known that in the moist Dutch climate – with a mean annual precipitation of about 700 mm – most of these salts are washed out from well-drained soils in one or at most two years (REINDERS, 1876; SWAVING, 1899; HISSINK, 1907 *b*; SMEDING, 1921; ZUUR, 1938). So the excessive salinity could not be the cause of the long-lasting ill effects of an inundation.

The second harmful factor – the collapse of soil structure – is especially operative after the bulk of the soluble salts has been removed from the topsoil. This bad structure may persist for 8 years or even more.

As we know now this deterioration of soil structure is due to a deflocculated state of the soil colloids caused by the large amounts of exchangeable Na present. This deflocculation begins as soon as the concentration of the soil solution has fallen below a certain limit.

Ion exchange in soils was discovered as early as about 1850 (THOMSON, 1850; WAY, 1850; DEUEL & HOSTETTLER, 1950) and soon afterwards these investigations became known in Holland [1]. But although REINDERS had observed in 1876 that ion exchange occurred in soils which were brought into contact with sea water, it was not before the 20th century that its importance for the behaviour of inundated soils was clearly understood. Moreover colloid chemistry was at first not sufficiently developed to be of much use for the explanation of the facts observed: it was not before the 20th century that the rules of SCHULZE (1882) and HARDY (1900) for the flocculation and deflocculation of hydrophobic colloids became generally known.

Therefore the first investigations on the structure of flooded soils had to be entirely empirical. Observations were made in the field and also the farmers' experiences were recorded (VAN BEMMELEN, 1872; MAYER, 1879*a*; DIRECTIE VAN DEN LANDBOUW, 1916; SMEDING, 1921). These observations nearly all confirmed PONSE's opinions, though of course they enlarged the knowledge considerably. So – among other things – it was observed that on old meadows, even if they are broken up after the inundation, a good soil structure is maintained.

Meanwhile MAYER observed during laboratory tests that after percolation of a column of clay soil with a NaCl solution the permeability of the soil fell almost to zero when the salt solution was followed by pure water (MAYER, 1879 *b*). On the other hand this large decline of permeability for water did not occur after the soil had been percolated with lime water instead of NaCl. These results were later explained by EHRENBERG (1909) from the rules of flocculation and deflocculation of colloids, as formulated by HARDY (1900).

Quite unaware of the work of MAYER and EHRENBERG, HISSINK (1907 *a*), after the stormflood of 1906, started a series of experiments which closely resembled those of MAYER. HISSINK percolated columns of clay soil with different salt solutions, which were followed by distilled water. His results were substantially the same as MAYER's: after NaCl the permeability for water fell almost to zero, whereas after $CaCl_2$ it remained on a fair level. The experiments of MAYER and HISSINK confirmed the observation that in many cases a breakdown of structure did not occur before the second year after the inundation, when the soluble salts had been largely removed from the topsoil (MAYER, 1879 *a*).

The inundations of 1916 renewed HISSINK's interests in the problem and among other things he analysed the soils flooded in 1906 on their contents of exchangeable cations. From these analyses it appeared that these soils – especially those with a poor structure – still contained considerable amounts of exchangeable sodium which brought about a deflocculated state of the soil colloids (HISSINK, 1918).

The soils in question had a high natural content of calcium carbonate, but obviously this calcium compound could not bring about a rapid replacement of exchangeable sodium by calcium. This conclusion was confirmed by earlier observations that the ordinary forms of lime dressing such as calcium carbonate or hydroxide – of

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[1] According to WIKLANDER (1946) ion exchange in soils being in touch with sea water was first mentioned by the Danish investigator FORCHHAMMER in 1850.

which the latter quickly passes into the carbonate – did not improve the structure of flooded soils. So HISSINK concluded that a more soluble calcium compound – e.g. gypsum – had to be used. This he tried in 1918 on an experimental field in the polder Anna Paulowna, which had been flooded two years earlier. In this field experiment calcium carbonate and hydroxide did not give any improvement, whereas the plots which had received gypsum were characterized by a better structure (HISSINK, 1922 *a*). Nevertheless different circumstances – not least the high price of gypsum shortly after World War I – prevented its use on a large scale.

The results of HISSINK's field experiments were in accordance with an earlier observation made by MAYER (1879 *a*) that in calcareous flooded soils sulphuric acid is able to increase crop yields in the second year after an inundation. MAYER, however, failed to recognize the connection of this observation with his laboratory experiments (MAYER, 1879 *b*).

After HISSINK's observations only one problem remained unsolved, viz. the fact that newly reclaimed Dutch saline soils seldom show a decline of soil structure. These soils are either consisting of bare or almost bare mud (*slik* soils) or of saline outmarshes already overgrown with a vegetation of halophytes (*schor* soils). The slik soils are in an almost completely reduced state at the moment of their drainage. HISSINK (1924) recognized that after drainage of such soils oxidation of ferrous sulphides, rendering sulphuric acid, will ultimately produce gypsum by subsequent reaction with calcium carbonate. Remarkably enough the importance of this process for soil structure was not clearly understood before 1936 (ZUUR & BAKKER, 1936; ZUUR, 1952).

In the schor soils, which are embanked from marine outmarshes the topsoil is usually already oxidized. Consequently its content of readily oxidizable sulphides is usually much lower than in the slik soils (c.f. HARMSEN, 1954). Therefore further oxidation can only result in the formation of small amounts of gypsum, which are insufficient to secure a good soil structure. That also in these schor soils a breakdown of soil structure seldom occurs must be attributed to the preserving action of the remnants of the vegetation, present at the moment of embanking. Just as in flooded old meadow soils, the organic matter of these remnants will protect soil structure even after the soil is broken up. Breakdown of soil structure may occur in such newly embanked schor soils only if layers less rich in plant residues and organic material are brought to the surface by too deep tillage. The danger involved in deep tillage of these soils was already known to VIERLINGH.

Whilst these facts became known in Holland, investigations abroad – especially concerning alkali soils in Hungary, Russia and in U.S.A. – led to similar results (HILGARD, 1906; 'SIGMOND, 1927; GEDROIZ, 1929; 'SIGMOND & ARANY, 1929; KELLEY, 1933, 1951). Also on these soils application of gypsum or other substances which turn into gypsum in the soil met with good results; in Hungary gypsum had been tried as early as 1893 ('SIGMOND, 1927) and in U.S.A. its beneficial effects were described by HILGARD (1906).

In Great-Britain an elaborate description of the agricultural behaviour of flooded soils was published in 1899 (DYMOND & HUGHES, 1899) and after an inundation near the Humber estuary in 1921 further studies were made by PAGE & WILLIAMS (1926). Though the results of these British investigations were generally in accordance with the Dutch, there were some remarkable differences; thus DYMOND & HUGHES recorded that the best results were obtained after fallowing and repeated ploughing, whereas all Dutch authors stress the necessity of reducing tillage to the utmost. Further the experiments of PAGE & WILLIAMS with gypsum on a heavy clay soil were not successful, though this might have been due to the relatively small amounts used in their trial.

In the past 30 years also the analytical methods for the determination of exchangeable cations were greatly improved. At first such determinations were only possible in soils which did not contain appreciable amounts of either calcium carbonate, gypsum or soluble salts. But in 1920 HISSINK published a method for taking account of the presence of calcium carbonate, which was later simplified by TIURIN (HISSINK, 1920, 1922 *b*; TIURIN, 1927; JARUSSOV, 1933). The presence of soluble salts remained a problem until ZUUR (1938) developed a method for taking them into account by putting the soil under high pressure and analysing the expressed fluid obtained for cations and for Cl. It was assumed that the ratios of these cations to Cl found in the expressed fluid are the same as those in the entire soil solution. By determining the total amount of Cl ions present in the soil the amounts of cations in the soil solution could be calculated and accounted for.

Thus by 1939 the following knowledge had been gained:

I. Soil salinity is one of the causes of the bad agricultural results on soils flooded with sea water, but on well-drained Dutch soils its effects are limited to one or at most two years after the inundation.

II. Bad soil structure, mainly occurring after most of the soluble salts had been washed out, may hamper agriculture for several years. It originates from a high percentage of sodium among the exchangeable cations of the soil, which causes a deflocculated state of the soil colloids. Calcium carbonate, generally present in Dutch polder soils, cannot bring about a quick replacement of this sodium by calcium. On former meadows, however, a good soil structure is maintained, even if they are broken up after the inundation.

III. Application of more soluble calcium compounds – e.g. gypsum – may improve soil conditions. However, the amounts to be given and the best ways of application were still unknown.

IV. Newly embanked Dutch saline soils, though also containing much exchangeable sodium, do not suffer from a decline of structure. In the slik soils consisting of bare mud, oxidation of ferrous sulphides in the presence of calcium carbonate leads to a large production of gypsum which causes a rapid exchange of sodium against calcium. On newly embanked schor soils, where this proces is less important, soil structure is preserved by the large amounts of organic matter originating from the outmarsh vegetation.

V. Analytical methods were so far developed that also in soils containing calcium carbonate, gypsum and soluble salts the amounts of exchangeable cations could be reliably estimated.

1.2. THE INUNDATIONS DURING THE PERIOD 1939–1953 AND THEIR INVESTIGATION

During World War II and again in 1953 large areas in the S.W. of the Netherlands were inundated with salt or brackish water. After the war their reconstruction was one of the major problems of Dutch agriculture.

In the period mentioned the following inundations occurred in the S.W. of the country:

1. The inundation of nearly 3000 ha with salt water by the Dutch army in 1939 and early 1940. These areas fell dry again in the early summer of 1940. After these floodings, gypsum supplied by the government was used for the first time on a large scale (RAPPORT, 1945; VAN VLIET, 1945).
2. The flooding of a part of the polder Wilhelmina (530 ha) with salt water after a so-called "dijkval" [1] in 1943. After a few days the greater part of this polder could be protected by an emergency dike, but the remainder was flooded for about four months.
3. The inundation of about 50,000 ha with salt or brackish water by the German army in spring 1944. This area was divided by the front line during the winter 1944–1945. South of this line the flooded polders were made dry again in autumn 1944, whereas in the North they remained inundated till early summer 1945 (WESTERHOF, 1947).
4. The flooding of the island of Walcheren (14,500 ha) after an Allied bombardment of its dikes. The greater part of the island was reclaimed in autumn 1945, though a small part remained flooded till spring 1946 (WESTERHOF, 1947).
5. The flooding of the small polder "Oost-Beveland" (90 ha) with salt water after a "dijkval" in 1945. For about 16 months this polder was flooded at each high tide and ran dry again at low tide.
6. The flooding of about 107,000 ha by salt and brackish water during the stormflood of February 1st, 1953. Most of the areas involved were drained within a period varying between a few days and two months, though some parts, totalling about 12,500 ha were not re-embanked before late summer or even autumn 1953.

A general review of the areas involved in these inundations is given in fig. 1.

All these inundations were followed by a study of the flooded soils, especially regarding their salinity, the changes in their exchangeable cations, the deterioration of their structure, their agricultural behaviour and the effects of gypsum. The areas flooded in 1939/40 and 1943 were investigated by the "Directie van de Wieringermeer", a government service with the task of carrying out the agricultural reclamation of the newly gained polders in the Zuiderzee area (RAPPORT, 1945; VOORDRACHTEN, 1946). During this work its research department had gained much experience with saline soils.

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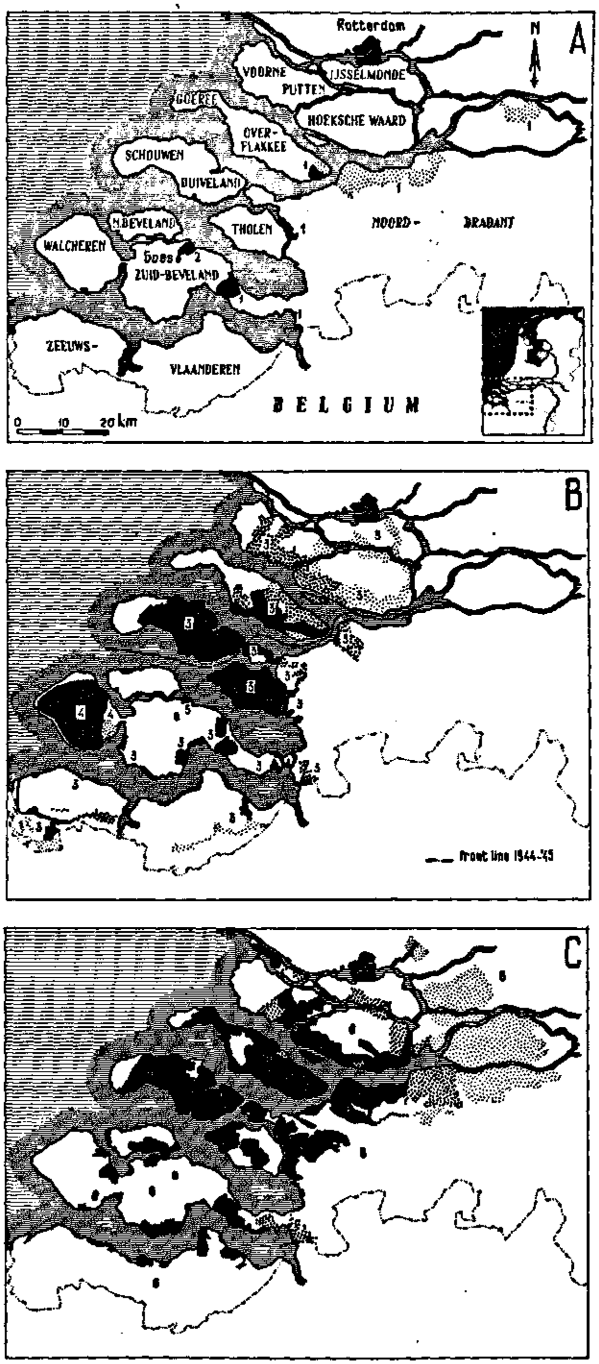
[1] Some estuaries in the S.W. of the Netherlands locally possess steep banks, which are attacked by tidal currents. At low tide such a slope may become unstable so that a landslide occurs. Often a part of a polder dike is also lost ("dijkval"), after which the polder concerned is flooded at the next high tide.



■ Flooded with salt water (> 10 g/l NaCl)

▨ Flooded with brackish water (3–10 g/l NaCl)

░ Flooded with fresh water (< 3 g/l NaCl)

A. 1939–1943
1. Flooded by the Dutch army in 1939/40
2. Flooded after a "dijkval" in 1943

B. 1944–1946
3. Flooded by the German army
4. Flooded by Allied bombardment of dikes in 1944
5. Flooded after a "dijkval" in 1945

C. 1953
6. Flooded during the stormflood of Febr. 1st., 1953

Fig. 1. Areas flooded in the S.W. of the Netherlands during the period 1939–1953

After the war such extensive problems had to be solved that a special government service, the "Rijksdienst voor Landbouwherstel" was created, charged with the task of restoring Dutch agriculture, including the repair of the flooded areas. Though "Landbouwherstel" itself only carried out part of the investigations, it acted also as a sponsor and co-ordinator for other research institutes and for the regional advisory services ("Rijkslandbouwconsulentschappen").

By combined effort an extensive research programme was set up, which started immediately after the war. As part of this programme a number of trial fields were laid out on which observations were made on exchangeable cations, soil structure and crop response. After the floodings of 1953 a similar programme was started, though on a somewhat smaller scale.

The experimental fields laid out in 1945/46 belonged to 4 different types, viz.:

1. G.T.-fields on which different amounts of gypsum were compared, usually in the ratio 0 : 1 : 2 : 3. Most of these fields were single ones, but some of them were laid out in duplicate. On non-calcareous soils gypsum was sometimes combined with lime.
2. A.G.-fields, on which gypsum was applied at different times. On these fields four different amounts of gypsum (0, 3, 6, 12 tons/ha) were given on four different occasions (e.g. autumn 1945, spring 1946, spring 1947 and spring 1948). These A.G.-fields were usually laid out with five replications.
3. S.M.-fields, on which different agents, usually in varying quantities, were compared (gypsum, sulphur, calcium chloride, hydroxide and carbonate, and sometimes other chemicals as well).
4. G.V.-fields, on which the effects of grass, lucerne and red clover, either with or without gypsum, were tested.

These experimental fields were laid out in autumn 1945 and spring 1946 by the regional advisory services in co-operation with the farmers. Except for the G.V.-series they shared in the crop rotation and the management of the field on which they were situated, though of course they were harvested separately. The observations were continued until the differences between the treatments had disappeared or until the farmer, tired of the bad spots in his field caused by the controls, refused further co-operation.

Some diagrams of such experimental fields are represented in fig. 2. Table 1 gives a review of the numbers of trial fields investigated for exchangeable sodium in different years.

TABLE 1. Numbers of experimental fields (series 1945/46) investigated for exchangeable sodium.

Year	G.T.-fields	A.G.-fields	S.M.-fields	G.V.-fields
1945	14	14	—	—
1946	40	15	6	7
1947	28	11	8	8
1948	21	8	5	3
1949	13	4	7	1
1950	7	2	4	1
1951	6	1	1	—
1952	5	1	3	—
1953	—	—	—	—
1954	3	—	1	—

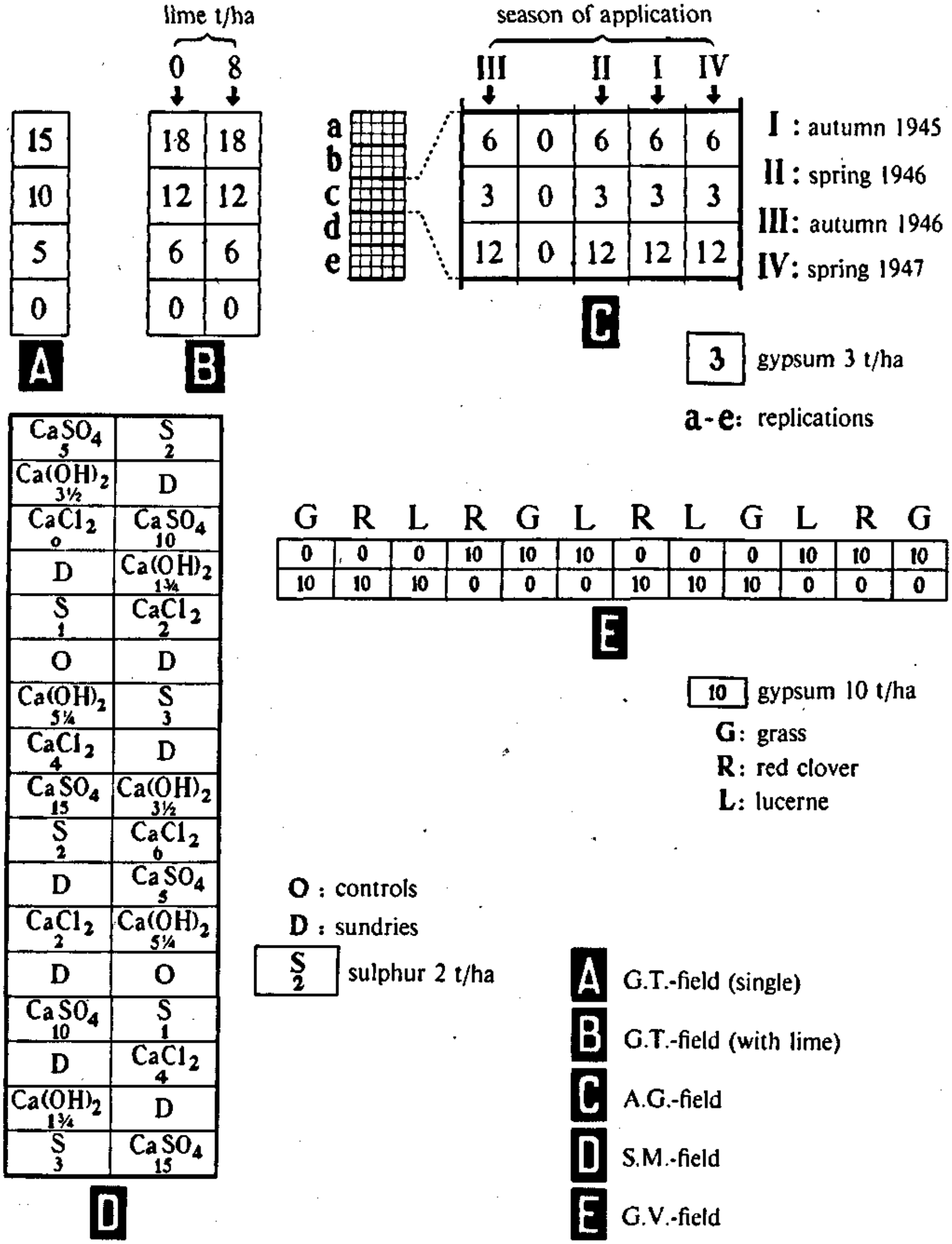


FIG. 2. Diagrams of trial fields

In addition to these investigations a small number of fixed sampling spots situated in ordinary fields were periodically examined for exchangeable cations.

This large programme involved numerous analyses, which were all carried out in the laboratory of the "Directie Wieringermeer" at Kampen. The analytical methods for determining the exchangeable cations in these saline, generally calcareous and often gypsum-containing soils were greatly improved by DOMINGO. So the laborious "expressed fluid" method mentioned in section 1.1. was replaced by washing out the soluble salts with alcohol. The tedious chemical determinations of Na and K were avoided by using a flame-photometer and recently complexometric titrations for Mg and Ca were substituted for the classical chemical procedures. All these new methods yielded the same results as the old ones, but generally the experimental error was reduced and much labour saved. More detailed information about the analytical methods used is given in the Appendix. In table 2 a review is given of the numbers of samples analysed after the different inundation-periods.

TABLE 2. Numbers of samples analysed for exchangeable cations after the inundations of 1939/1940, 1943 and 1944/1945.

Inundation period	Exchangeable Na only		Exchangeable Na, K, Mg and Ca	
	"Expressed fluid" method	Alcohol method	"Expressed fluid" method	Alcohol method
1939/1940	83	—	57	—
1943	—	—	46 [1]	45 [1]
1944/1945	19 [2]	4394 [2]	46 [3]	589 [3]

[1] For comparison 45 samples were analysed by both methods.
[2] For comparison 16 samples were analysed by both methods.
[3] For comparison 46 samples were analysed by both methods.

For the greater part the analyses mentioned in table 2 were completed by determinations of soil texture, salinity and pH. In addition to these analyses the soil structure on different objects of the trial fields was visually observed and described. Finally the crop response to different treatments was investigated, i.a. by determinations of crop yields.

1.3. SCOPE OF THIS TREATISE

In this treatise only the results of the investigations on exchangeable cations in flooded soils will be discussed. This discussion will be mainly limited to the analyses made after the inundations of 1944/45, though sometimes older results (from the inundations of 1939/40 and 1943) or recent experiences gathered after the stormflood of 1953 will be taken into consideration. Some reference will be made to similar investigations on soils in the newly drained Zuiderzee polders.

The results of the investigations on the salinity of the flooded soils and on crop response to salinity have already been published (VERHOEVEN, 1952; VAN DEN BERG, 1950, 1952; DORSMAN & WATTEL, 1951). The results of the observations concerning soil structure and crop response to this factor are to be published by WESTERHOF.

In this treatise the treatment of the subject-matter is mainly deductive in nature. Therefore the general theoretical principles involved in ion exchange will be reviewed first. In the following chapter a description will be given of the soils in the investigated areas and their main properties, especially with regard to their exchange characteristics. After that the changes brought about by flooding with salt or brackish water and the natural regeneration occurring after drainage will be described, followed by a review of the ways in which this regeneration may be promoted by different treatments. In an appendix the analytical methods used will be shortly described.

Readers who are only interested in the practical aspects of the problem may omit the entire chapter 2 and most of chapter 3 with the exception of the sections 3.1, 3,7 and 3.8.

2. THEORETICAL CONSIDERATIONS

The phenomena involved in ion exchange in soils may be considered from different points of view. The first of these is the equilibrium between the adsorbed ions and the ions in solution. As however the soil moisture is moving, the kinetics of ion exchange and the fact that the soil will behave as an ion exchange column must also be taken into account. Recent reviews of the subjects mentioned have been given by WIKLANDER (1946), KELLEY (1948), NACHOD (1949), KUNIN & MYERS (1950), SAMUELSON (1952), LEDERER & LEDERER (1953), WIKLANDER (1955).

2.1. ION EXCHANGE EQUILIBRIA; ADSORPTION ISOTHERMS

The equilibria between adsorbed ions and ions in solution are often of a complicated nature. In the simple case that only two kinds of ions are involved, their mutual relations may be expressed in the following way: the fraction of total adsorbed ions formed by one type of ions is plotted against the corresponding ionic fraction in solution. The curve thus obtained is known as an adsorption isotherm; some examples may be found in figs. 13, 15 and 17 (section 3.5).

The exchange equilibria, especially if obtained with complex exchangers like soils, are so complicated, that no adequate theoretical description of the experimental evidence is yet available. Among the many attempts made to solve this problem two main ways of theoretical approach may be distinguished, one of which is based upon thermodynamic principles, whereas the other makes use of model considerations. As however neither is quite satisfactory the exchange phenomena observed in special cases must often be described by more or less empirical equations.

2.11. *Thermodynamical considerations; the* DONNAN *equilibrium*

From a thermodynamic point of view the soil may be assumed to be equivalent with a DONNAN system, which in its simplest form consists of two phases, I and II, separated by a membrane (fig. 3). One of these phases contains large ions – e.g. the anions R^- – which cannot pass through the membrane, though the latter is permeable to the solvent (water) and to an added electrolyte, e.g. NaCl.

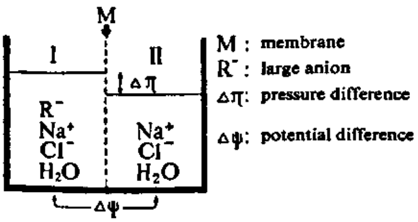


FIG. 3. DONNAN equilibrium

In such a system an equilibrium is set up, which is characterized by an unequal distribution of the ions of the electrolyte, by an osmotic pressure difference $\triangle \pi$ and by an electric potential difference $\triangle \psi$. By making two assumptions, viz. that the compressibility of the solution may be neglected and that the pressure difference $\triangle \pi$ is not too large, the following relation is obtained for the distribution of a monovalent electrolyte over both phases:

$$a'_+ a'_- = a''_+ a''_- \qquad (2.01)$$

in which a_+ and a_- denote the activities of cation and anion respectively, whereas $'$ and $''$ refer to the phases I and II (DONNAN & GUGGENHEIM, 1932; KLAARENBEEK, 1946).[1]

The pressure difference $\triangle \pi$ may be expressed by:

$$\triangle \pi = \pi'' - \pi' = \frac{RT}{\bar{v}_{H_2O}} \ln \frac{a'_{H_2O}}{a''_{H_2O}} \tag{2.02}$$

whereas the potential difference $\triangle \psi$ appears to be:

$$\triangle \psi = \frac{RT}{F} \ln \frac{a''_+}{a'_+} = \frac{RT}{F} \ln \frac{a'_-}{a''_-} \tag{2.03}$$

in which: R: Gas constant
T: Absolute temperature
$\bar{v}_{H_2O}$: Partial molal volume of water in the solution
a'_{H_2O}, a''_{H_2O}: Activities of water in both phases
F: The Faraday

In general, for ions with arbitrary valency z, equation (*2.03*) may be written as:

$$\triangle \psi = \frac{RT}{zF} \ln \frac{a''_i}{a'_i} \tag{2.04}$$

In general more than one electrolyte is present in ion exchange reactions. Thus in equilibria with sea water the ions Na, K, Mg, Ca, Cl and SO_4 are taking part. The fact that the potential difference $\triangle \psi$ has a constant value for any given system will lead to the following relation:

$$\frac{a''_{Na}}{a'_{Na}} = \frac{a''_K}{a'_K} = \sqrt{\frac{a''_{Mg}}{a'_{Mg}}} = \sqrt{\frac{a''_{Ca}}{a'_{Ca}}} = \frac{a'_{Cl}}{a''_{Cl}} = \sqrt{\frac{a'_{SO_4}}{a''_{SO_4}}} = \ldots\ldots = \lambda \tag{2.05}$$

in which λ is the DONNAN distribution coefficient.

The ionic activities mentioned above in equations (*2.01*)–(*2.05*) are running more or less parallel to the concentrations, but differ from them by the activity coefficient f.

Therefore we may put:

$$a_+ = f_+ m_+ \text{ and } a_- = f_- m_- \tag{2.06}$$

where f_+, f_- denote the activity coefficients of cation and anion respectively and m_+, m_- their concentrations, expressed as molalities (mols per 1000 g. of solvent).

Hence, equation (*2.01*) may be written as:

$$f'_+ f'_- m'_+ m'_- = f''_+ f''_- m''_+ m''_- \tag{2.07}$$

By definition the mean activity coefficient $f_\pm$ of a monovalent electrolyte is equal to:

$$f_\pm = \sqrt{f_+ f_-} \tag{2.08}$$

Hence, (*2.07*) may also be written as:

$$f^{2\prime}_\pm m'_+ m'_- = f^{2\prime\prime}_\pm m''_+ m''_- \tag{2.09}$$

---

[1] cf. KORTÜM & BOCKRIS, 1951, II, 368.

Assuming the mean activity coefficients $f_{\pm}$ to be equal in both phases, equation (*2.09*) changes into the "classical" form of the DONNAN equilibrium:

$$m'_{+}m'_{-} = m''_{+}m''_{-} \qquad (2.10)$$

But the assumption that $f'_{\pm}$ and $f''_{\pm}$ are equal is not justified for equilibria in which colloids take part, so that equation (*2.10*) may not be used for such systems. From the work of DAVIS (1942) on clay suspensions and of KLAARENBEEK (1946) on a Na-arabinate sol it became clear that especially for equilibria with dilute electrolyte solutions $f'_{\pm}$ is considerably smaller than $f''_{\pm}$.

In the colloid-free phase II the mean activity coefficient $f''_{\pm}$ may be determined, e.g. by vapour-pressure or freezing-point measurements. Moreover extensive tables are available for the mean activity coefficients of many electrolytes in aqueous solution (HARNED & OWEN, 1950; KORTÜM & BOCKRIS, 1951; CONWAY, 1952). But for the phase containing the colloid, $f_{\pm}$ is unknown and may only be evaluated from equation (*2.09*). Consequently a prediction of the ionic distribution becomes virtually impossible.

Another method of evaluating the ionic activities in phase I is the measurement of the potential difference $\Delta\,\psi$ between both phases. But in fact this potential difference cannot be measured by purely thermodynamic methods, and the reliability of measurements of $\Delta\,\psi$ with the help of KCl salt bridges is still uncertain (cf. COLEMAN et al., 1950; PEECH & SCOTT, 1950; PEECH, OLSEN & BOLT, 1953; BLOKSMA, 1955).

As the membrane forms no essential part of a DONNAN system, the same conclusions may be applied to any system in which one charged component is not freely movable. Consequently, in considering the equilibrium between a layer adjacent to a soil particle (phase I) and the bulk of the soil solution (phase II), the same reasoning may be followed (fig. 4). In fact a third phase (I_A) – e.g. a transition layer – may be present between the phases I and II, but as this third phase will be in equilibrium with both, it will not disturb their mutual relations.

In the derivation of equation (*2.01*), however, it is supposed that the osmotic pressure difference between the two phases examined is only small. As appears from equation (*2.02*) this condition implies that the activity of the solvent in both phases is approximately the same. This assumption is probably not justified in soils, where in the vicinity of the soil particles the water is known to be subjected to a strong field of force (EDLEFSEN & ANDERSON, 1943). This force field will substantially decrease its activity so that even the validity of the equations (*2.01*), (*2.03*), (*2.04*) and (*2.05*) may be questioned.

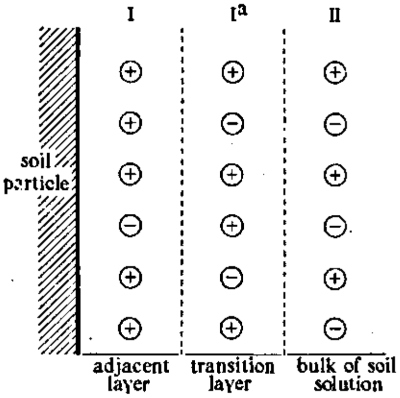


FIG. 4. Equilibrium in the vicinity of a soil particle

With all these uncertainties involved, the direct utility of the DONNAN equilibrium for the calculation of ion exchange equilibria in soils is small. Nevertheless its formulae, and especially equation (*2.05*), may be used as a base from which other relations may be derived by introducing some more or less plausible assumptions.

2.12. *Equations for ion exchange derived from the* DONNAN *equilibrium*

In the exchange phenomena occurring in flooded soils only the cations Na, K, Mg and Ca play a prominent part, whereas Cl is the leading anion. According to the theory of the DONNAN equilibrium their mutual relations may be described by equation (*2.05*), from which it follows that:

$$\frac{f''_{Na} \cdot m''_{Na}}{f'_{Na} \cdot m'_{Na}} = \frac{f''_{K} \cdot m''_{K}}{f'_{K} \cdot m'_{K}} = \left[\frac{f''_{Mg} \cdot m''_{Mg}}{f'_{Mg} \cdot m'_{Mg}}\right]^{\frac{1}{2}} = \left[\frac{f''_{Ca} \cdot m''_{Ca}}{f'_{Ca} \cdot m'_{Ca}}\right]^{\frac{1}{2}} = \frac{f'_{Cl} \cdot m'_{Cl}}{f''_{Cl} \cdot m''_{Cl}} \qquad (2.11)$$

Hence, after multiplication by $\frac{f''_{Cl}}{f'_{Cl}}$:

$$\frac{f''_{Na} \cdot f''_{Cl} \cdot m''_{Na}}{f'_{Na} \cdot f'_{Cl} \cdot m'_{Na}} = \frac{f''_{K} \cdot f''_{Cl} \cdot m''_{K}}{f'_{K} \cdot f'_{Cl} \cdot m'_{K}} = \left[\frac{f''_{Mg} \cdot f^{2''}_{Cl} \cdot m''_{Mg}}{f'_{Mg} \cdot f^{2'}_{Cl} \cdot f'_{Mg}}\right]^{\frac{1}{2}} = \left[\frac{f''_{Ca} \cdot f^{2''}_{Cl} \cdot m''_{Ca}}{f'_{Ca} \cdot f^{2'}_{Cl} \cdot m'_{Ca}}\right]^{\frac{1}{2}} = \frac{m'_{Cl}}{m''_{Cl}} \qquad (2.12)$$

Furthermore, the mean activity coefficients $f_\pm$ are defined by:

$$\left.\begin{array}{l} f_\pm = \sqrt{f_+ . f_-} \text{ for a 1–1 electrolyte (e.g. NaCl)} \\ f_\pm = \sqrt[3]{f_+ . f^2_-} \text{ for a 2–1 electrolyte (e.g. CaCl}_2\text{)} \end{array}\right\} \qquad (2.13)$$

Denoting both phases by the subscripts I and II instead of by ′ and ″ it is found that for the Na–K equilibrium:

$$\left[\frac{f^2_{\pm\,NaCl} \cdot m_{Na}}{f^2_{\pm\,KCl} \cdot m_K}\right]_I = \left[\frac{f^2_{\pm\,NaCl} \cdot m_{Na}}{f^2_{\pm\,KCl} \cdot m_K}\right]_{II} \qquad (2.14)$$

Furthermore, the equilibrium Na–Ca is found from equations (*2.12*) and (*2.13*) to be:

$$\left[\frac{f^2_{\pm\,NaCl} \cdot m_{Na}}{f^{3/2}_{\pm\,CaCl_2} \cdot \sqrt{m_{Ca}}}\right]_I = \left[\frac{f^2_{\pm\,NaCl} \cdot m_{Na}}{f^{3/2}_{\pm\,CaCl_2} \cdot \sqrt{m_{Ca}}}\right]_{II} \qquad (2.15)$$

Finally, for the equilibrium Mg–Ca:

$$\left[\frac{f^3_{\pm\,MgCl_2} \cdot m_{Mg}}{f^3_{\pm\,CaCl_2} \cdot m_{Ca}}\right]_I = \left[\frac{f^3_{\pm\,MgCl_2} \cdot m_{Mg}}{f^3_{\pm\,CaCl_2} \cdot m_{Ca}}\right]_{II} \qquad (2.16)$$

As the colloid-free phase II consists of a mixed solution of two or more electrolytes the mean activity coefficients are generally not known. But they may be fairly accurately estimated, because the activity coefficient of a given electrolyte in a mixture, is known to be approximately the same as in a pure solution of the same electrolyte possessing the same ionic strength. This ionic strength is defined by:

$$I = \tfrac{1}{2} \Sigma z^2_i m_i \qquad (2.17)$$

in which the summation must be carried out for all ions present. Except for very concentrated solutions the molalities m_i may be replaced by the concentrations c_i. Expressing the latter as milli-equivalents per litre their mutual relation is found to be:

$$c_i \cong 1000\, z_i\, m_i \tag{2.18}$$

Hence,

$$I = \frac{1}{2000} \Sigma z_i c_i \tag{2.19}$$

If the mixed solution contains only two electrolytes with a common anion (e.g. NaCl and $CaCl_2$) the mean activity coefficients of both may be still more accurately estimated from an equation given by GLUECKAUF (1949 *a*). For mixed solutions of the chlorides of two cations possessing the same valency this theory leads to simple equations. Thus, for solutions containing NaCl + KCl:

$$\frac{f_{Na}}{f_K} = \left[\frac{f^2_{\pm NaCl}}{f^2_{\pm KCl}}\right]_m = \left[\frac{f_{\pm NaCl}}{f_{\pm KCl}}\right]_s \tag{2.20}$$

and for solutions containing $CaCl_2$ + $MgCl_2$:

$$\frac{f_{Mg}}{f_{Ca}} = \left[\frac{f^3_{\pm MgCl_2}}{f^3_{\pm CaCl_2}}\right]_m = \left[\frac{f^{3/2}_{\pm MgCl_2}}{f^{3/2}_{\pm CaCl_2}}\right]_s \tag{2.21}$$

in which the index m refers to mixed solutions and the index s to single salt solutions of the same ionic strength.

For the chlorides of cations of unequal valency no such simple relationship is obtained. In that case the original, rather complicated equation has to be used.

On the other hand the activity coefficients in the phase influenced by the colloid anion (phase I) are unknown, and even their approximate evaluation is impossible. So the only way of evaluating the laws of ionic distribution will be the introduction of hypotheses for the quotient of the mean activity coefficients involved.

As may be easily shown some simple assumptions for this quotient will lead to the most commonly used equations for ion exchange (cf. KRISNAMOORTHY & OVERSTREET, 1949). So it may be supposed that the quotient of the activity coefficients is a constant or, in other words, that the activities of the ions in the adsorbed state are proportional to their molalities. In that case the equations (*2.14*), (*2.15*) and (*2.16*) will turn into:

$$\left[\frac{m_{Na}}{m_K}\right]_I = K \left[\frac{f^2_{\pm NaCl} \cdot m_{Na}}{f^2_{\pm KCl} \cdot m_K}\right]_{II} \tag{2.22}$$

$$\left[\frac{m_{Na}}{\sqrt{m_{Ca}}}\right]_I = K \left[\frac{f^2_{\pm NaCl} \cdot m_{Na}}{f^{3/2}_{\pm CaCl_2} \cdot \sqrt{m_{Ca}}}\right]_{II} \tag{2.23}$$

$$\left[\frac{m_{Mg}}{m_{Ca}}\right]_I = K \left[\frac{f^3_{\pm MgCl_2} \cdot m_{Mg}}{f^3_{\pm CaCl_2} \cdot m_{Ca}}\right]_{II} \tag{2.24}$$

Obviously the constants K are reciprocal to the ratios of the mean activity coefficients in phase I.

The equations mentioned above are generally named after KERR.

The same equations may be easily derived from the Law of Mass Action. Thus, for the reaction

$$(Na)_{ads} + \tfrac{1}{2}\, Ca^{\cdot\cdot} \rightleftarrows Na^{\cdot} + \tfrac{1}{2}\,(Ca)_{ads}$$

this law may be written as:

$$\frac{m'_{Na} \cdot \sqrt{m''_{Ca}}}{m''_{Na} \cdot \sqrt{m'_{Ca}}} = K \tag{2.25}$$

or

$$\left[\frac{m_{Na}}{\sqrt{m_{Ca}}}\right]_I = K \left[\frac{m_{Na}}{\sqrt{m_{Ca}}}\right]_{II} \tag{2.26}$$

This equation was first used by KERR (1928). After introducing activity coefficients in phase II equation (*2.23*) will be obtained. As however in dilute solutions the difference between concentration ratios and activity ratios is small, (*2.23*) may be considered as a slightly improved modification of (*2.26*). The same reasoning may be applied to (*2.22*) and (*2.24*).

In the following sections of this treatise the ionic concentrations in solution will usually be expressed as milli-equivalents per litre, whereas the adsorbed ions will be expressed as milli-equivalents per 100 g of exchanger. Denoting both by c_i it follows from equation (*2.18*) that the equations (*2.22*), (*2.23*) and (*2.24*) remain unchanged after replacing m_i by c_i and become equal to:

$$\left[\frac{c_{Na}}{c_K}\right]_I = K \left[\frac{f^2_{\pm NaCl} \cdot c_{Na}}{f^2_{\pm KCl} \cdot c_K}\right]_{II} \tag{2.27}$$

$$\left[\frac{c_{Na}}{\sqrt{c_{Ca}}}\right]_I = K \left[\frac{f^2_{\pm NaCl} \cdot c_{Na}}{f^{3/2}_{\pm CaCl_2} \cdot \sqrt{c_{Ca}}}\right]_{II} \tag{2.28}$$

$$\left[\frac{c_{Mg}}{c_{Ca}}\right]_I = K \left[\frac{f^3_{\pm MgCl_2} \cdot c_{Mg}}{f^3_{\pm CaCl_2} \cdot c_{Ca}}\right]_{II} \tag{2.29}$$

In the application of these equations to soils use may be made of the experimentally established fact that for a given soil the sum of adsorbed metal cations is only slightly dependent upon the kind of ions present and upon the concentration in the equilibrium solution, provided that the soil pH remains unchanged. Denoting this constant sum by S_s this condition may be written as:

$$\sum_{\substack{\text{metal}\\\text{cations}}} c'_i = S_s \tag{2.30}$$

Moreover in soils with a pH above 7, as is the case in the presence of free $CaCO_3$, this sum is approximately equal to the exchange capacity U_s of the soil, so that:

$$\sum_{\substack{\text{metal}\\\text{cations}}} c'_i = S_s \cong U_s \qquad (pH \geqq 7) \tag{2.31}$$

in which S_s and U_s are expressed as mval per 100 g of soil (dry matter).

As several assumptions have been used in the derivation of the KERR equations it is not surprising that sometimes large deviations in the constancy of K are observed.

An alternative assumption for the ionic activities in the adsorbed state, might be that they are proportional to their molar fractions N_i instead of proportional to their molalities m_i (VANSELOW, 1932).

These molar fractions are defined by:

$$N_i = \frac{m_i}{m_1 + m_2 + \ldots + m_i + \ldots} = \frac{m_i}{\Sigma m} \tag{2.32}$$

By applying this assumption to the basal equations (*2.14*), (*2.15*) and (*2.16*) the latter will turn into:

$$\left[\frac{N_{Na}}{N_K}\right]_I = K\left[\frac{f^2_{\pm NaCl} \cdot m_{Na}}{f^2_{\pm KCl} \cdot m_K}\right]_{II} \tag{2.33}$$

$$\left[\frac{N_{Na}}{\sqrt{N_{Ca}}}\right]_I = K\left[\frac{f^2_{\pm NaCl} \cdot m_{Na}}{f^{3/2}_{\pm CaCl_2} \cdot \sqrt{m_{Ca}}}\right]_{II} \tag{2.34}$$

$$\left[\frac{N_{Mg}}{N_{Ca}}\right]_I = K\left[\frac{f^3_{\pm MgCl_2} \cdot m_{Mg}}{f^3_{\pm CaCl_2} \cdot m_{Ca}}\right]_{II} \tag{2.35}$$

As however $\frac{N_{Na}}{N_K} = \frac{m_{Na}}{m_K} = \frac{c_{Na}}{c_K}$ and $\frac{N_{Mg}}{N_{Ca}} = \frac{m_{Mg}}{m_{Ca}} = \frac{c_{Mg}}{c_{Ca}}$ the equations (*2.33*) and (*2.35*) are obviously identical with the KERR equations (*2.22*), (*2.27*) and (*2.24*), (*2.29*) respectively. Thus for exchange between ions of equal valency the molar fraction hypothesis will give the same results as the earlier assumption based on molalities.

On the other hand, a different result is obtained for the exchange between ions of unequal valency. So it follows from (*2.32*) and (*2.34*) that for the Na-Ca exchange:

$$\left[\frac{m_{Na}}{\sqrt{m_{Ca} \cdot \Sigma m}}\right]_I = K\left[\frac{f^2_{\pm NaCl} \cdot m_{Na}}{f^{3/2}_{\pm CaCl_2} \cdot \sqrt{m_{Ca}}}\right]_{II} \tag{2.36}$$

If Na and Ca are the only ions present, (*2.36*) may be written as:

$$\left[\frac{m_{Na}}{\sqrt{m_{Ca}(m_{Na} + m_{Ca})}}\right]_I = K\left[\frac{f^2_{\pm NaCl} \cdot m_{Na}}{f^{3/2}_{\pm CaCl_2} \cdot \sqrt{m_{Ca}}}\right]_{II} \tag{2.37}$$

After replacing the molalities m_i by the concentrations c_i (expressed as milliequivalents per litre) and after making an appropriate change in the numerical value of K, equation (*2.37*) will become:

$$\left[\frac{c_{Na}}{\sqrt{c_{Ca}(c_{Na} + 0.5\, c_{Ca})}}\right]_I = K\left[\frac{f^2_{\pm NaCl} \cdot c_{Na}}{f^{3/2}_{\pm CaCl_2} \cdot \sqrt{c_{Ca}}}\right]_{II} \tag{2.38}$$

The equations (*2.36*), (*2.37*) and (*2.38*) were first used by VANSELOW (1932).

A third assumption might be that the activities of the adsorbed ions are proportional to their equivalent fractions instead of proportional to their molar fractions. For homovalent exchange this will make no difference, but in the case of heterovalent exchange – e.g. the exchange Na-Ca – this assumption will lead to:

$$\left[\frac{c_{Na}}{\sqrt{c_{Ca} \cdot \Sigma c_i}}\right]_I = K\left[\frac{f^2_{\pm NaCl} \cdot c_{Na}}{f^{3/2}_{\pm CaCl_2} \cdot \sqrt{c_{Ca}}}\right]_{II} \tag{2.39}$$

As however, according to equation (*2.30*) $\Sigma c_i = S_s$, (*2.39*) is only a modification of the KERR equation (*2.28*), the only difference being the numerical value of the constant K. If Na and Ca are the only ions present (*2.39*) may be written as:

$$\left[\frac{c_{Na}}{\sqrt{c_{Ca}(c_{Na}+c_{Ca})}}\right]_{I}=K\left[\frac{f^{2}{}_{\pm\,NaCl}\cdot c_{Na}}{f^{3/2}{}_{\pm\,CaCl_2}\cdot\sqrt{c_{Ca}}}\right]_{II} \qquad (2.40)$$

Recently, KRISNAMOORTHY, DAVIS & OVERSTREET (1948) drew attention to the fact that two Na ions may occupy any two available positions on an exchanging surface, whereas one Ca ion always must take up two neighbouring exchange positions. Taking account of these restrictions KRISNAMOORTHY, DAVIS & OVERSTREET obtained a new equation for heterovalent exchange. After making some assumptions for the pattern of exchange positions KRISNAMOORTHY & OVERSTREET (1949, 1950 *a*) found for the exchange Na-Ca:

$$\left[\frac{m_{Na}}{\sqrt{m_{Ca}(m_{Na}+1.5\,m_{Ca})}}\right]_{I}=K\left[\frac{f^{2}{}_{\pm\,NaCl}\cdot m_{Na}}{f^{3/2}{}_{\pm\,CaCl_2}\cdot\sqrt{m_{Ca}}}\right]_{II} \qquad (2.41)$$

Hence, after introduction of the concentrations c_i and making an appropriate adjustment of the constant K:

$$\left[\frac{c_{Na}}{\sqrt{c_{Ca}(c_{Na}+0.75\,c_{Ca})}}\right]_{I}=K\left[\frac{f^{2}{}_{\pm\,NaCl}\cdot c_{Na}}{f^{3/2}{}_{\pm\,CaCl_2}\cdot\sqrt{c_{Ca}}}\right]_{II} \qquad (2.42)$$

As may be seen by comparison of (*2.42*) with (*2.38*) and (*2.40*), this equation of KRISNAMOORTHY & OVERSTREET takes up an intermediate position between those of KERR (*2.40*) and VANSELOW (*2.38*).

Thus three groups of equations have been derived from the DONNAN equilibrium of from the Law of Mass Action. For homovalent exchange they all give the same results, viz. the equations (*2.22*), (*2.24*), (*2.27*) and (*2.29*) which are generally known as KERR's. For heterovalent exchange however three different types of equations are obtained, viz. those of KERR: (*2.23*), (*2.28*), (*2.39*), (*2.40*), VANSELOW: (*2.36*), (*2.37*), (*2.38*) and KRISNAMOORTHY & OVERSTREET: (*2.41*), (*2.42*).

2.13. *Model considerations; the electric double layer*

The problem of ion exchange may also be studied by analysing the conditions in the vicinity of a soil particle. As such a particle carries negative charges, it will attract cations and repulse anions by electrostatic forces. Thus, in the immediate vicinity of a soil particle, a large excess of cations will be found, which, together with the negatively charged particle-wall will form an electric double layer. Recently, the fundamental properties of such double layers have been extensively reviewed by OVERBEEK (1952).

As a first approximation the double layer may be regarded as a charged plate condensor in which one plate is formed by the particle itself, the other by the counter ions (HELMHOLZ double layer). As, however, the ions are subjected to thermal motion they will rather be arranged in a more diffuse way, forming a kind of atmosphere around the charged particles. In this diffuse double layer an equilibrium is set up between the electrostatic force field and the thermal kinetic forces in the solution (GOUY-CHAPMAN double layer).

By assuming that only electrostatical and thermal kinetic forces are present, that the ionic dimensions may be neglected, and that the dielectric constant in the double layer is the same as in pure water, this equilibrium may be calculated. From such calculations it appears that the electric potential – and together with it the excess of cations over anions – falls approximately exponentially with increasing distance to the charged particle. This potential drop is located in a layer possessing a thickness of a few times the parameter $\frac{1}{\varkappa}$, which for aqueous solutions at room temperature may be evaluated from:

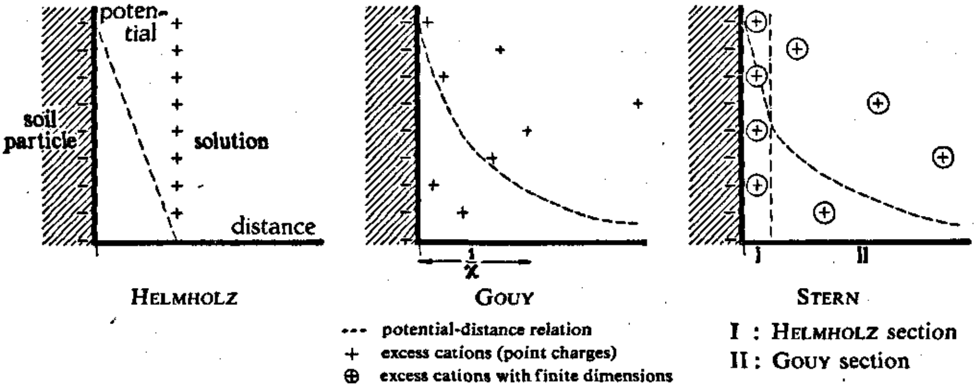
$$\frac{1}{\varkappa} = 3.0 \sqrt{\frac{1}{I}} \quad (\text{A.U.}) \tag{2.43}$$

in which I denotes the ionic strength of the solution and A.U. the Ångström unit, whereas $\frac{1}{\varkappa}$ is generally known as the "thickness" of the double layer.

In applying the GOUY-CHAPMAN theory to DONNAN equilibria on a Na-arabinate sol KLAARENBEEK (1946) could achieve a satisfactory explanation of the observed ionic distributions. More recently the same theory has also been applied to the conditions in soil-water systems (ERIKSSON, 1952; BOLT & PEECH, 1953). In these systems however the specific properties of the ions may certainly not be neglected, as it is well-known that soils show different affinities for different kinds of ions, even if the ions are of the same valencies. This preference is often, but not always, in accordance with the lyotropic series (SCHACHTSCHABEL, 1940; WIKLANDER, 1946).

That this GOUY-CHAPMAN theory, at least for equilibria with rather concentrated solutions, is inadequate, can be seen from equation (*2.43*). In solutions where I is near unity (e.g. 1 normal solutions of monovalent electrolytes) the thickness of the double layer will be of the same order as the ionic dimensions in aqueous solutions, viz. a few A.U. In that case nearly all adsorbed ions will be located in the immediate vicinity of the soil particles, so that their own dimensions may certainly not be neglected. Further it is doubtful whether in this layer the dielectric constant of the solvent is still approximately the same as in the pure solution. Finally other attractive forces, such as LONDON-VAN DER WAALS forces and forces due to ionic polarization, may come into play.

Making allowance for the ionic dimensions, STERN (1924) assumed that adjacent to the negatively charged particle a monolayer of cations is adsorbed, whereas at a greater distance a diffuse equilibrium is set up. Therefore in this picture of the double layer two different sections may be distinguished, an interior or HELMHOLZ section in the vicinity of the particle and an exterior or GOUY section at a greater distance (fig. 5). In the HELMHOLZ section the ionic dimensions will determine the distance of closest approach to the particle. Besides the electrostatic forces other attractive forces may be present in this section. This combined force-field is characterized by a single



HELMHOLZ GOUY STERN

--- potential-distance relation
+ excess cations (point charges)
⊕ excess cations with finite dimensions

I : HELMHOLZ section
II : GOUY section

FIG. 5. Diagrams of the electric double layer according to different theories

potential, the STERN adsorption potential φ. As the specific properties of the ions – such as their dimensions and polarizability – will cause differences in their adsorption potentials, the theory gives an adequate explanation for specific adsorption phenomena.

In the limiting case that all adsorbed ions are monovalent and located in the HELMHOLZ section of the double layer, the following relation exists between the exchange constant K and their adsorption potentials:

$$K = \exp \frac{\varphi_1 - \varphi_2}{kT} \qquad (2.44)$$

in which φ_1 and φ_2 denote the STERN potentials of the ions involved, k BOLZMANN's constant and T the absolute temperature (VERWEY, 1934).

As may be seen from equation *(2.43)* the HELMHOLZ section of the double layer will be most important in equilibria with concentrated solutions, whereas with increasing dilution of the equilibrium solution the GOUY section will gain importance.

In this GOUY section the ionic dimensions may be neglected, whereas it may be assumed that the non-specific electrostatic forces will strongly dominate. Therefore it may be expected from the STERN theory that specific effects in ion exchange will be most pronounced in equilibria with rather concentrated solutions, whereas with more dilute solutions the specific differences between the ions will become less important. In other words, the exchange constant K for homovalent exchange (equations *2.22* and *2.24*) must depend on the concentration of the equilibrium solution and will approach unity at increasing dilution of the latter.

There is, however, little experimental evidence for this phenomenon. A slight tendency in this direction may be observed in SCHACHTSCHABEL's measurements on the equilibria Li-NH_4 and K-NH_4 on montmorillonite (SCHACHTSCHABEL, 1940). Also in our own measurements of the equilibria K-Na and Ca-Mg on Dutch clay soils the exchange constant K was approaching unity at increasing dilution of the equilibrium solution (sections 3.51 and 3.53). On the other hand, however, WIKLANDER (1946) observed no effects of this kind in the exchange K-NH_4 on a synthetic exchange resin.

The order of affinity of the soil for different cations is usually in accordance with the lyotropic series. This sequence may be explained from the decreasing radii of the hydrated ions and from the increasing ionic polarizability in this series. The decreasing radii will cause an increased effect of all attractive forces present in the HELMHOLZ section of the double layer, whereas the increasing polarizability will cause an extra increase in the polarization forces.

There are, however, some marked exceptions to the rule mentioned above: the hydronium ion $(H_3O^{\cdot})$ is more vigourously adsorbed than would follow from its dimensions, whereas in soils containing minerals of the mica type also a preferential adsorption of potassium occurs (SCHACHTSCHABEL, 1940).

The abnormal behaviour of these ions may be readily explained from their ability to enter into special types of bonding with soil constituents. So the H_3O ion is capable of forming covalent bonds with active groups of soil particles. In fact these particles may be regarded as macro-anions with the character of weak polybasic acids. As a consequence of this covalent bonding H_3O ions are not only adsorbed in preference to metal cations, but their adsorption is also more complicated. So it appears impossible to describe ion exchange equilibria in which these ions are involved with the equations treated in section 2.12 (KRISNAMOORTHY & OVERSTREET, 1950 *b*).

It may be assumed as a first approximation that, at a given pH, the total exchange capacity U, corresponding with the total number of acidic groups present, will be partially occupied by a definite amount of H_3O ions. The remaining exchange capacity S than represents the number of exchange positions available to metal cations (c.f. equation *2.30*).

The majority of the flooded Dutch soils investigated possess a pH well above 7; in that case the acid groups are so largely dissociated that the difference between S and U is small (c.f. equation *2.31*).

The large affinity of clay minerals of the mica type for K ions may be explained from the fact that these minerals contain K as a lattice constituent. In some illitic soils this affinity is so pronounced, that adsorbed K ions will readily pass into non-exchangeable form by uptake into the mineral lattices.

The soils occurring in the investigated areas, though largely illitic in nature, are not known to possess K fixing properties. Nevertheless these soils show such a large preference for K over Na that lattice affinity probably plays a part in K adsorption.

2.14. *Equations for ion exchange derived from model considerations*

Thus far no quantitative evaluation of ion exchange, based upon the STERN picture of the double layer, has been given, though other models have been used as a base for deriving exchange equations. So GAPON (1933) used the replacement of an adsorbed liquid by another liquid as a model for ion exchange. In doing so, he arrived at an equation for heterovalent exchange which, after introducing activities in the solution, may be written as:

$$\left[\frac{m_{Na}}{m_{Ca}}\right]_{I} = K\left[\frac{f^{2}_{\pm\,NaCl}\cdot m_{Na}}{f^{3/2}_{\pm\,CaCl_2}\cdot\sqrt{m_{Ca}}}\right]_{II} \qquad (2.45)$$

By replacing *molalities* by *concentrations* (expressed as *milli*-equivalents) and after making an appropriate change in the numerical value of the constant K this equation changes into:

$$\left[\frac{c_{Na}}{c_{Ca}}\right]_{I} = K\left[\frac{f^{2}_{\pm\,NaCl}\ \cdot\ c_{Na}}{f^{3/2}_{\pm\,CaCl_2}\cdot\sqrt{c_{Ca}}}\right]_{II} \qquad (2.46)$$

As has been shown by Kelley (1948) the same reasoning, applied to exchange between monovalent ion pairs will again lead to Kerr's equation (*2.22*).

Making allowance for the attractive and thermal kinetic forces acting upon an adsorbed ion, Jenny (1936) ascribed to such an ion a definite sphere of oscillation. *Exchange can only follow if a second ion enters this oscillation sphere and places* itself closer to the attractive spot than the ion originally present. Working out this model and introducing the laws of probability Jenny arrived at a rather complicated equation for homovalent exchange. After introducing a few simplifying assumptions this equation became identical with Kerr's (*2.22*). In Jenny's equation the exchange constant K denotes the ratio of the oscillation spheres of the two ions involved. For heterovalent exchange the same theory has been worked out by Davis (1945 *b*). It than leads to an equation which, after some simplifications approaches Gapon's (*2.45*). This oscillation-sphere theory bears a certain relation to the Stern theory of the double layer. According to the latter the oscillation spheres will be confined to the Helmholz section of the double layer in equilibria with concentrated solutions, whereas with more dilute solutions these volumes will be much larger and also include the Gouy section.

Finally also the adsorption isotherm derived by Langmuir (1917) for adsorption of gas molecules at a surface, may be used as a base for deriving exchange equations. A modification of this Langmuir adsorption isotherm has been applied to ion exchange by Vageler & Woltersdorff (1930). For exchange between ion pairs of equal valency this equation may be easily shown to be identical with Kerr's, whereas for heterovalent exchange, after introducing a few simplifying assumptions, the same result may be obtained (Boyd *et al*, 1947).

2.15. *Empirical equations*

As neither of the equations described in the preceding sections is quite satisfactory (Davis, 1945 *a*), frequent use is made of empirical relations. One of the best known equations of this group has been proposed by Rothmund & Kornfeld (1918). For homovalent exchange this equation may be written as:

$$\left[\frac{m_{Na}}{m_{K}}\right]_{I} = K\left[\frac{m_{Na}}{m_{K}}\right]^{p}_{II} \qquad (2.47)$$

which, after replacing molalities by concentrations and introducing activity coefficients in the solution, becomes:

$$\left[\frac{c_{Na}}{c_{K}}\right]_{I} = K\left[\frac{f^{2}_{\pm\,NaCl}\cdot c_{Na}}{f^{2}_{\pm\,KCl}\ \cdot c_{K}}\right]^{p}_{II} \qquad (2.48)$$

For heterovalent exchange this equation may be written as:

$$\left[\frac{c_{Na}}{\sqrt{c_{Ca}}}\right]_{I} = K\left[\frac{f^{2}_{\pm\, NaCl}\ \cdot\ c_{Na}}{f^{3/2}_{\pm\, CaCl_2}\cdot\sqrt{c_{Ca}}}\right]^{p}_{II} \tag{2.49}$$

In the corresponding Kerr equations (*2.27*) and (*2.28*) the coefficient p is obviously unity, whereas in the Rothmund-Kornfeld equations (*2.48*) snd (*2.49*) p may take any arbitrary value. The Rothmund-Kornfeld equations are therefore of a more general nature; often they give a fair description of the observed equilibria (Walton, 1941).

As a matter of fact also other empirical relations may be used. So in section 3.7 a quadratic empirical equation for the behaviour of exchangeable Na in inundated soils will be introduced.

2.16. *Comparison of ion exchange equations*

As appears from the foregoing all theoretical considerations concerning homovalent exchange lead to Kerr's equations (*2.27, 2.29*). In practice, however, it is sometimes necessary to employ the more general empirical equation of Rothmund & Kornfeld (*2.48*).

For heterovalent exchange different equations have been proposed, viz. those named after Kerr (*2.28*), Krishnamoorthy & Overstreet (*2.42*), Vanselow (*2.38*), Gapon (*2.46*), Rothmund & Kornfeld (*2.49*). The first three of this group are closely related, with the second occupying an intermediate position. The equation of Rothmund & Kornfeld for heterovalent exchange may be considered as a more general form of Kerr's equation, whereas the equation, proposed by Gapon occupies a rather isolated position.

All equations mentioned above have been tested for two characteristic soils from the investigated area. The results of this comparison will be discussed in the sections 3.51, 3.52, and 3.53.

2.2. ION EXCHANGE KINETICS

In soils in which the soil moisture is moving not only the laws of exchange equilibria are of interest, but also the velocity at which these equilibria are established. If the velocity of the reaction is too low, equilibrium with the moving soil moisture will not be reached. Under normal conditions however, it is highly improbable that non-equilibrium will occur in Dutch soils.

The first systematic investigations on ion exchange in soils already revealed that this phenomenon is proceeding rapidly (Way, 1850) and this observation has been confirmed by later investigations (c.f. Hissink, 1925; Borland & Reitemeier, 1950). Recently Krisnamoorthy & Desai (1953) observed that the exchange velocity is mainly controlled by the rate of ionic diffusion through a water film surrounding the particles.

In Dutch soils natural percolation is a slow process. During the winter months, when drainage is greatest, percolation only averages about 0.3 cm^3/cm^2–24 hrs, and even the highest values reach only few cm^3/cm^2–24 hrs. Therefore it may reasonably be assumed that equilibrium conditions are present. An exception must possibly be made for soils which are suddenly flooded, e.g. after a dikeburst, though even in that case the limited permeability of the soil will set limits to the infiltration rate.

The assumption that the reaction velocity is high enough to obtain equilibrium conditions in soils under natural conditions is supported by observations on synthetic exchange resin columns made by EKEDAHL *et al* (1950). In these experiments deviations due to limited reaction velocity did not occur before the streaming velocity surpassed the order of one cm^3/cm^2–min. This critical streaming velocity is much higher than that occurring in Dutch soils. As the exchange resins as well as the soils are reacting quickly such deviations may neither be expected in soils under natural conditions.

On the other hand streaming irregularities may play a more prominent part, especially in heavy soils where fissures are present. Part of the percolating water will rapidly move through these fissures, without reaching equilibrium with the bypassed layers. This process causes deviations from ideal column behaviour, especially in heavy soils (VAN DER MOLEN, 1956; c.f. also fig. 32 B, section 4.4).

At the slow flow rates occurring in soils another kinetic process will become important, viz. lateral diffusion in the soil solution. This diffusion will attempt to level out all differences in composition of the soil solution and consequently also all differences in the exchangeable cations of the soil. From theory (MAZURE, 1940; KIRKHAM & FENG, 1949) as well as from experiment (VERHOEVEN, 1950) this process appears to be very active over short distances. So in water-saturated soils, concentration differences in the soil moisture occurring at a mutual distance of 1 cm will be almost completely levelled out in 24 hrs, unless subsequent supply from other sources occurs. Over larger distances, however, the efficiency of this process decreases rapidly: theoretically the time needed to obtain a certain degree of equalization will be proportional to the square of the distance.

The consequences of lateral diffusion for ion exchange in columns will be further discussed in the next section.

2.3. ION EXCHANGE IN COLUMNS

In chemistry, ion exchange in columns has become an important tool for ionic separations (NACHOD, 1949; DAVIES, 1950; SAMUELSON, 1952). As this utilization of ion exchange closely resembles the use of adsorption in chromatography, it is usually denoted as ion exchange chromatography. As a rule synthetic exchange resins are employed for the separations mentioned above. The laws found for this process may immediately be applied to exchange reactions in soils profiles (RIBBLE & DAVIS, 1955).

Let us consider, as a simple case, a column of exchanger saturated with one kind

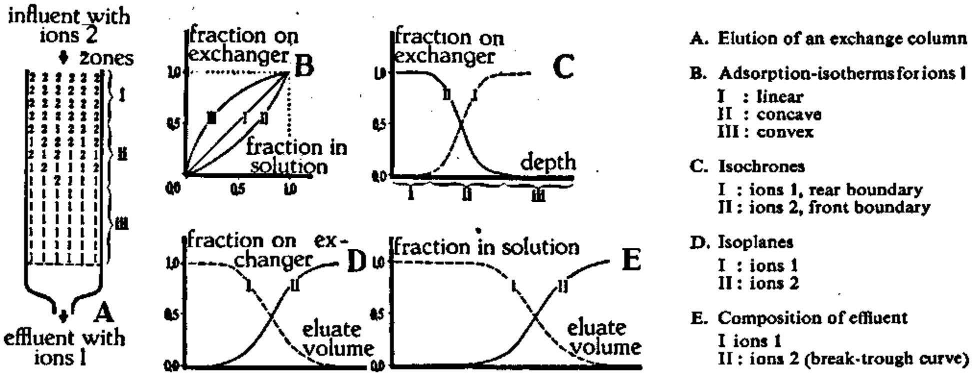


FIG. 6. Ion exchange in a column

of cations (1). If this column is eluted with a solution containing a second ionic species (2), the ions 2 present in the influent solution will gradually replace the ions originally present in the column (fig. 6). As this percolation will cause a repeated adsorption and desorption of ions the replacement of 1 by 2 will proceed from top to bottom. Thus, after the process has been operative for some time, the following three zones may be distinguished:

I. A zone where all ions 1 have been replaced by 2.

II. A transition zone where the ions 1 and 2 occur together and where the relative amount of 1 is increasing with depth.

III. A zone where still only ions 1 are present. A large part of these ions however are originating from ion exchange reactions higher in the column.

As long as the exchanger still contains all three zones only ions 1 will be found in the effluent. After a certain volume of solution has passed, zone I will reach the bottom of the column and ions 2 will appear in the effluent, or, as is generally said, the ions 2 will break through. If percolation is continued the proportion of ions 2 in the effluent will increase until the entire column has become completely saturated with ions 2 and the composition of the effluent has become equal to that of the influent.

The changes in the adsorbed cations may be graphically represented in two ways (SAMUELSON, 1952), viz.:

1. By isochrones, giving the change in adsorbed cations with depth at a given time. Isochrones referring to the ions being displaced from the column (ions 1 in fig. 6) are known as rear boundaries, whereas those referring to the influent ions (2 in fig. 6) are denoted as front boundaries.
2. By isoplanes giving the change in adsorbed cations with eluate volume (or, in the case of steady flow, with time) at a given depth.

In the same way the variations in solution composition may be represented. The isoplane of the solution, corresponding with the bottom of the column, gives a picture of the changes in the composition of the effluent; if this isoplane refers to the influent ion, it is generally known as the break-through curve. Finally the relation between adsorbed ions and ions in solution may be represented in the usual way by adsorption isotherms.

2.31. *Theories of column operation*

The theoretical investigations on ion exchange chromatography may be divided into two groups, viz. theories based on discontinuous variables on the one hand and those based on continuous variables on the other.

In the early work of MARTIN & SYNGE (1941) on partition chromatography discontinuous variables were used. In this kind of chromatography one or more solutes are divided between two immiscible solvents. One of these liquids is kept in a fixed position by adsorption on a column of a carrier substance, whereas the other is percolating through the column. The solutes are supposed to obey the NERNST partition law:

$$c' = a \, . \, c'' \tag{2.50}$$

in which a represents the NERNST partition coefficient and c′ and c″ the concentrations of the solute in both solvents.

MARTIN & SYNGE recognized the analogy of this process to column-distillation. Such a distillation column may be considered as being composed of a series of independent plates of equal height, at each of which an equilibrium is established between vapour and liquid. In applying this plate concept to partition chromatography MARTIN & SYNGE showed that the distribution of a solute obeys the laws of probability. In cases, that a substance, originally present only at the top of the column (fig. 7, I) is eluted, the binomial or BERNOULLI probability distribution is obtained (fig. 7, II). After a large amount of liquid has passed and after the substance has travelled through a large number of theoretical plates this BERNOULLI distribution will approach the normal curve of error (fig. 7, III). The top of this curve will move at a rate proportional to the eluate volume, though its standard deviation will gradually increase. As a consequence the band formed by the solute is travelling downward, becoming more diffuse at the same time.

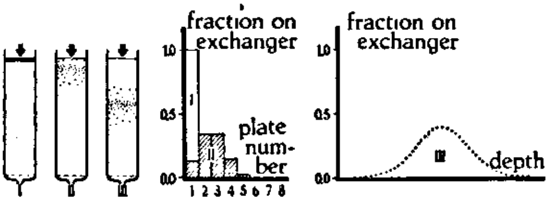


FIG. 7. Elution of a column loaded at the top, according to the theory of MARTIN & SYNGE

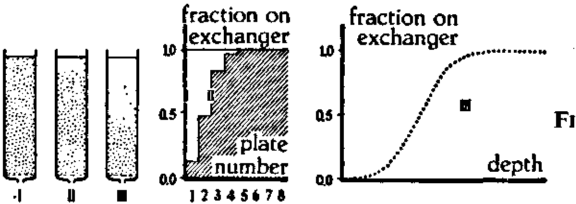


FIG. 8. Elution of a uniformly loaded column, according to the theory of MARTIN & SYNGE

If initially the column was evenly loaded with solute (fig. 8), the separate terms of the BERNOULLI distribution should be summated; when a large number of plates has been passed, the error curve should be integrated into the error function. In this case, the point at which the concentration has decreased to half its original value, is travelling downward with constant speed, whereas at the same time the boundary is gradually broadening.

These theories will be immediately applicable to ion exchange for cases in which a linear adsorption isotherm is present.

The cations are held by the exchanger, partially in the adsorbed state, and partially in the solution occurring in the pore spaces. When the adsorption isotherm is linear the amount of adsorbed ions may be represented by:

$$f^{*}(c_i) = a^{*} . c_i \tag{2.51}$$

in which $f^{*}(c_i)$ denotes the amount of exchangeable cations i and c_i their concentration in the equilibrium solution (expressed as milli-equivalents per g. of exchanger and per ml of solution respectively). If α represents the amount of liquid present in the pore space (in ml per g. of exchanger) the amount of ions i held in the solution is obviously equal to $\alpha . c_i$.

Consequently the total amount of ions i held per g. of exchanger, $f(c_i)$, is equal to:

$$f(c_i) = f^{*}(c_i) + \alpha . c_i = (a^{*} + \alpha)c_i = a . c_i \tag{2.52}$$

This total amount $f(c_i)$ is obviously also proportional to the concentration, so that equation (*2.52*) is completely analogous to the NERNST distribution law (*2.50*). Consequently, also the laws for column behaviour will be the same in both cases.

The drawbacks of this plate theory are: that the discontinuous BERNOULLI distribution function is rather cumbersome to handle, that the theoretical plate concept is somewhat artificial for continuous columns, and that extension of the theory to non-linear adsorption isotherms will be difficult.

Working with continuous variables WILSON (1940) and DE VAULT (1943) developed a theory for ion exchange chromatography in ideal columns, in which the thickness of the theoretical plates was assumed to be infinitesimal.

For a given volume of exchanger, the Law of Mass Conservation requires that the amount of ions i entering, less the amount leaving this volume, must correspond to the changes in the amount present.

For the case of zero plate thickness this condition, applied to an infinitesimal layer, leads to the differential equation:

$$\left[\frac{\partial f(c_i)}{\partial v}\right]_x + \left[\frac{\partial c_i}{\partial x}\right]_v = 0 \tag{2.53}$$

in which:

$f(c_i)$ total amount of ion i held by the exchanger (pore space included), (mval/g)

c_i concentration of ion i in solution (mval/ml)

v volume of influent passed through the column (ml/cm^2)

x depth (expressed as g/cm^2 of exchanger).

The points at which $f(c_i)$ and c_i [1] remain constant will move downward through the column at a rate, which may be calculated from:

$$\left[\frac{\partial v}{\partial x}\right]_c = \frac{df(c)}{dc} = f'(c) \tag{2.54}$$

or, after differentiation with respect to c:

$$\frac{\partial \left[\frac{\partial v}{\partial x}\right]_c}{\partial c} = \frac{df'(c)}{dc} = f''(c) \tag{2.55}$$

As appears from (*2.55*) the shape of the boundary depends on the shape of the adsorption isotherm. If the ions originally present in the column (ions 1 in fig. 6) posses a linear adsorption

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[1] In the following equations c_i is simplified to c.

isotherm, $f''(c)$ will be zero. Hence the velocity of zones of constant concentration will be independent of the concentration itself. For the rear boundary this concentration increases with depth; therefore the velocity at which the rear boundary moves down the column will be the same for all its points. As a consequence – at least for this ideal case – the shape of the boundary will remain constant.

In the case of a concave isotherm $f''(c)$ will be positive. Hence, according to equation *(2.54)*, $\left(\frac{\partial v}{\partial x}\right)_c$ will increase at increasing concentration. On the other hand the travelling rate $\left(\frac{\partial x}{\partial v}\right)_c$ will decrease at increasing concentration or, which comes to the same for a rear boundary, with depth. Thus the most forward points of such a boundary will move slower than points more backward or, in other words, the boundary will possess a self-sharpening tendency.

For a convex isotherm the reverse is true and the boundary will be broadening at its downward movement.

The differential equation *(2.53)* may be solved after inserting proper boundary conditions. For a rear boundary these conditions are:

$$\left.\begin{array}{llll} v = 0 & x \neq 0 & c = c_0 & f(c) = f_0 \\ v \neq 0 & x = 0 & c = 0 & f(c) = 0 \end{array}\right\} \qquad (2.56)$$

For the limiting case of ideal behaviour (infinitesimal plate thickness) the following curves are obtained for the isochrones and for the break-through curves:

1. For a linear adsorption isotherm: a sharp rear boundary, leading to a sudden breakthrough of the influent ions.
2. For a concave adsorption isoterm: a sharp rear boundary, leading to a sudden breakthrough of the influent ions.
3. For a convex adsorption isotherm: a diffuse, broadening boundary, leading to a slow breakthrough of the influent ions.

This theory of WILSON (1940) and DE VAULT (1943) has recently been applied to ionic exchange in soil profiles by RIBBLE AND DAVIS (1955).

In practice, however, not only the convex isotherms, but also the linear and concave ones will give rise to more or less diffuse boundaries. Apparently the ideal case of infinite plate thickness is not fulfilled in actual columns in which disturbing factors are operative, such as finite grain size, diffusion in the solution, and non-equilibrium.

These disturbing factors may be accounted for by introducing a finite plate thickness (MARTIN & SYNGE), but also by introducing appropriate corrections into the differential equation *(2.53)*.

For cases where finite grain size or diffusion act as disturbing factors GLUECKAUF (1949) derived the differential equation:

$$\left[\frac{\partial f(c)}{\partial v}\right]_x + \left[\frac{\partial c}{\partial x}\right]_v - k\left[\frac{\partial_2 c}{\partial x^2}\right]_v = 0 \qquad (2.57)$$

In this equation k represents half the thickness (in g/cm²) of the theoretical unit from the plate theory. For non-equilibrium cases another differential equation was obtained. In the foregoing section it has been argued that in soils non-equilibrium conditions may be neglected, whereas diffusion will be one of the major causes for deviations from ideal behaviour. Therefore equation (*2.57*) will probably apply to the conditions in soils.

In the case of a linear adsorption isotherm (equation *2.52*) the differential equation (*2.57*) will change into:

$$a\left[\frac{\partial c}{\partial v}\right]_x + \left[\frac{\partial c}{\partial x}\right]_v - k\left[\frac{\partial_2 c}{\partial x^2}\right] = 0 \tag{2.58}$$

For a front boundary this differential equation has been integrated by TAIT (GLUECKAUF, 1949) after introducing the boundary conditions:

$$\left.\begin{array}{lll} v = 0 & x \neq 0 & c = 0 \\ v \neq 0 & x = 0 & c = c_0 \end{array}\right\} \tag{2.59}$$

It was found that:

$$c = \frac{c_0}{2}\left[\operatorname{erfc}\frac{ax - v}{2v}\sqrt{\frac{v}{ak}} + e^{x/k}\operatorname{erfc}\frac{ax + v}{2v}\sqrt{\frac{v}{ak}}\right] \tag{2.60}$$

in which:

$$\operatorname{erfc} p = 1 - \frac{2}{\sqrt{\pi}}\int_0^p e^{-p^2}\,dp \tag{2.61}$$ [1]

For the rear boundary the conditions are given by equation (*2.56*). Though not given in the original paper, the equation for this case may be found by analogy to (*2.60*) as:

$$c = \frac{c_0}{2}\left[\operatorname{erfc}\frac{v - ax}{2v}\sqrt{\frac{v}{ak}} - e^{x/k}\operatorname{erfc}\frac{v + ax}{2v}\sqrt{\frac{v}{ak}}\right] \tag{2.62}$$

Introducing the number of theoretical plates above depth x:

$$N = \frac{x}{2k} \tag{2.63}$$

and putting:

$$\bar{v} = ax \tag{2.64}$$

equation (*2.62*) changes into:

$$c = \frac{c_0}{2}\left[\operatorname{erfc}\frac{v - \bar{v}}{2\sqrt{v\bar{v}}}\sqrt{2N} - e^{2N}\operatorname{erfc}\frac{v + \bar{v}}{2\sqrt{v\bar{v}}}\sqrt{2N}\right] \tag{2.65}$$

For large values of N the second term may be neglected, so that

$$c = \frac{c_0}{2}\operatorname{erfc}\frac{v - \bar{v}}{2\sqrt{v\bar{v}}}\sqrt{2N} \tag{2.66}$$

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[1] Values for the error integral $\frac{2}{\sqrt{\pi}}\int_0^n e^{-n^2}\,dn$ may be found in mathematical handbooks e.g. in JAHNKE & EMDE (1938).

The equations (*2.65*) and (*2.66*) predict a boundary, which is gradually broadening during its downward movement through the column and which finally approaches the symmetrical shape of the integrated normal curve of error:

$$c = \frac{c_0}{2} \operatorname{erfc} \frac{v - \bar{v}}{2\bar{v}} \sqrt{2N} \tag{2.67}$$

In the equations (*2.66*) and (*2.67*) $c = \frac{c_0}{2}$ for $v = \bar{v} = ax$. Therefore the points at which the original concentration has been reduced by half will move through the column at a rate proportional to the effluent volume. At a given depth, $\bar{v}$ obviously represents the volume of effluent needed for this reduction, so that it may be denoted as half-concentration volume.

At low values of N, near the top of the column, however, the influence of the second term in equation (*2.65*) causes the concentration $c = \frac{c_0}{2}$ to be reached already before $v = \bar{v}$, or, in other words, already at $\frac{v}{\bar{v}} < 1$. As may be seen from table 3, these deviations are less than 20% for $N \geqq 2$.

Table 3. Half-concentration volumes at low values of N.

N	$\frac{v}{\bar{v}}$ at which $c = \frac{c_0}{2}$ Exact equation (*2.65*)	$\frac{v}{\bar{v}}$ at which $c = \frac{c_0}{2}$ Approximate equation (*2.66*)	Deviation
0.5	0.55	1.00	0.45
1.0	0.69	1.00	0.31
2.0	0.80	1.00	0.20
4.5	0.90	1.00	0.10

In the theory mentioned above the behaviour of the column is determined by two parameters viz. a and k. Of these, a may be derived from the adsorption isotherm or calculated from equation (*2.52*). The constant k, however, must be evaluated by analysing the column performance, for which either the isochrones or the isoplanes may be used.

From the isochrones the value of k may be determined by estimating the slope $\frac{\partial c}{\partial x}$ of the curve at the depth $\bar{x}$ where $c = \frac{c_0}{2}$. As may be shown by differentiating equation (*2.67*), the number of theoretical plates above this half-concentration depth is equal to:

$$N = 2\pi \left[\frac{\bar{x}}{c_0} \cdot \frac{\partial c}{\partial x}\right]^2_{\bar{x}} \tag{2.68}$$

From the isoplanes the slope $\frac{\partial c}{\partial v}$ may be estimated at the volume $\bar{v}$ where $c = \frac{c_0}{2}$. In that case N may be evaluated from:

$$N = 2\pi \left[\frac{\bar{v}}{c_0} \cdot \frac{\partial c}{\partial v}\right]^2_{\bar{v}} \tag{2.69}$$

In flooded soils the Cl ions form an ideal object for testing the theory. As these ions are not adsorbed by the soil particles, but are only retained in the solution occurring in the pore spaces, the value of a^* (equation *2.52*) is obviously zero. Hence:

$$f(c) = (a^* + \alpha)c = \alpha c \tag{2.70}$$

Some examples in which this theory is applied to the desalinization of flooded soils and in which the value of k is evaluated from equations (*2.68*) and (*2.69*) have been published elsewhere (VAN DER MOLEN, 1956). As appears from these investigations the theory gives a fair description of the phenomena observed, especially in light-textured soils. The value of the theoretical plate thickness – 2k – is of the order of 7 g/cm², corresponding with a height of the theoretical plate of approximately 5 cm.

On the other hand also the penetration of sea water into the soil, occurring during an inundation, may be described by the theory. Some aspects of this penetration process, which will lead to the formation of a front boundary of Cl ions, will be treated in section 4.4.

For non-linear adsorption isotherms a general solution of the basic differential equation (*2.57*) is not yet available. However, in the important case that the adsorption isotherm of the ions originally present in the column is concave, a steady state will be reached. In this steady state the self-sharpening tendency of the boundary and the diffusing effects will balance each other. According to GLUECKAUF, BARKER & KITT (1949) this equilibrium state is characterized by a boundary moving with unchanged form, at a rate:

$$\left[\frac{\partial x}{\partial v}\right]_c = \frac{c_0}{f_0} \tag{2.71}$$

whereas the differential equation (*2.57*) changes into:

$$\left[\frac{\partial v}{\partial c}\right]_x = \frac{k \cdot \frac{f_0}{c_0}}{\frac{c_0}{f_0} \cdot f - c} \tag{2.72}$$

The case mentioned above occurs if in a soil profile exchangeable ions are replaced by other ions, coming from above and possessing a greater adsorption affinity. So for the replacement of Na by Ca in flooded Dutch soils the adsorption isotherm of the Na ions is approximately quadratic (section 3.7).

$$f(c) = b.c^2 \tag{2.73}$$

For this quadratic adsorption isotherm GLUECKAUF (1954) has given the following solution of the differential equations (*2.71*) and (*2.72*) for the case that the steady state has been established:

$$v = \frac{f_0}{c_0}\left[x + k \ln \frac{c_0 - c}{c}\right] \tag{2.74}$$

or:
$$\frac{c_0}{c} = \sqrt{\frac{f_0}{f}} = 1 + \exp\frac{\bar{x} - x}{k} \tag{2.75}$$

Due to the self-sharpening tendency of the boundary its gradient will be steeper than in the case of a linear adsorption isotherm; otherwise it has a similar shape.

The volume $\bar{v}$ at which the concentration in the solution becomes equal to half its original value is obviously:

$$\bar{v} = \frac{f_0}{c_0}x \tag{2.76}$$

On the other hand, due to the quadratic adsorption isotherm, the amount of adsorbed ions f will already be reduced by half at $c = \frac{c_0}{\sqrt{2}}$. The volume $\bar{\bar{v}}$ required for this halving of the adsorbed ions may therefore be calculated from:

$$\bar{\bar{v}} = \frac{f_0}{c_0}\left[x + k \ln(-1 + \sqrt{2})\right] = \frac{f_0}{c_0}\left[x - 0.882\,k\right] \tag{2.77}$$

For $x \gg k$, or in general for large values of x, this half-concentration volume $\bar{\bar{v}}$ will approach:

$$\bar{\bar{v}} \backsimeq \bar{v} = \frac{f_0}{c_0} . x \tag{2.78}$$

This expression (*2.78*) is analogous to equation (*2.64*) for a linear adsorption isotherm, in which a also represents $\frac{f_0}{c_0}$.

As in the soils studied a full development of the Ca/Na boundary is prevented by disturbing factors – i.a. by soil tillage – a stringent field test of the theory is impossible. Nevertheless it has been found in a few cases that the rear boundary of the Na ions has a steeper gradient with depth than the corresponding boundary of the Cl ions (c.f. fig. 42, section 5.2).

Thus, theoretical considerations about exchange equilibria may either be based upon the DONNAN equilibrium or upon molecular models. For homovalent exchange all considerations lead to the same result: the KERR equation, but for heterovalent exchange different equations are obtained. Besides, empirical relations are in frequent use. A summary of all these equations was given in section 2.16. In the next chapter they will be applied to exchange equilibria observed on soils from the investigated region. Moreover it will be tried to extend their use to equilibria involving more than two different kinds of ions.

In nature exchange reactions are accompanied by movements of soil moisture, and the soil will behave like an exchange column. Therefore the theory of column operation has been dealt with. Its application to the phenomena observed in flooded soils will be given in the chapters 4, 5 and 6.

3. THE SOILS AND THEIR PROPERTIES

In this chapter the soils occurring in the investigated area will be considered mainly with regard to their exchange properties. Prior to this, a short description of the landscape and its soils will be given, involving their origin, history and morphology.

The principal exchange characteristics of the soils involve adsorptive capacity, total amount of exchangeable metal cations, equilibria with salt solutions, and the ionic composition of unflooded soils. Among the equilibria with salt solutions those with sea- and brackish water are of special practical interest, as well as the equilibria occurring in soils after an inundation. For a better understanding of these rather complicated equilibria, their treatment will be preceded by a study of the equilibria with binary salt solutions.

3.1. GEOGENESIS AND PEDOMORPHOLOGY

The investigated area consists for the greater part of a number of islands, separated in the North by tidal rivers and in the South by wide estuaries. At about the beginning of the Christian era the entire region was mainly covered with peat and lying behind a ridge of dunes. From that time, however, the influence of the sea increased: in some districts the peat was covered by the Young Sea Clay, in others it was completely destroyed. Initially this sedimentation and erosion occurred during a few transgression periods; later, after about 1100 A.D., embankments succeeded in preserving some areas from further changes, though in others man has not been able to withstand the inroads of the sea. Thus large parts of the original landscape were lost; elsewhere however new accretions were formed, which were usually embanked and drained as soon as they had grown high enough. The embanked regions – old as well as new ones – are known as *polders.*

From the extensive soil surveys[1] made after 1945 the different phases of these Young Sea Clay sediments and their properties have become well-known (KUIPERS, 1948; EDELMAN, 1950; DE BAKKER, 1950; BENNEMA & VAN DER MEER, 1952). According to these investigations, the sediments may be divided into three groups, viz.:

1. Old-land sediments
2. Middle-land sediments
3. New-land sediments

During the formation of the old- and middle-land, creeks were scoured out in the peat landscape. Heavy marine sediments covered the remaining peat areas, whereas in a later stage the creeks themselves were filled up, at first with sand, finally with sandy clay.

After the land had been embanked the peat areas subsided, whereas the creek soils retained their original altitude. This process has led to an inversion of the land-

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[1] These surveys were made by "Stichting voor Bodemkartering" (Soil Mapping Institute) at request of "Landbouwherstel".

scape, by which the former creeks were transformed into ridges. Moreover, during the late Middle-Ages man dug out huge amounts of peat from under the clay cover for fuel and for salt-making [1], so that the natural differences in altitude were accentuated.

The *creek-ridge soils* generally consist of sandy clay, gradually changing into sand at some depth. The most ancient ones are more or less decalcified, whereas the younger creek ridges, belonging to the middle-land, still contain calcium carbonate, at least immediately below the ploughed layer. Most creek ridges are well-drained and in use as arable land, and in some localities the best of them are used for fruit growing (DE BAKKER, 1950).

The low lying clay-on-peat soils are known as *"pool"-soils*. The non-calcareous, often acid and sometimes permanently saline pool soils of the old-land, are in use as rather bad pastures. The corresponding middle-land pool soils, being of a somewhat better quality due to the presence of small amounts of calcium carbonate and a somewhat higher altitude, are in favourable cases used as arable land of moderate quality.

The *new-land sediments* were formed after the embankment of the old- and middle-land as accretions along the coast or even as newly-formed islands. In this new-land the peat is either lacking or compressed by a thick layer of younger sediments. Consequently no inversion of the landscape followed after the embankment, so that the former creeks in the new-land are still forming the lowest places. Except for the low-lying soils along these creeks, the well-drained and calcareous new-land soils are almost exclusively used as arable land, which is very productive in favourable cases. Their texture may vary widely and range from sand to heavy clay. As a rule these soils become more sandy with depth.

In the north-eastern part of the area the new-land soils have originated from brackish water instead of under pure marine conditions. This difference, due to the influence of the rivers, reveals itself in a more brownish colour and in certain small deviations in texture, which will be discussed in the next section. These brackish-water soils are generally known as *estuary soils*.

Outside the present dikes two main groups of soils may be distinguished, viz. *"schor" soils* and *"slik" soils*. The schor soils consist of outmarshes silted up above normal high tide level, which are only submerged during spring-tides and stormfloods, whereas the slik soils are either permanently submerged or only falling dry at low tide. In the marine region the outmarshes are covered with a vegetation of halophytes, whereas in the brackish-water regions this halophytic character is less pronounced. These outmarshes are oxidized in their topsoil; consequently their content of readily oxidizable ferrous sulphides is low. Therefore, after their embankment, gypsum-formation is negligible.

The *slik soils*, consisting of almost bare mud, are nearly completely reduced, with the exception of a few mm near their surface. Their content of readily oxidizable sulphides is high, so that they will form large amounts of gypsum after their embankment and subsequent drainage. The soils, found in the Zuiderzee-polders, which will be mentioned a few times, may be reckoned among this group of slik soils.

The investigations carried out after the inundations have been mainly restricted to the creek ridge and new-land soils, as the pool soils, due to their high content

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[1] For this purpose saline peat was burnt, after which common salt was extracted from the ashes.

of organic matter, showed no signs of structural decay. On the pool soils, therefore, observations were restricted to a few fixed sampling spots, which were regularly investigated for exchangeable cations. Occasionally data obtained from schor or slik soils, will be used for comparison.

3.2. MECHANICAL COMPOSITION; CLAY MINERALS

For a few typical cases the soil texture is given in table 4. This table of selected data illustrates a number of soil characteristics, found by different investigators.

The following characteristics are illustrated by table 4:

1. *Calcium carbonate* is present in appreciable amounts in new-land soils and also, though in smaller amounts, in the creek ridges of the old- and middle-land, especially in the latter. Usually this compound increases with depth, as weathering or – as it is generally called – ageing of the sediment under the influence of a humid climate has deprived the top-layers of a considerable part of their calcium carbonate. As this process of dissolution of calcium carbonate is of fundamental importance for the regeneration of flooded soils, it will be discussed in more detail in the next section. In addition to the calcium carbonate, also small amounts of calcium-magnesium carbonate (dolomite) are present in these soils (BRUIN, 1938; VAN DER MAREL, 1950). The pool soils are essentially non-calcareous, though the younger ones may contain small amounts of $CaCO_3$ in their subsoils.

2. *Organic matter* is low if the soil has been in use as arable land for a long time. Except for the light soils, where it is higher, the content of organic matter in the ploughed layer of such soils may be roughly estimated at 1/10 of the clay content (particles $< 2\,\mu$), whereas in deeper layers it is still less.
   On the other hand the pool soils, after having been covered with grass for centuries, have obtained a higher organic matter content in their topsoil.

3. *Clay content* may be expressed in different ways; it is usually defined either as the percentage of particles below $2\,\mu$ or as particles below $16\,\mu$. In the Netherlands the ratio between these two clay fractions is known to vary with the salt content of the water from which sedimentation occurred.
   As has been shown by ZUUR (1954) different chemical and physical properties of soils are more closely related to their content of particles below $2\,\mu$ than to particles below $16\,\mu$; therefore in this treatise the clay content will be expressed as the amount of particles smaller than $2\,\mu$, in accordance with international standards.
   As appears from table 4, clay content is low in the creek ridges and higher in the pool soils, whereas for the new-land soils no general rules may be given. According to BENNEMA & VAN DER MEER (1952) the old soils show signs of transport of clay particles from the topsoil to deeper layers. Evidence of this transport is given by a higher clay content and a higher ratio $0–2\,\mu$ to $0–16\,\mu$ immediately below the ploughed layer (c.f. the data for StW 13 in table 4). Even in new-land soils these phenomena are frequently met. The influence of sedimentary conditions on the ratio of the clay fractions is demonstrated by the examples of new-land soils in table 4. Whereas for pure marine new-land soils this ratio averages to about 0.70 and seldom falls below 0.65, for typical estuary soils its value is much smaller, being nearly always below 0.65.

The *clay minerals* of Dutch sea-clay soils have been investigated by FAVEJEE (1939) and by VAN DER MAREL (1950). From these investigations it appeared that these minerals are mainly illitic in nature, with kaolinite and montmorillonite as minor constituents. In the S.W. of the Netherlands the proportion of montmorillonite is slightly higher than in the north, causing the exchange capacity of the clay fraction to be somewhat higher. This exchange capacity will be further treated in section 3.4.

TABLE 4. Mechanical composition of some typical soils (weight-percentages of dry matter).

Soil type	Sampling spot	Depth cm	$CaCO_3$	Organic matter	Clay			$CaCO_3$ 20–40 cm	Remarks
					0–2 μ	0–16 μ	ratio		
Creek ridge soils									
old	AG 18 [1]	0–20	0.6	2.4	14.6	24.5	0.60	1.0	arable land
younger	StW 13 [2]	0–20	1.0	3.0	11.6	16.6	0.70	—	arable land
	StW 13	20–40	1.2	2.1	14.0	18.9	0.74	—	
Pool soils									
old	PP 1 [3]	0–10	0.0	21.3	20.2	31.5	0.64	0.0	pasture; acid
younger	St 71 [4]	5–20	0.0	7.3	24.3	36.1	0.67	1.4	pasture; acid topsoil
New-land soils									
sea clay	Ni 1 [5]	0–20	3.4	1.8	10.3	13.5	0.76	5.0	arable land
	St 68 [6]	5–20	6.8	3.3	36.7	53.4	0.69	7.9	young orchard
estuary clay	C 105 [7]	5–20	12.5	2.5	19.7	34.0	0.58	—	arable land
	St 7 [8]	0–20	1.8	5.3	42.0	69.5	0.60	6.2	arable land

[1] Zuid-Watering, Walcheren
[2] Zuid-Watering, Walcheren
[3] Polder Poortvliet, Tholen
[4] Poel van Goes, Zuid-Beveland
[5] Polder Nieuwlande, Zuid-Beveland
[6] Polder Strodorpe, Zuid-Beveland
[7] Zuidpolder Barendrecht, IJsselmonde
[8] Polder Louisa, Eiland van Dordrecht

3.3. RATE OF DECALCIFICATION

In the moist Dutch climate the soils will loose $CaCO_3$ by dissolution into the percolating rain water. For the area considered the $CaCO_3$-losses from the topsoil have been estimated by EDELMAN (1950) at 1% in 75 years. As will be published elsewhere, our observations suggest an average rate of decalcification of 1% of topsoil weight per 80 years.

If the annual water passage is known, the rate of decalcification may be used for estimating the average solubility of calcium carbonate in the soil solution, as it may be assumed, that all compounds in solution will be virtually washed out from the topsoil in the course of the year (c.f. the observations of the rate of desalinization mentioned in section 1.1). According to VERHOEVEN (1952) water passage in creek ridge and new-land soils averages about 200 mm a year. From this and from a loss of calcium carbonate from the topsoil of 1% in 80 years, the concentration of this compound in the soil solution may be estimated at 3.5 mval/l. Thus, all soils containing appreciable amounts of calcium carbonate will be percolated with a dilute solution of this compound. As a consequence, other exchangeable ions will be slowly replaced by Ca, a process which causes a slow natural regeneration of flooded soils. This reaction will be treated in more detail in chapter 5.

3.4. EXCHANGE CAPACITY AND SUM OF EXCHANGEABLE METAL CATIONS

The adsorptive properties of the soil are due to clay minerals and to organic matter. Per unit weight the organic matter possesses an exchange capacity of approximately three times that of the clay fraction (RAPPORT, 1945). Therefore it is usual to correlate the adsorptive properties of the soil with its content of active matter, defined by:

$$\text{active matter} = \text{clay } (< 2\mu) + 3 \text{ x organic matter} \qquad (3.01)$$

For the topsoil the active matter defined in this way possesses an exchange capacity U_a of about 68 mval per 100 g for Ca-ions at pH 8.0 (fig. 9). There is, however, a slight tendency it to be somewhat higher for light soils than for heavy ones. The frequency distribution for U_a given in fig. 11 shows that for the topsoil of arable land its value ranges between 65 and 75 mval per 100 g in the great majority of cases.

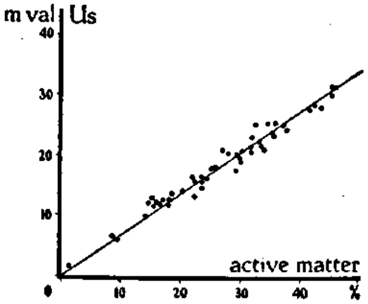


FIG. 9. Relation between content of active matter and exchange capacity U_s of the soil at pH 8.0 (mval per 100 g of dry matter). Topsoils of arable land on creek ridge and new-land soils

As for arable land humus and clay content are closely correlated, these soils are not well suited for testing the active matter concept expressed by equation (*3.01*). But old pastures, in which organic content is so much higher that it forms the principal exchanger, prove to be also in accordance with the generalizations formulated above (fig. 10).

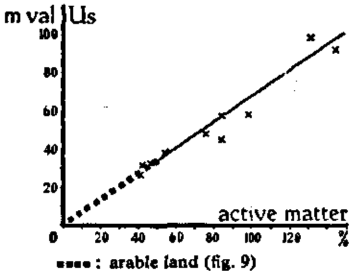


FIG. 10. Relation between content of active matter and exchange capacity U_a of the soil at pH 8.0 (*mval per 100 g of dry matter*). Topsoils of old pastures on pool soils

For the subsoil U_a is usually higher than for the topsoil, even in cases that their mechanical composition is similar (table 5). This difference may either be due to the clay fraction or to the organic matter. As it does not disappear after oxidation (table 5), it must arise from differences in the adsorptive properties of the clay fraction.

In newly drained polder soils, embanked from saline outmarshes, U_a is the same throughout the profile. But already in polders 150 years old (like St 68 and 69 in table 5) U_a is markedly increasing with depth (c.f. also table 6). It is not impossible that these changes are caused by soil-forming processes leading to alterations in the clay minerals; this question will need further investigation.

TABLE 5. Adsorptive capacity of the active matter in topsoils and subsoils of similar mechanical composition.

Sampling spot	Depth cm	Organic matter %	Clay (< 2 mu) %	Adsorptive capacity of active matter at pH 8.0; mval/100 g	
				Before oxidation	After oxidation
GT 55	10–20	2.2	16.2	63.2	72.8
GT 57	10–20	2.1	16.4	69.6	77.4
St 69	60–80	2.0	16.0	87.5	85.6
St 13	5–20	2.5	22.3	65.1	66.8
GT 56	10–20	2.0	22.7	69.7	70.5
St 69	40–60	2.3	22.3	73.6	80.3
GT 63	10–20	2.6	25.0	68.3	76.0
St 37	5–20	2.9	25.6	65.0	66.8
St 68	60–80	2.9	25.1	76.9	80.9

The adsorptive capacity of the soil may be considered as a measure for the number of exchange positions present on the surfaces of the clay minerals and the organic matter. These exchange positions will be partially occupied by metal cations – among which Na, K, Mg and Ca are the principal ones [1] – and partially by H_3O ions [2].

In calcareous soils the sum of the principal exchangeable metal cations, defined by:

$$S = \text{sum of exchangeable Na, K, Mg and Ca} \qquad (3.02)$$

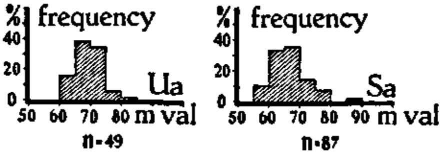
closely resembles the exchange capacity U. In acid soils however a large difference between S and U is observed (table 6).

TABLE 6. Sum of exchangeable Na, K, Mg and Ca (S) and exchange capacity (U) in two different soils.

Sampling spot	Depth cm	pH (H_2O)	$CaCO_3$ %	S_a [1]	U_a [1]
St 69 (new-land soil)	0– 5 5–20 20–40 40–60 60–80	8.2 8.1 8.2 8.1 8.3	7.9 7.9 8.7 8.9 7.7	65.7 66.1 64.9 75.8 89.2	66.6 66.4 65.2 73.6 87.5
PP 1 (old pool soil)	0–10	4.4	0.0	28.9	54.0

[1] mval per 100 g of active matter

For calcareous soils the close relation between S and U causes the laws for both quantities to be very similar. Thus the average value for S_a in these soils is approximately 65 mval per 100 g of active matter, whereas for U_a the corresponding value was about 68 mval. Also the frequency distributions for S_a and U_a bear close resemblance, though for S_a it is slightly shifted to lower values (fig. 11), with most cases ranging from 60 to 70. Moreover S_a shows the same particulars as U_a: it is slightly higher for light soils than for heavy ones and also increases with depth (c.f. St 69 in table 6).



U_a: exchange capacity at pH 8.0 (mval per 100 g of active matter). Topsoils of arable land (inundations 1953).

S_a: sum of metal cations (mval per 100 g of active matter). Topsoils of arable land; $CaCO_3 \geqq 1.0\,\%$ (inundations 1944/45).

n: number of observations.

FIG. 11. Frequency distributions of U_a and S_a

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[1] In the soils examined the amounts of exchangeable NH_4 may be neglected.

[2] Some observations indicate that in acid clays also exchangeable Al ions play a prominent part (HARWARD & COLEMAN, 1954).

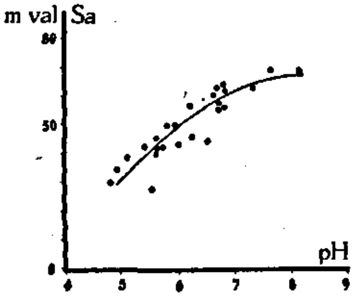

FIG. 12. Relation between pH and *sum of metal cations* S_a (mval per 100 g of active matter) in soils with less than 1 % $CaCO_3$

For non-calcareous soils is is well-known that S_a greatly depends on soil pH (fig. 12). But in the non-calcareous soils observed it may be considered approximately as constant during the exchange processes occurring after an inundation: whereas the individual amounts of Na, K, Mg and Ca may undergo great changes, their total remains approximately at the same level (c.f. table 34, section 5.2).

3.5. EXCHANGE CHARACTERISTICS; EQUILIBRIA WITH BINARY SALT SOLUTIONS

In order to study the exchange characteristics of the soils and especially to test the exchange equations mentioned in section 2.1 some observations have been made on exchanges involving the ion pairs Na-K, Na-Ca and Ca-Mg. These experiments were carried out with two soils from the investigated area. Each of them represents a commonly occurring soil series viz. the pool soils and the heavy newland soils, which largely differ in age, origin and agricultural value.

Further data concerning these two soils may be found in table 7.

TABLE 7. Characteristics of the soils used in testing the laws of ion exchange.

Soil	Sampling spot	Depth cm	Soil series	Year of embankment	Land-use	Agricultural quality
A	St 71	0–20	Pool soil	before 1200	Pasture	Moderate
B	St 68	0–20	Newland soil (Heavy clay)	1808	Young orchard on former arable land	Excellent

Soil	pH (H_2O)	$CaCO_3$ %	Organic matter %	Clay (< 2 μ) %	Active matter %	U (Ca ions at pH 8.0)	
						mval/100 g of soil	mval/100 g of active matter
A	5.8	0.1	8.1	27.4	51.7	34.9	67.5
B	7.7	7.0	3.6	38.9	49.7	30.9	62.2

Of these soils 10 g, mixed with 70 g of quartz sand were leached in a percolation tube with excess of a mixed solution containing the chlorides of the ions to be studied. During this process equilibrium was established between the exchanging components of the soil and the leaching solution. Afterwards the column was rinsed with alcohol (96 %) to remove the solution from the pore spaces. Finally the exchangeable cations were determined by leaching with a suitable solution (1 n NaCl or NH_4Cl) and analysis of the leacheate. In all cases where Ca ions were to be determined a correction was made for dissolved calcium carbonate by TIULIN's method; as a matter of fact this correction was very small for soil A and much larger for the calcareous soil B.

In general the exchange characteristics of the two soils proved to be very similar, indicating that no fundamental difference existed in their exchanging components (clay minerals and organic matter). The results of these investigations were studied in the following ways:

1. Adsorption isotherms were obtained by plotting the fraction of one of the components in the solution against the corresponding fraction on the exchanger.
2. The exchange equations mentioned in section 2.1 were tested by comparing the activity ratios in the solutions with the amounts of exchangeable cations.

For calculating the activities in mixed solutions use has been made of GLUECKAUF's equation (GLUECKAUF, 1949 *a*), which for solutions containing ions of equal valency reduces to equations (*2.20*) and (*2.21*), treated in section 2.12. The mean activity coefficients in single salt solutions of the same ionic strength needed for this calculation have been obtained from HARNED & OWEN (1950) and KORTÜM & BOCKRIS (1951), using graphical interpolation if necessary.

3.51. *Na-K equilibria*

These equilibria have been studied by leaching the soils with solutions of NaCl + KCl varying in ionic strength and in composition (table 8). The equilibrium amounts of exchangeable Na and K are represented in tables 9 and 10.

TABLE 8. Solutions of NaCl + KCl used for investigating the Na-K equilibria.

Solution no.	c_{Na} mval/l	c_K mval/l	c_{total} mval/l	Ionic strength I[1]	$\frac{c_{Na}}{c_{Na}+c_K}$	$\frac{f_{Na}}{f_K}$[2]	$\frac{a_{Na}}{a_K}$	Volume used for 10 g of soil ml
1	187	799	986	$\cong$ 1.0	0.190	1.08	0.253	250
2	480	488	968	$\cong$ 1.0	0.496	1.08	1.062	250
3	842	105	947	$\cong$ 1.0	0.889	1.08	8.64	250
4	885	48	933	$\cong$ 1.0	0.949	1.08	19.9	250
5	94	392	486	$\cong$ 0.5	0.194	1.04	0.250	500
6	240	243	483	$\cong$ 0.5	0.497	1.04	1.026	500
7	418	50	468	$\cong$ 0.5	0.893	1.04	8.70	500
8	17	79	96	$\cong$ 0.1	0.177	1.01	0.217	2500
9	49	50	99	$\cong$ 0.1	0.496	1.01	0.991	2500
10	84	10	94	$\cong$ 0.1	0.894	1.01	8.50	2500

[1] c.f. equation (*2.17*)

[2] Calculated from equation (*2.20*)

The *sum of exchangeable alkali metal cations* ($c_{Na} + c_K$) given in tables 9 and 10 obeys the following rules:

1. Comparing the sum $c_{Na} + c_K$ with the adsorptive capacities of the soils used (34.9 and 30.9 mval/100 g respectively) it appears that for soil A a large difference exists between these two. Obviously the neutral salt solutions have not been able to remove the bulk of the H_3O ions from this acid soil. For the calcareous

TABLE 9. Exchangeable Na and K after leaching soil A (pool soil) with the solutions mentioned in table 8.

Solution no.	c_{Na} mval/100 g	c_K mval/100 g	$c_{Na} + c_K$ mval/100 g	$\frac{c_{Na}}{c_{Na} + c_K}$	$\frac{c_{Na}}{c_K}$
1	1.2	21.9	23.1	0.052	0.055
2	3.4	19.7	23.1	0.147	0.173
3	13.1	9.4	22.5	0.582	1.39
4	16.5	5.8	22.3	0.740	2.84
5	1.5	21.1	22.6	0.066	0.071
6	4.8	18.0	22.8	0.210	0.266
7	14.3	8.4	22.7	0.630	1.70
8	2.5	18.6	21.1	0.118	0.134
9	5.7	15.2	20.9	0.273	0.375
10	13.8	6.9	20.7	0.666	2.00

TABLE 10. Exchangeable Na and K after leaching soil B (heavy new-land soil) with the solutions mentioned in table 8.

Solution no.	c_{Na} mval/100 g	c_K mval/100 g	$c_{Na} + c_K$ mval/100 g	$\frac{c_{Na}}{c_{Na} + c_K}$	$\frac{c_{Na}}{c_K}$
1	1.4	29.9	31.3	0.045	0.047
2	4.0	27.0	31.0	0.129	0.148
3	15.4	13.5	28.9	0.533	1.14
4	20.3	9.0	29.3	0.693	2.26
5	2.0	27.7	29.7	0.067	0.072
6	5.4	25.2	30.6	0.177	0.214
7	17.2	12.4	29.6	0.581	1.39
8	2.4	24.5	26.9	0.089	0.098
9	5.5	20.4	25.9	0.212	0.27
10	14.7	10.3	25.0	0.588	1.43

soil B the difference with the adsorptive capacity is only small and for the first two solutions even negligible.

2. The replacing power of the solution decreases at increasing dilution. For soil A the replacement of H_3O ions by metal cations is obviously lower at high dilution. For the calcareous soil B the sum $c_{Na} + c_K$ is influenced by Ca ions from $CaCO_3$ dissolved in the percolating liquid; this influence will increase with dilution.
3. At equal ionic strength solutions containing a high proportion of K (e.g. 1, 5, 8) posses a slightly stronger replacing power than solutions in which Na predominates (e.g. 3, 7, 10).

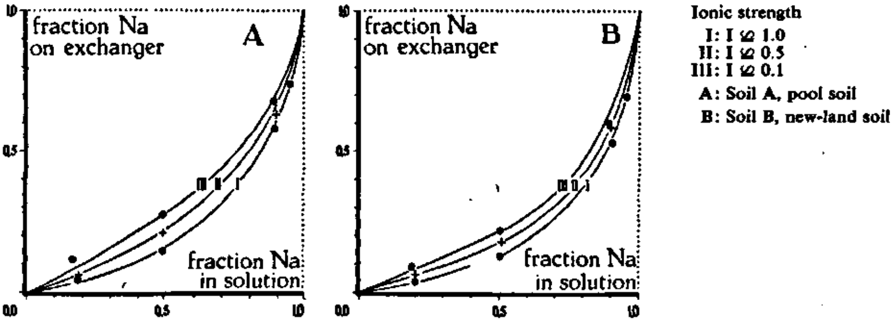

FIG. 13. Adsorption isotherms for the equilibrium Na–K

The adsorption isotherms obtained by plotting the fraction $\frac{c_{Na}}{c_{Na} + c_K}$ in the solution against the corresponding fraction on the exchanger are represented in fig. 13. For the two soils investigated these isotherms are very similar; they give a picture of the following exchange characteristics of the two soils studied:

1. Both soils show a marked preference for K over Na, in accordance with the lyotropic series and with the well-known preferential adsorption of K in illitic soils.
2. This preference diminishes at decreasing ionic strength, in accordance with the STERN theory mentioned in section 2.13.

In the adsorption isotherms the increasing affinity for Na at increasing dilution is slightly exaggerated by the diminishing value of $c_{Na} + c_K$. But this is not the major cause of the dilution effect as may be seen by comparing the values for exchangeable Na at equilibrium with solutions of equal Na/K ratio, listed in tables 9 and 10. These values for c_{Na} generally also increase at increasing dilution (c.f. the values for c_{Na} in equilibrium with the solution series 1-5-8, 2-6-9 and 3-7-10 of which only solution 10 forms an exception).

The *exchange equations* to be tested are those of KERR (eq. *2.27*) and ROTHMUND & KORNFELD (eq. *2.48*). Both may be written logarithmically as:

$$\log \left[\frac{c_{Na}}{c_K}\right]_I = \log K + p \log \left[\frac{f^2_{\pm NaCl} \cdot c_{Na}}{f^2_{\pm KCl} \cdot c_K}\right]_{II} \qquad (3.03)$$

in which the subscript I refers to the exchanger and II to the solution. Obviously the KERR equation is only satisfied if p = 1.

By plotting $\log \left[\frac{c_{Na}}{c_K}\right]_I$ against $\log \left[\frac{f^2_{\pm NaCl} \cdot c_{Na}}{f^2_{\pm KCl} \cdot c_K}\right]_{II}$ fig. 14 is obtained, from which it is evident that:

1. At equal ionic strength the linear relationship demanded by equation (*3.03*) is satisfied.
2. The condition for the KERR equation, p = 1, is obviously not fulfilled. Thus the results of the experiments may only be described by the ROTHMUND-KORNFELD equation.

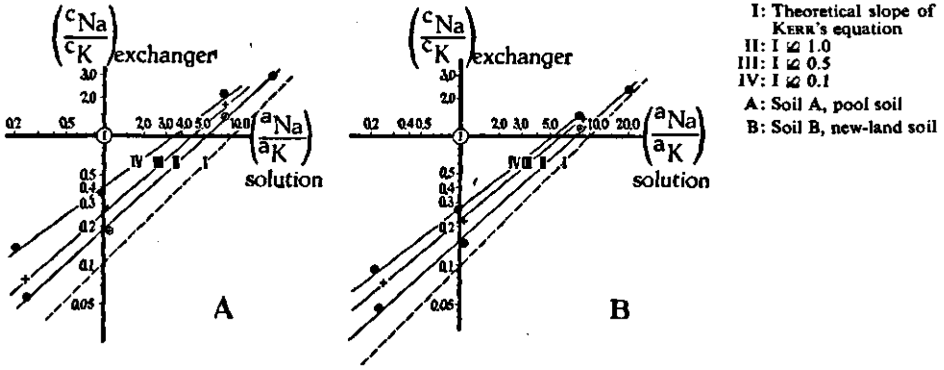

FIG. 14. Tests of theoretical equations for the equilibrium Na–K

3. The values of K and p are dependent upon the ionic strength of the solution. From the experimentally obtained values for these constants mentioned in table 11, it appears that K approaches unity at increasing dilution, though this is not the case for p.

TABLE 11. Values for the exchange constants K and p in the ROTHMUND-KORNFELD equation describing the Na-K equilibria:

$$\left[\frac{c_{Na}}{c_K}\right]_I = K\left[\frac{f^2_{\pm NaCl}\cdot c_{Na}}{f^2_{\pm KCl}\cdot c_K}\right]^p_{II}$$

I	Soil A		Soil B	
	K	p	K	p
0.1	0.40	0.76	0.28	0.76
0.5	0.25	0.88	0.22	0.82
1.0	0.18	0.92	0.16	0.89

For the range of I studied these values may be calculated from the following empirical equations:

Soil A (pool soil)

$$K = 0.18 - 0.22 \log I \qquad 0.1 < I < 1.0 \qquad (3.04)$$

$$p = 0.93 + 0.16 \log I \qquad ,, \qquad (3.05)$$

Soil B (new-land soil)

$$K = 0.17 - 0.11 \log I \qquad 0.1 < I < 1.0 \qquad (3.06)$$

$$p = 0.87 + 0.11 \log I \qquad ,, \qquad (3.07)$$

3.52. *Na-Ca equilibria*

These equilibria have been studied by leaching the soils with solutions of NaCl + $CaCl_2$ varying in ionic strength and in composition. Analogous to the investigations of the Na-K equilibria the sum of exchangeable Na and Ca was studied, adsorption isotherms were constructed and the equations for ion exchange tested (tables 12 and 13).

Table 12. Exchangeable Na and Ca after leaching soil A (pool soil) with mixed solutions of NaCl + $CaCl_2$.

Solution				Soil			
c_{Na} mval/l	c_{Ca} mval/l	Ionic strength I	$\frac{c_{Na}}{c_{Na}+c_{Ca}}$	c_{Na} mval/100 g	c_{Ca} mval/100 g	$c_{Na}+c_{Ca}$ mval/100 g	$\frac{c_{Na}}{c_{Na}+c_{Ca}}$
50	1013	≌ 1.5	0.047	0.7	24.2	24.9	0.028
294	827	≌ 1.5	0.26	0.9	24.2	25.1	0.036
848	416	≌ 1.5	0.67	8.0	18.4	26.4	0.30
1395	101	≌ 1.5	0.93	17.7	9.3	27.0	0.66
121	336	≌ 0.6	0.26	1.0	23.9	24.9	0.040
364	166	≌ 0.6	0.69	7.0	19.0	26.0	0.27
478	84	≌ 0.6	0.85	12.0	13.9	25.9	0.46
60	167	≌ 0.3	0.26	1.1	24.0	25.1	0.044
174	83	≌ 0.3	0.68	6.2	20.0	26.2	0.24
242	42	≌ 0.3	0.85	10.6	15.2	25.8	0.41
91	42	≌ 0.15	0.68	5.3	20.3	25.6	0.21

Table 13. Exchangeable Na and Ca after leaching soil B (heavy new-land soil) with mixed solutions of NaCl + $CaCl_2$.

Solution				Soil			
c_{Na} mval/l	c_{Ca} mval/l	Ionic strength I	$\frac{c_{Na}}{c_{Na}+c_{Ca}}$	c_{Na} mval/100 g	c_{Ca} mval/100 g	$c_{Na}+c_{Ca}$ mval/100 g	$\frac{c_{Na}}{c_{Na}+c_{Ca}}$
60	957	≌ 1.5	0.059	0.4	30.4	30.8	0.013
301	820	≌ 1.5	0.27	2.2	28.8	31.0	0.071
870	401	≌ 1.5	0.68	10.2	20.0	30.2	0.34
338	99	≌ 1.5	0.93	18.8	10.0	28.8	0.65
120	328	≌ 0.6	0.27	1.4	29.3	30.7	0.046
348	160	≌ 0.6	0.68	7.3	22.9	30.2	0.24
535	40	≌ 0.6	0.93	16.6	12.3	28.9	0.58
60	164	≌ 0.3	0.27	1.2	29.3	30.5	0.039
174	80	≌ 0.3	0.68	6.1	24.5	30.6	0.20
268	20	≌ 0.3	0.93	14.2	14.5	28.7	0.49
87	40	≌ 0.15	0.68	4.4	26.1	30.5	0.145

The *sum of exchangeable metal cations* ($c_{Na} + c_{Ca}$) is nearly independent of ionic strength over the range studied ($0.15 < I < 1.5$), whereas also the composition of the solution has little influence. For the non-calcareous, acid soil A this sum, though being slightly higher than the sum $c_{Na} + c_K$ treated in section 3.51 is still considerably below the exchange capacity: the average value of $c_{Na} + c_{Ca}$ is 25.7 mval/100 g, whereas the exchange capacity of this soil, U_s, is 34.9 mval/100 g. For the calcareous soil B the sum $c_{Na} + c_{Ca}$ appears to be nearly equal to the exchange capacity (30.9 mval/100 g), except for equilibria with solutions rich in Na, where it is slightly lower.

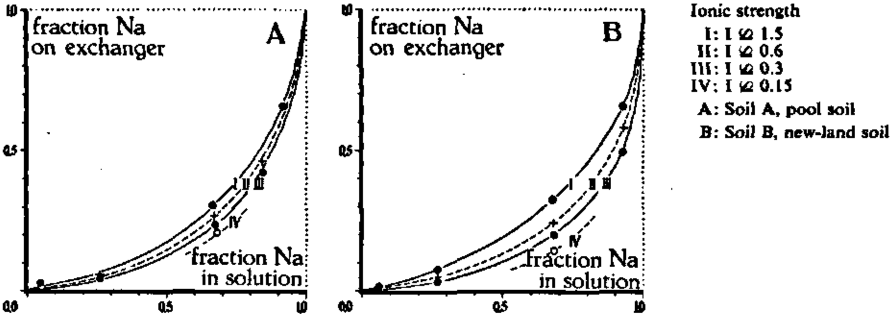

FIG. 15. Adsorption isotherms for the equilibrium Na–Ca

The *adsorption isotherms* represented in fig. 15 were obtained by plotting the fraction $\frac{c_{Na}}{c_{Na} + c_{Ca}}$ in the solution against the corresponding fraction on the exchanger. Again both soils show a quite similar behaviour, from which the following exchange characteristics may be derived:

1. In the range of concentrations studied ($0.15 < I < 1.5$) both soils posses a marked preference of Ca over Na, in accordance with the general rule that at ordinary concentrations bivalent ions are more strongly adsorbed than monovalent ones.
2. This preference for Ca is increasing at increasing dilution. This effect must be ascribed to the influence of the valency, predicted by all equations for heterovalent exchange, treated in chapter 2.

The *exchange equations* to be tested are those of KERR (*2.28*), KRISNAMOORTHY & OVERSTREET (*2.42*), VANSELOW (*2.38*), GAPON (*2.46*) and ROTHMUND & KORNFELD (*2.49*).

All these equations may be written as:

$$F\,(Na, Ca)_I = K \left[\frac{f^2_{\pm\,NaCl} \cdot c_{Na}}{f^{3/2}_{\pm\,CaCl_2} \cdot \sqrt{c_{Ca}}}\right]^p_{II} \qquad (3.08)$$

or, logarithmically as:

$$\log F\,(Na, Ca)_I = \log K + p \log \left[\frac{f^2_{\pm\,NaCl} \cdot c_{Na}}{f^{3/2}_{\pm\,CaCl_2} \cdot \sqrt{c_{Ca}}}\right]_{II} \qquad (3.09)$$

in which F (Na, Ca)$_l$ denotes a function of the adsorbed cations. The coefficient p should be unity except for the ROTHMUND & KORNFELD equation. For the equations mentioned above F (Na, Ca)$_l$ may be written as:

$$F_{Kerr} = \frac{c_{Na}}{\sqrt{c_{Ca}}};\ p = 1 \tag{3.10}$$

$$F_{K.\&O.} = \frac{c_{Na}}{\sqrt{c_{Ca}\,(c_{Na} + 0.75\, c_{Ca})}};\ p = 1 \tag{3.11}$$

$$F_{Vans.} = \frac{c_{Na}}{\sqrt{c_{Ca}\,(c_{Na} + 0.5\, c_{Ca})}};\ p = 1 \tag{3.12}$$

$$F_{Gapon} = \frac{c_{Na}}{c_{Ca}};\ p = 1 \tag{3.13}$$

$$F_{R.\&K} = \frac{c_{Na}}{\sqrt{c_{Ca}}};\ p \neq 1 \tag{3.14}$$

As an illustration the tests of these formulae for soil B are shown in fig. 16. It appears that the equations of KERR, KRISNAMOORTHY & OVERSTREET and VANSELOW

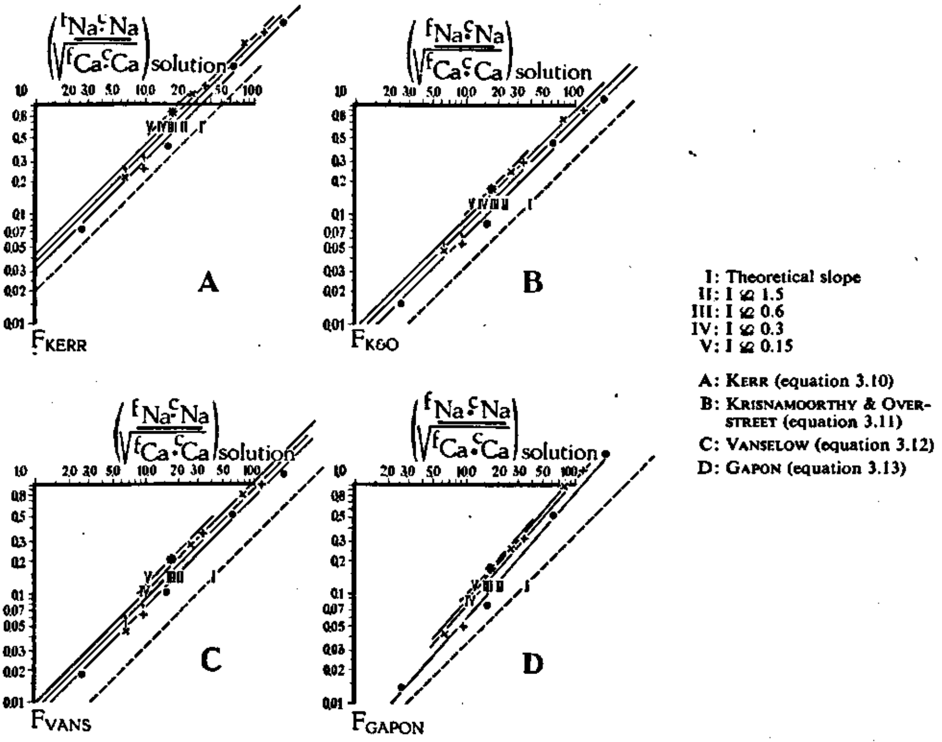

FIG. 16. Tests of theoretical equations for the equilibrium Na–Ca. Soil B, new-land soil

all give straight lines with a slope of 1 : 1. Consequently these equations are suitable for describing the observed equilibria. As their mutual differences are slight compared to the experimental errors it is impossible to make a choice from the available experimental evidence. In these circumstances KERR's equation (*2.28*) is to be preferred for its simplicity. For the GAPON equation the coefficient p markedly differs from unity; therefore this equation is obviously inadequate.

It also appears from fig. 16 that the value of the exchange constant K distinctly depends upon the ionic strength of the solution. Thus, after eliminating the valency effect, the preference for Ca over Na is highest in equilibria with the most concentrated solutions, resulting in a lower value of the exchange constant K (table 14). Possibly this effect is analogous to the dilution effect in the Na-K equilibria mentioned in section 3.51, which was ascribed to diminishing specific influences at lower ionic strength, as predicted by the STERN theory. Although this effect counteracts the valency effect – by which Ca will be held more strongly at low concentrations – the latter apparently predominates, as may be seen from the adsorption isotherms (fig. 15).

For the non-calcareous pool soil (soil A) similar results were obtained.

TABLE 14. Values for the exchange constant K in the KERR equation describing the Na-Ca equilibria:

$$\left[\frac{c_{Na}}{\sqrt{c_{Ca}}}\right]_{I} = K \left[\frac{f^{2}_{\pm\,NaCl} \cdot c_{Na}}{f^{3/2}_{\pm\,CaCl_2} \cdot \sqrt{c_{Ca}}}\right]_{II}$$

I	K	
	Soil A	Soil B
0.15	0.067	0.050
0.3	0.050	0.044
0.6	0.036	0.038
1.5	0.030	0.031

For soil B and for the range of I studied the following empirical relationship between K and I may be employed:

Soil B (new-land soil)

$$K_{Kerr} = 0.034 - 0.0195 \log I \tag{3.15}$$

For soil A no such simple relationship could be formulated; moreover, due to experimental errors, the data for K are less reliable in this case. If necessary, graphical interpolation between the values given in table 14 may be used.

3.53. *Mg-Ca equilibria*

Values for these equilibria studied by the same methods as the foregoing ones, are given by tables 15 and 16.

TABLE 15. Exchangeable Mg and Ca after leaching soil A (pool soil) with mixed solutions of $MgCl_2 + CaCl_2$.

Solution				Soil			
c_{Mg} mval/l	c_{Ca} mval/l	Ionic strength I	$\frac{c_{Ca}}{c_{Mg} + c_{Ca}}$	c_{Mg} mval/100 g	c_{Ca} mval/100 g	$c_{Mg} + c_{Ca}$ mval/100 g	$\frac{c_{Ca}}{c_{Mg} + c_{Ca}}$
193	803	$\cong 1.5$	0.81	2.8	20.3	23.1	0.88
509	500	$\cong 1.5$	0.50	6.2	16.3	22.5	0.72
821	199	$\cong 1.5$	0.20	12.0	10.4	22.4	0.46
913	105	$\cong 1.5$	0.103	15.2	6.9	22.1	0.31
101	404	$\cong 0.75$	0.80	3.1	19.9	23.0	0.87
259	257	$\cong 0.75$	0.50	6.9	15.9	22.8	0.70
410	100	$\cong 0.75$	0.20	12.7	9.4	22.1	0.42
458	53	$\cong 0.75$	0.103	15.8	6.2	22.0	0.28
20	80	$\cong 0.15$	0.80	3.2	19.5	22.7	0.86
51	50	$\cong 0.15$	0.50	7.3	15.1	22.4	0.68
80	21	$\cong 0.15$	0.20	13.5	8.5	22.0	0.39
91	10.5	$\cong 0.15$	0.104	16.2	5.5	21.7	0.25

TABLE 16. Exchangeable Mg and Ca after leaching soil B (heavy new-land soil) with mixed solutions of $MgCl_2 + CaCl_2$.

Solution				Soil			
c_{Mg} mval/l	c_{Ca} mval/l	Ionic strength I	$\frac{c_{Ca}}{c_{Mg} + c_{Ca}}$	c_{Mg} mval/100 g	c_{Ca} mval/100 g	$c_{Mg} + c_{Ca}$ mval/100 g	$\frac{c_{Ca}}{c_{Mg} + c_{Ca}}$
193	803	$\cong 1.5$	0.81	5.2	24.3	29.5	0.82
509	500	$\cong 1.5$	0.50	10.3	18.8	29.1	0.65
821	199	$\cong 1.5$	0.20	17.6	10.8	28.4	0.38
913	105	$\cong 1.5$	0.103	21.1	7.2	28.3	0.25
101	404	$\cong 0.75$	0.80	4.7	24.8	29.5	0.84
259	257	$\cong 0.75$	0.50	10.5	18.5	29.0	0.64
410	100	$\cong 0.75$	0.20	18.0	10.1	28.1	0.36
458	53	$\cong 0.75$	0.103	21.7	6.5	28.2	0.23
20	80	$\cong 0.15$	0.80	4.6	24.8	29.4	0.84
51	50	$\cong 0.15$	0.50	10.9	18.0	28.9	0.62
80	21	$\cong 0.15$	0.20	18.9	9.9	28.8	0.34
91	10.5	$\cong 0.15$	0.104	22.7	5.6	28.3	0.198

The *sum of exchangeable cations*, $c_{Mg} + c_{Ca}$, is only slightly dependent on the ionic strenth and composition of the equilibrium solution and obeys the same rules as in the case of the Na-Ca exchange equilibria treated in the foregoing section.

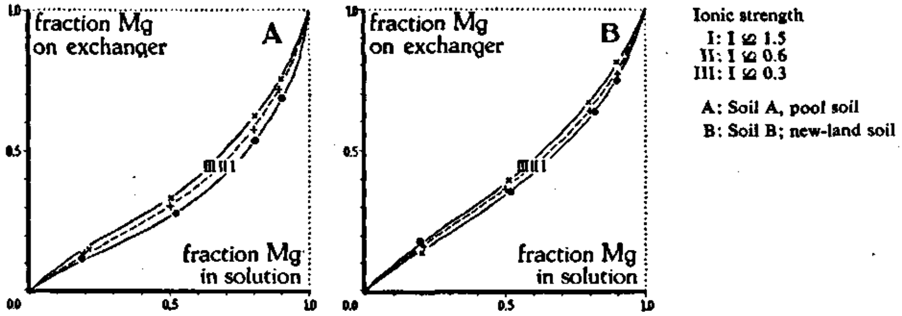

FIG. 17. Adsorption isotherms for the equilibrium Mg–Ca

The *adsorption isotherms* represented in fig. 17 show that both soils studied have a slight preference for Ca over Mg, in accordance with the lyotropic series. The curvature of the isotherms is greater for soil A, which will be probably caused by the high organic content, which is known for its specific affinity for Ca (c.f. SCHACHTSCHABEL, 1940). Just like in the homovalent Na-K exchange this preference diminishes at decreasing ionic strength, which is in accordance with the STERN double layer theory.

The *exchange equations* to be tested are those of KERR (eq. *2.29*) and ROTHMUND-KORNFELD (eq. *2.48*). Both of these may be written logarithmically as:

$$\log \left[\frac{c_{Mg}}{c_{Ca}}\right]_{I} = \log K + p \log \left[\frac{f^3_{\pm\, MgCl_2} \cdot c_{Mg}}{f^3_{\pm\, CaCl_2} \cdot c_{Ca}}\right]_{II} \qquad (3.16)$$

in which only $p = 1$ satisfies the KERR equation.

As may be seen from fig. 18 this condition is obviously not fulfilled: as p distinctly differs from unity only the ROTHMUND-KORNFELD equation gives an adequate description of the equilibria observed.

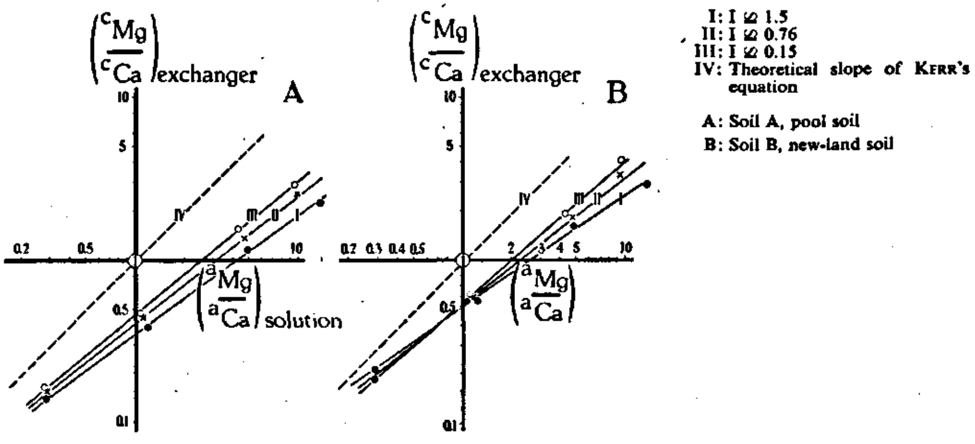

FIG. 18. Tests fo theoretical equations for the equilibrium Mg–Ca

The exchange constants K and p occurring in this equation are listed in table 17. As may be derived from these figures both K and p decrease at increasing ionic strength.

TABLE 17. Values for the exchange constants K and p in the ROTHMUND-KORNFELD equation describing the Mg-Ca equilibria:

$$\left[\frac{c_{Mg}}{c_{Ca}}\right]_I = K\left[\frac{f^3_{\pm\,MgCl_2}\cdot c_{Mg}}{f^3_{\pm\,CaCl_2}\cdot c_{Ca}}\right]^p_{II}$$

I	Soil A		Soil B	
	K	p	K	p
0.15	0.47	0.80	0.58	0.86
0.76	0.40	0.78	0.55	0.78
1.52	0.34	0.75	0.51	0.71

The differences between the values given in table 13 are rather small. Hence it seems hardly justified to derive empirical relations from these data.

Thus, the following generalizations may be made:

1. The behaviour of the two soils tested (pool soil and new-land soil) is very similar.
2. The homovalent exchange equilibria Na-K and Mg-Ca may be described by equations of the ROTHMUND-KORNFELD type.
3. The heterovalent exchange equilibrium Na-Ca may be described by the equations of KERR, KRISNAMOORTHY & OVERSTREET, and VANSELOW.
4. The parameters in the exchange equations are slightly dependent upon the ionic strength of the equilibrium solution. This is probably due to the STERN effect which tends to reduce the individual differences between different kinds of ions at increasing dilution.

3.6. EQUILIBRIA WITH SEA WATER AND BRACKISH WATER

The exchange equilibria treated in the foregoing sections are only of limited value for the study of inundated soils, as in these soils four ions, viz. Na, K, Mg and Ca are involved in the equilibria. Of the numerous variations possible in such a system two are of practical importance, viz. equilibria with sea- or brackish water and equilibria occurring in inundated soils during the regeneration period.

The equilibria with sea- and brackish water are of special interest as they represent the conditions occurring after a long inundation. They have been studied by investigating the exchange equilibria of the same soils as used in the previous experiments, obtained after leaching with excess amounts of the solutions mentioned in table 18.

TABLE 18. Solutions used for investigating the equilibria with sea water and brackish water.

Solution no.	Composition	Ratio	Salinity C[1]	I
1	Sea water (North Sea)	—	29.5	0.64
2	Sea water + distilled water	2 : 1	19.8	0.43
3	Sea water + distilled water	1 : 1	15.0	0.32
4	Sea water + distilled water	1 : 2	9.8	0.21
5	Sea water + distilled water	1 : 5	5.0	0.11
6	Sea water + distilled water	1 : 9	3.0	0.06
7	Brackish water (Volkerak)	—	8.4	0.19
8	Brackish water (Hollands Diep)	—	5.2	0.12

[1] Content of Cl ions, calculated as NaCl (g/l).

TABLE 19. Ionic composition of the solutions mentioned in table 18.

Solution no.	Composition	Percentage of cations			
		Na	K	Mg	Ca
1–6	Sea water (diluted)	77.2	1.8	17.6	3.4
7	Brackish water (C = 8.4)	76.4	1.7	16.5	5.4
8	Brackish water (C = 5.2)	75.4	1.6	16.6	6.4

TABLE 20. Ionic composition of soils in equilibrium with the solutions mentioned in table 18.

Soil	Solution			Percentage of exchangeable metal cations			
	No.	Composition	Salinity C	Na	K	Mg	Ca
A[1]	1	Sea water	29.5	41.0	9.3	33.7	16.0
	3	Sea water (diluted)	15.0	34.3	8.1	40.4	17.2
	5	Sea water (diluted)	5.0	25.1	5.8	48.9	20.2
B[2]	1	Sea water	29.5	40.8	11.8	34.9	12.5
	2	Sea water (diluted)	19.8	34.3	10.6	38.5	16.6
	3	Sea water (diluted)	15.0	30.3	10.2	41.4	18.1
	4	Sea water (diluted)	9.8	27.2	9.3	44.7	18.8
	5	Sea water (diluted)	5.0	21.6	7.8	50.9	19.7
	6	Sea water (diluted)	3.0	17.8	7.2	54.1	20.9
B[2]	7	Brackish water	8.4	25.1	8.8	41.5	24.6
	8	Brackish water	5.2	20.9	8.0	42.1	29.0

[1] Pool soil.

[2] Heavy new-land soil.

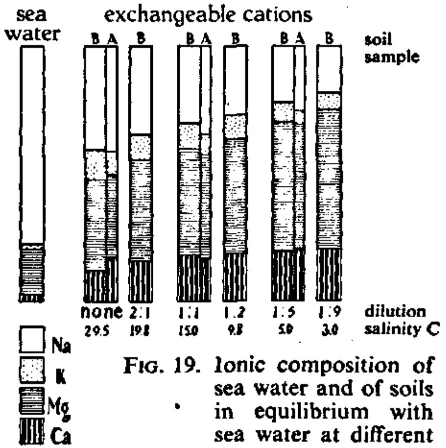

FIG. 19. Ionic composition of sea water and of soils in equilibrium with sea water at different dilutions

3.61. *General aspects of the equilibria*

The percentages of the four main cations in these solutions and the corresponding equilibrium percentages of the exchangeable cations are represented in tables 19 and 20, and in figs. 19 and 20. As appears from these data the equilibria show the following characteristics:

1. The behaviour of the two soils A and B (table 7) is almost identical.
2. Of the ions present in sea water K is preferentially adsorbed: among the exchangeable cations of soils in equilibrium with sea water the percentage of K is about 6 times as high as in the sea water itself. The same holds to a less extent for Ca and Mg, whereas for Na the reverse is true. Obviously under these circumstances the adsorption increases in the order: Na < Mg < Ca < K.
3. At increasing dilution of the sea water the percentages of adsorbed bivalent ions increase at the expense of the monovalent ones. This valency effect is in accordance with theory and with the results for the Na-Ca equilibrium treated in section 3.52.

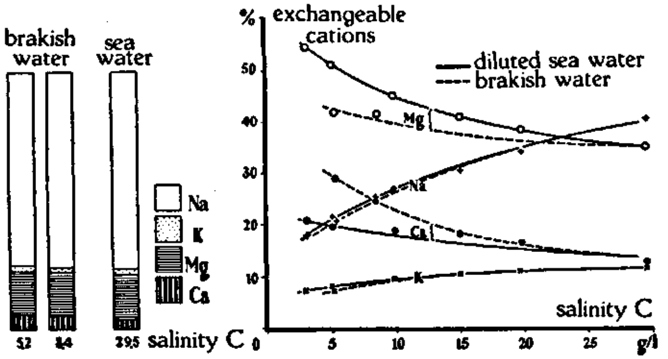

FIG. 20. Ionic composition of brackish water and sea water and percentages of exchangeable cations in soils in equilibrium with diluted sea water or brackish water

4. Brackish water contains a higher proportion of Ca ions than pure sea water. Consequently soils, brought into equilibrium with brackish water, contain a relatively higher proportion of exchangeable Ca (fig. 20).

3.62. *Theoretical aspects of the equilibria*

Theoretically these equilibria must obey the DONNAN distribution, given by equation (*2.05*). If it is assumed that in the adsorbed state the activities of the cations are proportional to their equivalent fractions, the following extended KERR equation is obtained:

$$[K_1c_{Na} : K_2c_K : K_3\sqrt{c_{Mg}} : K_4\sqrt{c_{Ca}}]_I = [f_{Na}\,c_{Na} : f_K\,c_K : \sqrt{f_{Mg}\cdot c_{Mg}} : \sqrt{f_{Ca}\cdot c_{Ca}}]_{II} \qquad (3.17)$$

in which K_1, K_2, K_3 and K_4 denote constants, one of which may be chosen arbitrarily.

Inserting the mean activity coefficients instead of the unknown individual ionic activity coefficients and considering Cl as the leading anion, this equation changes into:

$$\begin{gathered}[K_1c_{Na} : K_2c_K : K_3\sqrt{c_{Mg}} : K_4\sqrt{c_{Ca}}]_I = \\ [f^2_{\pm\,NaCl}\cdot c_{Na} \;:\; f^2_{\pm\,KCl}\cdot c_K \;:\; f^{3/2}_{\pm\,MgCl_2}\cdot\sqrt{c_{Mg}} \;:\; f^{3/2}_{\pm\,CaCl_2}\cdot\sqrt{c_{Ca}}]_{II}\end{gathered} \qquad (3.18)$$

The mean activity coefficients mentioned above may be calculated according to the ionic strength principle. In these complicated solutions a refinement of this method by employing GLUECKAUF's equation is not possible, but it may be expected that the errors will not be too large.

As one of the exchange constants K may be chosen at will, K_1 has been put equal to 100. In this way the values for K_2, K_3 and K_4 listed in table 21, have been obtained from the available data.

TABLE 21. Relative values for the exchange constante K_1, K_2, K_3 and K_4 in the extended KERR equation (*3.18*) describing the equilibria of soil B with diluted sea water.

Solution no.	Dilution ratio	I	Exchange constants			
			K_1 [1] (Na)	K_2 (K)	K_3 (Mg)	K_4 (Ca)
1	none	0.64	100	7.2	7.7	5.0
2	2 : 1	0.43	100	7.0	7,4	4.5
3	1 : 1	0.32	100	6.4	7.2	4.3
4	1 : 2	0.21	100	6.4	7.7	4.9
5	1 : 5	0.11	100	6.3	8.2	5.6
6	1 : 9	0.06	100	5.7	8.4	5.8
Average			100	6.5	7.8	5.0

[1] Arbitrary value.

It is clear from this table that the value of the exchange constants K is little affected by dilution of the solution. Reciprocally their average value may be employed for predicting the equilibria with other solutions of similar composition e.g. for equilibria with brackish water.

For the calculation of equilibria from known values of the constants K, equation (*3.18*) may be written as:

$$\left.\begin{aligned}
[c_{Na}]_I &= p\left[\frac{f^2_{\pm NaCl}\cdot c_{Na}}{K_1}\right]_{II} = k_1 . p \\
[c_K]_I &= p\left[\frac{f^2_{\pm KCl}\cdot c_K}{K_2}\right]_{II} = k_2 . p \\
[c_{Mg}]_I &= p^2\left[\frac{f^3_{\pm MgCl_2}\cdot c_{Mg}}{K_3^2}\right]_{II} = k_3 . p^2 \\
[c_{Ca}]_I &= p^2\left[\frac{f^3_{\pm CaCl_2}\cdot c_{Ca}}{K_4^2}\right]_{II} = k_4 . p^2
\end{aligned}\right\} \qquad (3.19)$$

in which p is an arbitrary constant.

On the other hand the condition required by equation (*3.02*) must be fulfilled, viz.:

$$[c_{Na} + c_K + c_{Mg} + c_{Ca}]_I = S_s$$

Hence:

$$(k_3 + k_4)\, p^2 + (k_1 + k_2)\, p - S_s = 0 \qquad (3.20)$$

from which p and consequently also c_{Na}, c_K, c_{Mg} and c_{Ca} may be calculated.

As a matter of fact the equilibria with diluted sea water, calculated from the average values of the constants K and the observed values of S_s, closely approach the observed values. But also for the equilibria with brackish water fair results were obtained, though the calculated values for Ca are slightly too high (table 22).

TABLE 22. Calculated and observed equilibria of soil B (new-land soil) with brackish water.

Solution no. [1]	Salinity C		Exchangeable cations mval/100 g of soil				
			Na	K	Mg	Ca	S_s
7	8.4	calculated [2]	7.9	2.5	12.4	8.8	31.6
		observed	7.9	2.8	13.1	7.8	
8	5.2	calculated [2]	6.1	2.0	12.8	10.9	31.8
		observed	6.7	2.5	13.4	9.2	

[1] c.f. table 18.

[2] Calculated from the average values of the exchange constants obtained from the sea water dilution experiments (table 21).

On the other hand, as will be shown in the next section, it appears that this method is inadequate for solutions differing greatly from sea water in ionic composition. This inconsistency must be ascribed to mutual interference of the cations involved.

This mutual disturbance may be demonstrated in still another way. If the ratios of the exchangeable cations in the sea water dilution experiment are more closely examined, it appears that – at least for soil B – the Na/K ratios decrease at increasing dilution (table 23). This behaviour is just opposite to that observed in the pure Na-K equilibria treated in section 3.51. Hence it may be concluded, that the foreign ions[1] Mg and Ca will disturb the Na-K equilibrium: at increasing dilution their replacing power increases, obviously chiefly at the cost of the weakly bound Na ions. Further evidence of this influence of the foreign ions becomes apparent if the ionic ratios c_{Na}/c_K are calculated from the equations for exchange equilibria with binary salt solutions given in section 3.5. By comparing these calculated c_{Na}/c_K ratios with the observed values it appears that the calculated ratios are too high (table 23).

This confirms the specific influence of the foreign ions – Mg and Ca – on the equilibria; obviously these foreign ions reduce the amounts of exchangeable Na more than the amounts of exchangeable K. On the other hand the c_{Mg}/c_{Ca} ratios are found to be as calculated; apparently this equilibrium is only slightly influenced by the presence of Na and K ions.

TABLE 23. Calculated and observed ionic ratios in soil B after equilibrium with diluted sea water.

Solution no.	Dilution ratio	Ratios of exchangeable cations		
		Ratio	calculated	observed
1	none	c_{Na}/c_K	5.1 [1]	3.5
5	1 : 5	c_{Na}/c_K	5.0 [1]	2.8
1	none	c_{Mg}/c_{Ca}	2.5 [2]	2.8
4	1 : 2	c_{Mg}/c_{Ca}	2.6 [2]	2.4

[1] Calculated from equations (*3.03*), (*3.06*) and (*3.07*).
[2] Calculated from equation (*3.16*) and table 17.

These mutual effects extensively studied by WIKLANDER (1946), make it extremely difficult to predict the exchange equilibria with solutions containing several electrolytes. Only for a group of solutions with kindred ionic composition, is a calculation based on empirically established constants possible (c.f. the calculation of brackish water equilibria from equilibria with diluted sea water, given in table 22).

3.63. *Equilibria with limited amounts of sea water*

In flooded soils full equilibrium with sea or brackish water, as described in the preceding section, is seldom reached. Only after very prolonged inundations or in cases where flooded soils are falling dry at each low tide and are flooded again at the next high tide, is this full equilibrium approached. In all other cases where limited amounts of flood water penetrate, the ionic composition of this penetrating water is considerably altered by ion exchange with the active matter of the soil.

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[1] Ions interfering with equilibria between two cationic species will be denoted as foreign ions, whereas all ions which interfere with the adsorption of one particular ionic species will be called complementary ions.

The equilibria with limited amounts of sea water, being of considerable practical importance, have been studied both empirically and theoretically.

In the experiments usually 140 g of dry soil, corresponding with approximately 100 cm^3 in its natural position, has been thoroughly mixed with 100 or 200 cm^3 of sea water. These amounts correspond to amounts of sea water of 100 and 200 mm respectively, coming into equilibrium with the upper 10 cm of a flooded soil. After standing for 24 hrs. and removal of the supernatant liquid the soil was washed out with alcohol (96%) and investigated for exchangeable cations. In some experiments this procedure was repeated once or twice.

In these equilibria the ions originally present in the soil as well as the ions added with the sea water take part. In other words, the total amounts of cations of different kinds present in the system are redistributed between the soil and the solution. As in the new-land soil used in the experiments (soil B) the Ca ion is strongly predominant, the solution is enriched with Ca, whereas the soil itself is enriched with Na, K and Mg ions (table 24; fig. 21). These changes, though considerable, are less than those brought about by percolation with excess amounts of sea water.

Theoretically the equilibria for this soil may be calculated from the extended KERR equation (*3.18*), using the empirical exchange constants derived from the diluted sea water experiments (table 21).

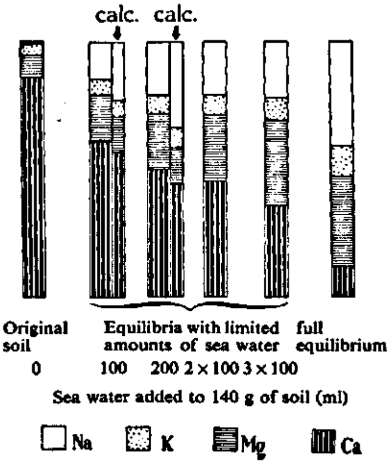

FIG. 21. Ionic composition of soil B equilibrated with limited amounts of sea water

TABLE 24. Ionic composition of soil B equilibrated with limited amounts of sea water.

Experiment no.	Soil g	Sea water ml	Percentages of exchangeable metal cations			
			Na	K	Mg	Ca
1 [1]	—	—	0.2	5.3	8.3	86.2
2	140	100	14.5	6.4	17.9	61.2
3	140	200	20.9	7.1	21.2	50.8
4	140	2×100	20.6	7.9	25.8	45.7
5	140	3×100	22.1	8.9	33.0	36.0
6 [2]	—	excess	40.8	11.8	34.9	12.5

[1] Original soil.

[2] Full equilibrium after percolation with excess sea water (table 20).

This calculation may be carried out in the following way. Suppose that P grammes of soil are equilibrated with Q litres of sea water. The amounts of cations present in the system may be denoted as in table 25.

TABLE 25. Amounts of cations present in the equilibrium of P grams of soil with Q litres of sea water.

Ion	Before equilibrium			After equilibrium			
	Soil (P g.) mval	Solution (Q l.) mval	Total mval	Soil (P g.) mval	Solution (Q l.) mval	(c_i) exchanger mval/100 g	(c_i) solution mval/l
Na	a_1	b_1	t_1	x_1	t_1-x_1	$\frac{100\,x_1}{P}$	$\frac{t_1-x_1}{Q}$
K	a_2	b_2	t_2	x_2	t_2-x_2	$\frac{100\,x_2}{P}$	$\frac{t_2-x_2}{Q}$
Mg	a_3	b_3	t_3	x_3	t_3-x_3	$\frac{100\,x_3}{P}$	$\frac{t_3-x_3}{Q}$
Ca	a_4	b_4	t_4	x_4	t_4-x_4	$\frac{100\,x_4}{P}$	$\frac{t_4-x_4}{Q}$

Utilizing equation (*3.18*) gives, after some rearrangements:

$$\frac{f^2_{\pm NaCl}}{100\,K_1} \cdot \frac{P}{Q} \cdot \left[\frac{t_1}{x_1} - 1\right] = \frac{f^2_{\pm KCl}}{100\,K_2} \cdot \frac{P}{Q} \cdot \left[\frac{t_2}{x_2} - 1\right] =$$

$$\frac{f^{3/2}_{\pm MgCl_2}}{10\,K_3} \cdot \sqrt{\frac{P}{Q}} \cdot \sqrt{\frac{t_3}{x_3} - 1} = \frac{f^{3/2}_{\pm CaCl_2}}{10\,K_4} \cdot \sqrt{\frac{P}{Q}} \cdot \sqrt{\frac{t_4}{x_4} - 1} \qquad (3.21)$$

Finally, according to equation (*3.02*)

$$x_1 + x_2 + x_3 + x_4 = \Sigma x = \frac{P}{100} \cdot S_s \qquad (3.22)$$

The four unknowns $x_1 \ldots\ldots x_4$ may be easily found by inserting different values for x_1 into (*3.21*), calculating the corresponding values of $x_2 \ldots\ldots x_4$ and selecting the set of values obeying equation (*3.22*) by graphical interpolation. An example of this procedure may be found in table 26.

TABLE 26. Calculation of the equilibrium of 140 g of soil B with 100 cm³ of sea water.

	x_1	x_2	x_3	x_4	Σx observed	Σx required
Trial values for x_1	6.0	1.6	2.2	11.1	20.9	
	8.0	1.8	3.8	17.2	30.8	
	10.0	1.9	5.5	22.6	40.0	42.0
	12.0	1.9	7.2	27.0	48.1	
x_1 by graphical interpolation	10.5	1.9	6.0	23.8	42.2	

The ionic distributions calculated in this way are also indicated in fig. 21. It is clear that for these cases the observed ionic compositions differ from those calculated: the calculated amounts of Na are far too high, whereas Mg and Ca are too low. As the ionic composition of the equilibrium solutions differs greatly from that of sea water it is not astonishing that foreign ion effects will interfere with the calculations.

3.7. EMPIRICAL ADSORPTION ISOTHERMS IN FLOODED SOILS

Due to the disturbing effects mentioned in the foregoing section, the calculation of the complicated four-ion equilibria proves to be hardly possible. The only remaining way of predicting such equilibria will be the formulation of empirical rules for the behaviour of different ions in soils flooded with sea water.

Until about 1946 all samples investigated for exchangeable cations were analysed by the "expressed fluid" method, outlined in section 1.1 and described in more detail in the Appendix. In this method the exchangeable cations of the soil are determined with the help of an analysis of the soil moisture, squeezed out at a pressure of several hundreds of atmospheres. These data allow the investigation of equilibria between the adsorbed ions and the ions in solution.

Since 1946, however, nearly all samples have been investigated by the alcohol method, by which the ionic composition of the soil moisture cannot be determined. Therefore the empirically established relations between adsorbed ions and ions in solution are based mainly upon the data gathered after the inundation periods 1939/40 and 1943. Nevertheless the cases available are numerous enough to draw conclusions about the relations between the adsorbed ions and the ions in the soil solution in flooded soils shortly after the inundation and during the regeneration period. In the following discussions these conclusions will be presented in the form of empirical adsorption isotherms.

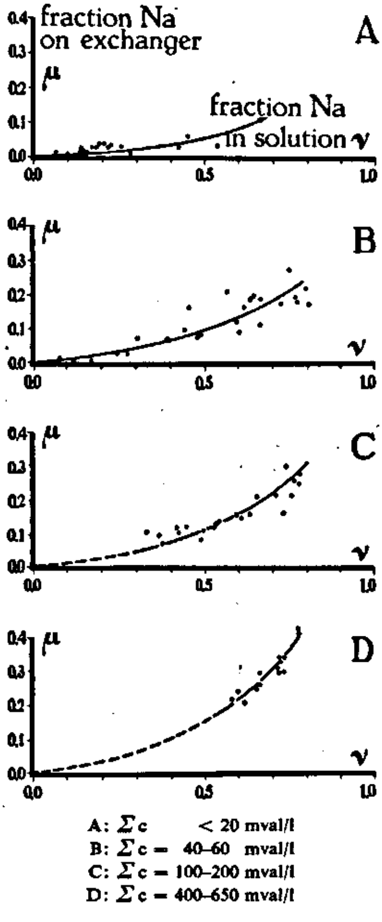

FIG. 22. Empirical Na adsorption isotherms in soils flooded with sea water

As will be shown in another treatise to be published by WESTERHOF the physical properties of flooded soils are mainly determined by the amounts of exchangeable Na, as the other ions present in excess (Mg and, to a less extent, K) cause much less deterioration of soil structure. Consequently the behaviour of the Na ions may be considered as the most important. Moreover, as will be shown in chapter 5, the only reaction occurring with noticeable speed during the regeneration of flooded soils, is the replacement of exchangeable Na by Ca; the replacement of excess K and Mg is extremely slow. In this respect also the behaviour of the Na ions deserves most attention.

The *Na adsorption isotherms* of flooded soils are reproduced in figs. 22 and 23. As appears from these diagrams the isotherms are concave, with a curvature depending on the total concentration of the solution. This concentration-dependence is due to the valency effect, as the replacing power of the principal complementary[1] ions – Mg and Ca – increases with dilution. In fig. 22 a few examples of the Na adsorption isotherms are

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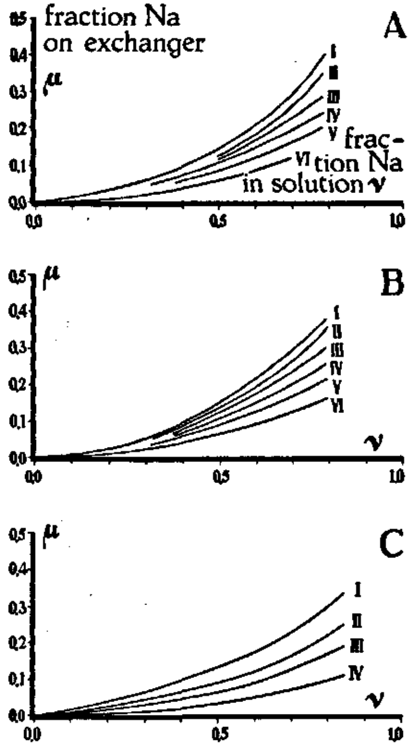
[1] C.f. footnote on page 56.



A I: $\Sigma c = 400\text{–}650$
II: $\Sigma c = 200\text{–}400$
III: $\Sigma c = 100\text{–}200$
IV: $\Sigma c = 40\text{–}100$
V: $\Sigma c = 20\text{–}40$
VI: $\Sigma c = < 20$

B I: $\Sigma c = 500$
II: $\Sigma c = 300$
III: $\Sigma c = 150$
IV: $\Sigma c = 70$
V: $\Sigma c = 30$
VI: $\Sigma c = 15$

C I: $\Sigma c = 500$
II: $\Sigma c = 150$
III: $\Sigma c = 70$
IV: $\Sigma c = 15$

A: Observed
B: Calculated from eq. (*3.23*)
C: Calculated from the Na–Ca equilibria of soil B (eq. *3.08*, *3.10* and *3.15*).

FIG. 23. Comparison of the observed Na adsorption isotherms with the empirical relation (*3.23*) and with the adsorption isotherms calculated from the Na–Ca equilibria of soil B (equations *3.08*, *3.10* and *3.15*)

given, and fig. 23 gives a synopsis of all observations. Within the range studied the empirical isotherms, pictured in fig. 23 obey the following quadratic expression (c.f. equation *2.73*):

$$\mu = 0.22\,\nu^2 \log \Sigma c \qquad (3.23)$$

in which $\mu = \frac{c_{Na}}{S}$ represents the fraction of Na among the exchangeable cations whereas $\nu = \frac{c_{Na}}{\Sigma c}$ is the corresponding fraction in the solution, Σc being the total concentration of the latter in mval/l.

The expression (*3.23*) has been tested for the range:

$$10 < \Sigma c < 650; \; \nu < 0.80$$

The empirical isotherms approximate closely to those calculated from (*3.23*) (fig. 23 A, B). Nevertheless this equation is theoretically inadequate as it does not for all values of Σc fulfill the condition:

$$\mu = 1.00 \text{ at } \nu = 1.00 \qquad (3.24)$$

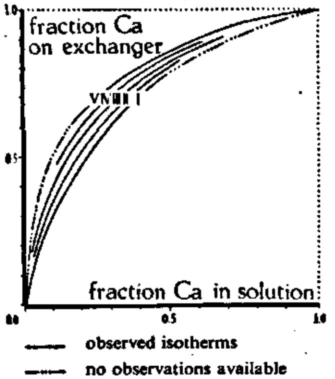
As, however, in all cases observed $\nu = \frac{c_{Na}}{\Sigma c} < 0.80$ the relation may be assumed applicable for describing the conditions prevailing in inundated soils.

In flooded soils the complementary ions K, Mg and Ca all possess a stronger replacing power than the Na ion. The K ion is quantitatively unimportant. Between Mg and Ca there is no large difference in replacing power, both ions being more strongly adsorbed than is Na.

Thus the relative amounts of complementary ions present do not exert great influence upon the Na adsorption isotherms.

If the Na adsorption isotherms described by equation (*3.23*) are compared with the pure Na-Ca equilibria treated in section 3.52 and represented by equations (*3.08*), (*3.10*) and (*3.15*), a difference is observed (fig. 27, B, C). Although the isotherms are similar in shape, less Na is adsorbed in pure Na-Ca equilibria on soil B. This difference may be explained from the fact that in flooded soils also Mg plays a prominent part; in many cases the soil solution contains more Mg than Ca, so that its replacing power for Na is lower than in pure Na-Ca equilibria.

As the quadratic relation (*3.23*) has been derived directly from analyses of flooded soils this relation is to be preferred. Moreover it is easier to handle in the mathematical treatment of column behaviour (c.f. section 2.31).



I: Σc = 200–650 mval/l
II: Σc = 60–200 mval/l
III: Σc = 40– 60 mval/l
IV: Σc = 20– 40 mval/l
V: Σc < 20 mval/l

FIG. 24. Empirical Ca adsorption isotherms in soils flooded with sea water

The *Ca adsorption isotherms* show a behaviour just opposite to that of the Na isotherms, being strongly convex (fig. 24). Due to the valency effect their curvature increases with dilution. As Ca is more strongly adsorbed than all other ions taking part in the equilibrium – with the exception of the quantitatively unimportant K ion in concentrated solutions – the relative amounts of these complementary ions will not greatly interfere with the shape of the Ca isotherms. Therefore, like those for Na, the Ca adsorption isotherms show a simple conduct, their shape being dependent only on the total ionic concentration of the solution Σc.

The *K adsorption isotherms* are more complicated. The K ion possesses a stronger replacing power than Na, but on the other hand is itself replaced by Mg and Ca, at least in equilibria with dilute solutions. Thus two effects may be expected to determine the shape of the isotherms, viz.:

1. The valency effect: adsorption of the monovalent K ions will increase with concentration.
2. Complementary ion effects: K will be strongly adsorbed from solutions in which Na is the predominating complementary ion, but much less if Mg and Ca are present in large amounts.

   It is, however, not easy to trace these effects from the available data.

Among the cations present – either as exchangeable cations or as ions in solution – K is always a minor constituent, which only seldom makes up more than 10% of the total. The analyses of the expressed fluid for K [1] were very inaccurate at low concentrations, and from the data it appears that trustworthy results have been obtained only for $\Sigma c > 100$ mval/l. At lower values for Σc the experimental errors are so large that the points indicating the relationship between adsorbed K and K in solution are widely scattered. As a consequence it is hardly possible to draw the adsorption isotherms at low concentrations.

Nevertheless, the isotherms are markedly dependent upon concentration, in accordance with the valency effect mentioned under (1) (fig. 25). It must be kept in mind, however, that for $\Sigma c < 100$ the isotherms are uncertain and are therefore shown in fig. 25 by dotted lines.

The effects of the complementary ions are difficult to assess, because noticeable variations in their proportions occurred only at low concentrations, at which levels chemical analyses were inaccurate.

The *Mg adsorption isotherms* are influenced by the valency effect as well as by the relative amounts of complementary ions present.

1. The valency effect will cause a diminishing Mg adsorption at increasing concentration of the equilibrium solution. This tendency may be expected to be most pronounced in solutions containing a high proportion of the monovalent Na ions.
2. Complementary ion effects will cause a strong adsorption of Mg from solutions – especially diluted ones – in which the weakly adsorbed Na ions predominate, whereas in equilibria with solutions rich in Ca the reverse will be true. Neglecting K it may be supposed that the slope of the Mg isotherm will depend on the Na/Ca ratio in the equilibrium solution.

As Mg is present in larger quantities than is K, the errors in analyses are less [2]. Both effects mentioned above are apparent from the empirical adsorption isotherms, reproduced in figs. 26 and 27. From fig. 26 the great influence of the Na/Ca ratio is manifest, and for solutions rich in Na the valency effect also is operative (fig. 27).

3.8. EXCHANGEABLE CATIONS IN UNFLOODED SOILS

In the area involved, dikebursts have occurred so frequently in historical times that, except for the youngest polders, it is virtually impossible to find soils which have not been flooded after their embankment.

Nevertheless it may be expected that the changes, brought about by such inundations are wiped out in the course of time and that for the topsoil this process will be almost completed in about one century. Thus in soils which have not been flooded since the beginning of the 19th century, the exchangeable cations will be subject only to very gradual changes.

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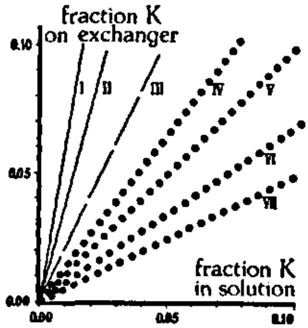
[1] The analyses of the expressed fluid were carried out before the introduction of the flame photometer in our laboratory. K was determined gravimetrically as K-cobalt-nitrite in these analyses.

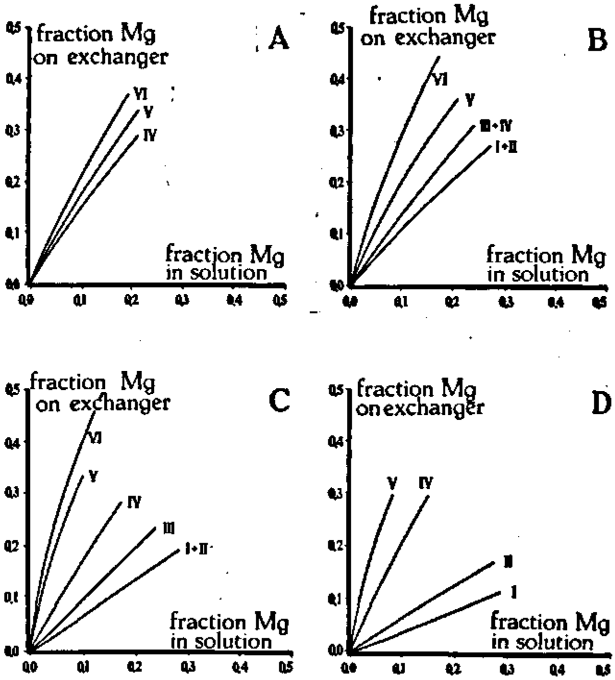
[2] Mg was estimated by gravimetric determination as Mg pyrophosphate.



I: $\Sigma c = 400\text{–}650$
II: $\Sigma c = 200\text{–}400$
III: $\Sigma c = 100\text{–}200$
IV: $\Sigma c = 60\text{–}100$
V: $\Sigma c = 40\text{–}60$
VI: $\Sigma c = 20\text{–}40$
VII: $\Sigma c = < 20$

$$\left(\frac{c_{Na}}{\Sigma c} > 0.5\right)$$

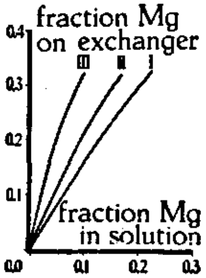
FIG. 25. Empirical K adsorption isotherms in cases where Na is the predominating complementary ion in the soil solution



I: $\left(\frac{c_{Na}}{c_{Ca}}\right)$ solution $< \frac{1}{2}$
II: $\left(\frac{c_{Na}}{c_{Ca}}\right)$ solution $\frac{1}{2}\text{– }1$
III: $\left(\frac{c_{Na}}{c_{Ca}}\right)$ solution $1\text{– }2$
IV: $\left(\frac{c_{Na}}{c_{Ca}}\right)$ solution $2\text{– }4$
V: $\left(\frac{c_{Na}}{c_{Ca}}\right)$ solution $4\text{–}10$
VI: $\left(\frac{c_{Na}}{c_{Ca}}\right)$ solution > 10

A: $\Sigma c = 400\text{–}650$ mval/l
B: $\Sigma c = 100\text{–}200$ mval/l
C: $\Sigma c = 40\text{– }60$ mval/l
D: $\Sigma c = 20\text{– }40$ mval/l

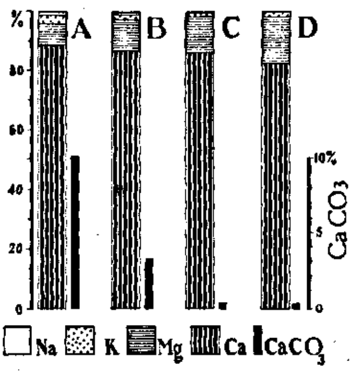
FIG. 26. Empirical Mg adsorption isotherms in soils flooded with sea water



I: $\Sigma c = 400\text{–}650$ mval/l
II: $\Sigma c = 200\text{–}400$ mval/l
III: $\Sigma c = 20\text{– }60$ mval/l

$$4 < \left(\frac{c_{Na}}{c_{Ca}}\right) \text{solution} < 10$$

FIG. 27. Empirical Mg adsorption isotherms in soils where Na is the predominating complementary ion in the soil solution



A: DN 1 New-land, age 190 years
B: Ni 1 New-land, age 300 years
C: SM 11 Middle-land creek ridge, age over 650 years
D: Kl 1 Middle-land pool soil, age over 650 years

FIG. 28. Exchangeable cations in unflooded soils. Different sampling spots; 0–20 cm depth

Of such "unflooded" soils a few analyses have been made. In these soils Ca appears to be the principal metal cation, followed by Mg and K, whereas only traces of exchangeable Na are present (fig. 28; fig. 30 A). Except for K, which becomes concentrated in the topsoil, the exchangeable cations show no systematic variation with depth (fig. 30 A, section 4.3). This concentration of K in the topsoil is attributed to the uptake of K ions by plants from the entire soil profile, but only the topsoil receives K supplies from plant residues and manuring (MASCHHAUPT, 1936).

From the investigations of unflooded soils it is also obvious that the amounts of exchangeable Mg increase at the cost of Ca as the soils grow older (fig. 28) (c.f. HISSINK, 1935). The cause of this phenomenon is still unknown, though several possibilities have been proposed.

For the gradual increase in Mg the following explanations may be given:

1. Mg is slowly liberated by weathering of clay minerals (HISSINK, 1935).
2. Mg is slowly liberated by dissolution of dolomite in the percolating rain water. As long as calcite is present this compound, which has a higher solubility than dolomite, will keep up a high proportion of Ca among the ions present in the soil solution. But if calcite becomes exhausted by the process of decalcification, Mg will become a relatively more important constituent. This higher proportion of Mg in the soil solution will also cause an increase in exchangeable Mg (BRUIN, 1938).
3. The excess Mg ions present in old soils are remnants from former inundations with sea or brackish water. In calcareous soils these excess ions will be gradually, though slowly, replaced by Ca originating from the dissolution of calcium carbonate. But in soils poor in lime this process may be too slow to bring about noticeable changes. Such a preservation of Mg is the more likely as the low permeability and bad drainage of these soils greatly reduce water-passage, without which no substantial changes in ionic composition will occur (c.f. chapter 5).
4. The excess Mg ions present in old soils are remnants from the exchangeable cations present at the time of sedimentation (VEENENBOS & VAN SCHUYLENBORGH, 1951). If this sedimentation has occurred from sea water and still the more so if the soil has been settled from brackish water, the original Mg content must have been high (MÜLLER, 1955). If, moreover, the original sediment was already non-calcareous (e.g. by decalcification during the sedimentation-period), and water-passage is low, it may be assumed that at least part of the exchangeable cations originally present, have been preserved ever since.

Additional research will be needed to distinguish between these possibilities. For our purpose, however, the picture of the exchangeable cations in unflooded soils, as given by fig. 28 and fig. 30 A, is sufficiently accurate to describe the situation prior to the inundations. An exception to this general picture is found in most pool soils belonging to the old-land. These soils nearly always have a saline subsoil, and in some cases salinity even reaches the topsoil. In such cases much larger contents of exchangeable Na and Mg may be expected than in normal soils. Though no analyses of "unflooded" soils of this kind were available, the large amounts of exchangeable Na and soluble salts found in their subsoils after an inundation clearly prove the presence of permanent salinity prior to the floodings (c.f. fig. 35 E, section 4.5).

Thus, the main properties of the soils occurring in the investigated areas have been dealt with, especially with regard to ion exchange. Whereas in simple cases, like equilibria with binary salt solutions, ion exchange may be described by the theoretical equations mentioned in chapter 2, these equations fail in describing the behaviour of more complicated systems, like flooded soils. Their inadequacy must be ascribed to mutual interference of different ionic species.

For flooded soils, however, empirical rules may be derived from experimental evidence. These rules, especially those found for the exchange of Na ions, will be frequently used in the following chapters, which will deal with ion-exchange processes occurring during and after an inundation with sea- or brackish water.

For estimating the magnitude of the changes brought about by an inundation, the ionic composition of soils should be compared before and after flooding. For this comparison, a review has been given of the ionic composition of unflooded soils. In the next chapter the changes caused by flooding will be considered.

4. CHANGES OCCURRING DURING INUNDATION

If a polder is flooded with sea water part of this water will penetrate into the soil, causing considerable changes in the composition of the soil moisture and consequently also in the distribution of the exchangeable cations. These processes will enrich the soil with Cl, Na, K and Mg ions. As column effects are operative, the changes will be usually largest in the topsoil. The correlation between exchangeable Na and Cl, found in the topsoil after drainage, is of considerable practical interest for the estimation of gypsum requirements.

In this chapter the changes caused by flooding will be treated both from a theoretical and an empirical point of view. As their magnitude depends on the amounts of penetrating water, this subject will be reviewed first.

4.1. Amounts of penetrating water

The amounts of penetrating water are dependent upon several factors, like pore space, moisture content and height of the ground-water table at the moment of flooding. Moreover, for inundations of short duration (less than a few weeks) the condition of the soil surface also plays a prominent part: freshly ploughed land appears to take up much larger amounts of water than land possessing a more closed surface, like unploughed arable land or pasture.

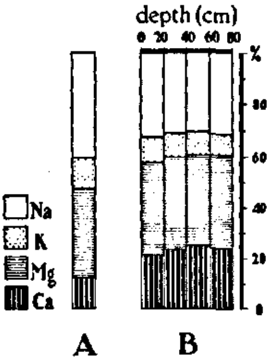
After the changes brought about by this penetration, further alterations may be caused only by diffusion, which is a rather slow process. Consequently in the soils flooded during the inundation period 1944–'45, which for the greater part remained under water for more than one year, only limited amounts of salt water could enter. Usually these amounts were of the order of 200–300 mm.

For inundations of a few weeks' duration, as were common after the stormflood of 1953, the amounts of penetrating water are still lower, and usually range from 100–200 mm, depending on the condition of the soil surface and the duration of flooding.

If, however, soils are flooded at each high tide and are drained at each low tide, much larger amounts of water will enter. Such soils were found in 1945–'46 in the polder Oost Beveland, where a large dike breach occurred. At low tide these soils, falling dry, could discharge their excess water through the existing tile drains. These soils were therefore submitted to an intense natural percolation with almost pure sea water for about 16 months.

4.2. Theoretical considerations

Soils subjected to natural percolation will soon reach complete equilibrium with the inundating water. Therefore the distribution of the exchangeable cations in such soils will readily approach the values found in the percolation experiments mentioned in section 3.61 (figs. 19 and 20). This complete equilibrium will not only be set up in the topsoil, but also in all deeper layers which are reached by the percolating water. In the polder Oost Beveland this has been the case in all layers sampled. Throughout the profile, up to a depth of 80 cm, the ionic distribution found after the inundation closely resembled that observed in laboratory percolation experiments with sea water (fig. 29).



A. Laboratory percolation experiment with a heavy new-land soil (table 20, section 3.6).

B. Sampling spot OB 13, polder Oost Beveland, after natural percolation for about 16 months.

FIG. 29. Ionic composition of soils after artificial and natural percolation with sea water

In the laboratory experiments, the amounts of exchangeable Na are slightly higher and those of exchangeable Ca slightly lower than in the polder Oost Beveland; this difference may be caused by a difference in flow rate. In the laboratory experiments this flow rate is high compared with the streaming velocity under natural conditions. Consequently, in these calcareous soils, dissolution of $CaCO_3$ in the percolating sea water might play a more prominent part in nature, increasing the content of exchangeable Ca at the expense of Na. As the dissolution of $CaCO_3$ increases with depth it may be expected that the deviations from the laboratory experiments will also increase with depth. Another explanation might be that even in the polder Oost Beveland full equilibrium with sea water was not yet entirely reached.

Apart from this simple, though exceptional case of natural percolation the theoretical treatment of the exchange processes during an inundation is very complicated, even virtually impossible. This is due to several complications viz.:

1. Even in the top layers the penetrating amounts of sea water are insufficient to establish full equilibrium. Consequently equilibria of this kind may only be described by empirical rules, like those formulated in section 3.7.
2. During the penetration of the water, column effects will be operative. But the high flow rate occurring during the penetration of the flooding water may be expected to cause considerable streaming irregularities, which will prevent a normal column performance. Especially in heavy soils part of the penetrating water may rapidly pass downward through existing fissures, without reaching equilibrium with the soil moisture in the bypassed layers [1].
3. During the process strongly adsorbed Ca ions will be replaced by less strongly

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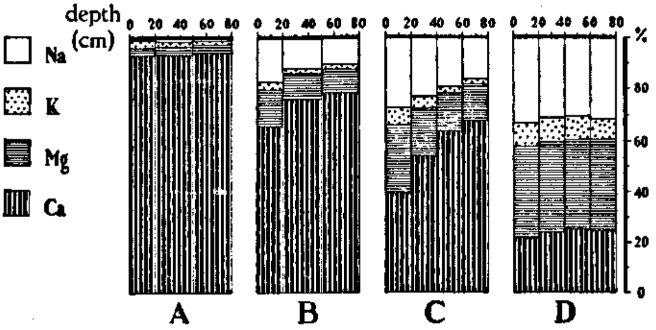
[1] A typical example of this effect was observed by WESTERHOF immediately after an inundation of short duration in 1953: the groundwater which accumulated in a newly dug-out hole was found to possess a higher salt concentration than the moisture in the surrounding soil.

adsorbed Na and Mg ions. In this case the rear boundary of Ca, and consequently also the front boundaries of Na and Mg, will become diffuse, even in the ideal case of zero theoretical plate thickness (section 2.31). This diffuse character will be accentuated by the streaming irregulaties mentioned under (2) and by lateral diffusion in the soil solution. Thus far no theoretical description of the phenomena occurring under these circumstances is available.

In view of the above complications, a rigid theoretical treatment of the exchange processes occurring during an inundation is virtually impossible, but some general rules may be derived from the field observations. In the next section these observations will be shortly reviewed, after which the behaviour of the Na and Cl ions will be more closely examinated, both from an experimental and a semitheoretical point of view.

4.3. EXCHANGEABLE CATIONS AFTER AN INUNDATION; GENERAL ASPECTS

Immediately after the floodings of 1943, 1944–'45 and 1953 some soil profiles were sampled and analysed for exchangeable cations. As the ionic composition of normal soils is well known (section 3.8) the changes brought about by the penetration of the inundating water could be derived from these investigations.



A. Sampling spot WP 17a; polder Wilhelmina, not inundated
B. Sampling spot WP 29, polder Wilhelmina, after an inundation of short duration (about 2 weeks)
C. Sampling spot J 1, polder Jonge, after prolonged inundation (about 1 year)
D. Sampling spot OB 13, polder Oost Beveland, after natural percolation with sea water for about 16 months

FIG. 30. Ionic composition of new-land soils before and after inundation with sea water

Some examples of ionic distributions in soils sampled immediately after being flooded with sea water, are given in fig. 30. For comparison the ionic composition of a comparable unflooded soil has been included (fig. 30, A). As appears from fig. 30 the amounts of exchangeable Na, K, and Mg have been considerably increased during the inundation, at the cost of the exchangeable Ca. The magnitude of these changes depends on the duration of the floodings or – which for this case comes to the same – on the amounts of sea water penetrated into the soil (fig. 30, B, C). Moreover, in these cases, the changes are greatest in the topsoil and gradually decrease with depth. This indicates that column effects play a prominent part during the penetration of the sea water.

Finally, in the limiting case of natural percolation with sea water, in which very large amounts of sea water have entered into the soil, the ionic composition of all layers sampled has become uniform again (fig. 30, D) and will approach full equilibrium with sea water (c.f. fig. 29, section 4.2). Moreover in this case the changes are much larger than in normal inundations, even if the latter have extended for over a year.

If the soils have been flooded with brackish water instead of sea water, the changes in their ionic composition may be expected to be less. For Na and K this will already be the case if the soil reaches full equilibrium with the inundating water, but on the other hand a higher proportion of exchangeable Mg may be expected in brackish water equilibria (c.f. the laboratory experiments described in section 3.61).

Such full equilibria with brackish water however were not established during the inundations investigated, as a brackish-water equivalent of the polder Oost Beveland was lacking. Nevertheless these full equilibria may be studied by analysis of soils from outmarshes or from estuary bottoms in brackish-water regions. The few available analyses from these soils have been mentioned in table 28.

TABLE 28. Ionic composition of soils being in natural equilibrium with sea water and brackish water (soils of outmarshes and estuary bottoms).

Sampling locality	Salinity of the water C[1]	Exchangeable cations %			
		Na	K	Mg	Ca
Brakman	≌ 25	31.7	7.7	36.0	24.6
Ooltgensplaat	≌ 11	25.2	6.5	37.8	30.5
Hellegat	≌ 6	18.2	5.4	29.6	46.8
Zuiderzee-bottom	≌ 4	13.8	6.6	42.8	36.8
Hellegat	≌ 3	14.5	4.4	29.4	51.7

[1] Content of Cl ions, calculated as NaCl (g/l).

From this table the same general trends may be observed as those appearing from the laboratory experiments mentioned in section 3.61, viz.:

1. The percentages of exchangeable Na and K decrease at decreasing salinity of the water.
2. At least in some cases the percentages of exchangeable Mg have the tendency to increase with decreasing salinity. Other cases, however, are not in accordance with this generalization.
3. The percentages of exchangeable Ca show a marked increase at decreasing salinity. This effect is due not only to the bivalent character of this ion, but also to the relatively higher Ca content of brackish water as compared with sea water (c.f. fig. 20, section 3.61).

In most inundations with brackish water only limited amounts, and of low ionic concentration, penetrate the soil, so that the amount of exchangeable Na found in the soil is lower than that found after sea water inundations. Likewise for Mg, the amount of ions entering the soil is not enough to reach the high values of exchangeable Mg found in soils in full equilibrium with brackish water. Consequently differences in ionic composition between flooded and unflooded soils will become less and less marked as the salinity of the flood water decreases (table 29).

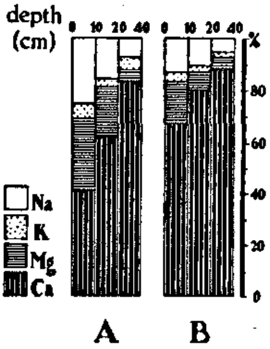
TABLE 29. Ionic composition of soils inundated for about a year with water of different salinity.

Sampling spot	Depth cm	Salinity of flooding water C[1]	Exchangeable cations %			
			Na	K	Mg	Ca
J 1	0–20	≌ 25	27.0	6.4	26.6	40.0
AG 7	0–20	≌ 25	20.4	6.3	25.2	48.1
OT 2	0–20	≌ 22	20.4	4.6	23.5	51.5
GT 33	0–20	≌ 11	9.6	4.0	18.2	68.2
AG 11	0–20	≌ 7	8.6	3.2	16.2	72.0
DN 1	0–20	≌ 0[2]	1.0	3.5	4.9	90.6

[1] Average Cl content during the summer of 1944, calculated as NaCl. (g/l).

[2] Inundated with fresh water for a short period.

As in sea water inundations, column effects play a prominent part, as appears from the distribution of the exchangeable cations over the soil profile: near the soil surface the changes in ionic composition are much larger than in deeper layers (fig. 31).



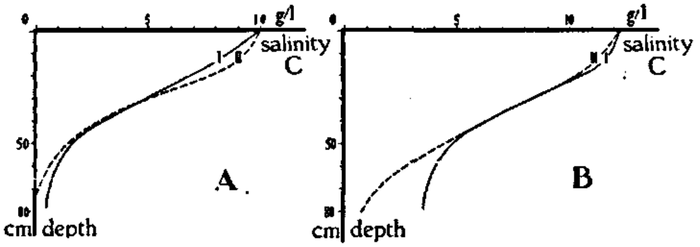
A. Sampling spot OT 2, polder Oude Tonge; salinity C of flood water ± 22 g/l
B. Sampling spot NS 1, polder Nieuwe Stad; salinity C of flood water ± 5 g/l

FIG. 31. Ionic composition of soils after inundation with brackish water

4.4. BEHAVIOUR OF CL AND NA IONS DURING AN INUNDATION

In addition to the general aspects of the exchange processes described in the foregoing section, the behaviour of the Cl and Na ions will be treated in more detail. Both ions are virtually absent in normal soils. Moreover their adsorptive behaviour is well known, Cl being not adsorbed by the soil particles, Na obeying the empirical adsorption equation (*3.23*) mentioned in section 3.7.

The Cl ions may serve as an indicator for the column processes during the penetration of the inundating water. If all this water could rapidly penetrate into the soil and subsequently mix with the soil moisture already present, uniform distribution of the Cl ions would be set up. If, on the other hand the penetrating water mixed with the soil moisture during its downward movement, the Cl content of the soil would decrease with depth. Observations indicate the predominance of the second process. Therefore, as appears from fig. 32, the distribution of the Cl ions found immediately after an inundation may be fairly well described by the theory of column performance treated in section 2.31 (equation *2.60*).



I: observed
II: calculated with 2 k = 11 cm

I: observed
II: calculated with 2 k = 15 cm

A: Sampling spot St 22, polder Den Bommel (light soil)
B: Sampling spot St 5, polder Grijpland (heavy soil)

FIG. 32. Observed and calculated salinity-depth curves immediately after an inundation of short duration (1953)

A direct application of the column theory to the penetration processes meets with difficulties as the moisture content of the soil varies greatly during the inundation. If the inundation takes place in winter the initial moisture content of the soil will not be far from field capacity. During the inundation, however, the soil will be near to saturation with water. After drainage of the flooded soil field capacity is usually reached again within a few days, provided that the drainage system has remained intact. These changes in moisture content – and consequently also in the liquid-filled pore-space α – will prevent a direct application of the theory. Nevertheless good results are obtained by supposing the entire process to proceed at field capacity (fig. 32, A). From the available observations – most of which were gathered after inundations of short duration in 1953 – the theoretical plate thickness of the soils, calculated from equation (*2.68*), was found to be of the order of 10–15 cm. This value is 2–3 times higher than that found from the desalinization of a saline soil under the influence of rainfall (VAN DER MOLEN, 1956); undoubtedly this divergence is caused by streaming irregularities during the rapid penetration of the inundating water. Moreover, especially in heavy soils, the Cl content of deeper layers, found after the inundation, is higher than may be expected from the column theory (fig. 32 B). This effect must be ascribed to rapid passage of part of the penetrating water through existing fissures.

The Na ions will accompany the Cl ions in their penetration into the soil. In sea water – and in brackish water as well – the numbers of both ions are approximately equal, the equivalent ratio Na/Cl being about 0.9–1.0. In the soil, however, many of the invading Na ions will readily enter into exchange reactions. Consequently the ratio $\delta = \frac{\Sigma \text{Na}}{\Sigma \text{Cl}}$ found in the topsoil after an inundation should be higher than in the inundating water. For reasons of balance the reverse should be true in the subsoil (table 30).

Table 30. Amounts of Na and Cl present in soils immediately after a short inundation with sea water (1943).

Sampling spot	Depth cm	mval/100 g of soil		$\delta = \frac{\Sigma \text{Na}}{\Sigma \text{Cl}}$
		ΣNa[2]	ΣCl[2]	
Sea water	—	—	—	0.9–1.0
WP 9[1]	0– 5	10.9	8.0	1.4
	5–20	7.3	5.8	1.3
	20–50	5.1	5.0	1.0
	50–80	3.5	3.9	0.9
WP 29[1]	0– 5	8.8	8.4	1.1
	5–20	6.6	6.7	1.0
	20–50	3.4	3.9	0.9
	50–80	2.4	2.9	0.8

[1] Light soils.

[2] ΣNa and ΣCl denote the total amounts (exchangeable + water-soluble) of both ions present in the soil (mval/100 g).

Apart from this distinct, but slight shift in the Na/Cl ratios, the behaviour of both ions appears to be rather similar: due to column effects both Na and Cl strongly decrease with depth. This similarity is not as surprising at it looks at first sight: upon closer examination it appears that in these soils the majority of the Na ions present – roughly 2/3 of the total – exist in solution, hence the influence of the adsorbed ions is relatively small.

The distribution of the total amount of Na ions – ΣNa – over the soil solution and the exchange seats, already touched upon, is rather complicated. It may be investigated by using the Na adsorption isotherms expressed by the empirical equation (*3.23*). According to this equation:

$$\mu = 0.22\, \nu^2 \log \Sigma c \qquad (4.01)$$

in which the μ and ν refer to the fractions of Na ions among the adsorbed ions and the ions in solution respectively. Consequently

$$\nu = \left[\frac{c_{\text{Na}}}{\Sigma c}\right]_{\text{solution}} \qquad (4.02)$$

whereas, if the sum of the exchangeable metal cations S is expressed as mval per 100 g of dry matter (S_s), the amount of exchangeable Na, expressed as mval per 100 g of dry matter (Na_s), may be derived from:

$$Na_s = \mu \,.\, S_s = 0.22\, S_s \,.\, \nu^2 \,.\, \log \Sigma c \qquad (4.03)$$

If the moisture content of the soil is A ml per 100 g of dry matter, the amount of Na ions in solution per 100 g of dry matter will obviously be equal to:

$$Na_{sol} = \frac{A}{1000}\left[c_{\text{Na}}\right]_{sol} = \frac{A \,.\, \nu \,.\, \Sigma c}{1000} \qquad (4.04)$$

The total amount of Na, present per 100 g of dry matter will be:

$$\Sigma \text{Na} = Na_s + Na_{sol} = 0.22\, S_s\, \nu^2 \log \Sigma c + \frac{A \,.\, \nu \,.\, \Sigma c}{1000} \qquad (4.05)$$

The fraction of the Na ions present in the adsorbed state, φ_{Na}, may be expressed by:

$$\varphi_{Na} = \frac{Na_s}{\Sigma Na} = \frac{1}{1 + \frac{A}{220\, S_s \,.\, \nu} \cdot \frac{\Sigma c}{\log \Sigma c}} \qquad (4.06)$$

This equation will determine the distribution of the ions between the adsorber and the solution. In a soil profile φ_{Na} may either increase or decrease with depth, depending on the variations of the quantities A, S_s, ν and Σc. The fraction φ_{Na} wil be increased by an increase in S_s and ν and decreased by an increase in A and Σc (at least for the values of Σc normally occurring in soils after flooding with sea water).

Some tests of equation (*4.06*) have been reproduced in table 31, which shows that the calculated values of φ_{Na} are in close agreement with the values directly observed. The data from table 31 clearly illustrate the mutual relations between the different factors governing the Na distribution between the exchanger and the soil solution, although they only prove that the equation (*4.01*) is closely obeyed in this case.

TABLE 31. Calculated and observed values for φ_{Na}, immediately after inundation with sea water (1943).

Sampling spot	Depth cm	A ml/100 g	S_s mval/100g	ν	Σc mval/l	φ_{Na}	
						calculated	observed
WP 9	0– 5	23.8	15.8	0.651	460	0.36	0.35
	5–20	22.8	16.0	0.591	336	0.41	0.39
	20–50	21.9	13.4	0.536	277	0.39	0.36
	50–80	23.9	10.3	0.456	210	0.32	0.34
WP 29	0– 5	22.8	12.7	0.618	448	0.31	0.28
	5–20	21.9	12.6	0.562	382	0.33	0.29
	20–50	22.2	10.7	0.482	219	0.35	0.32
	50–80	24.5	9.6	0.421	151	0.34	0.33

The soils mentioned in table 31 are light-textured new-land soils, but they may be taken as representative of the creek-ridge soils as well. As in nearly all creek-ridge and new-land soils in the area, their clay- and humus-contents decrease with depth. Consequently their amounts of exchangeable metal cations S_s, which in these calcareous soils are approximately equal to their adsorptive capacity U_s, will also decrease with depth. On the other hand, the moisture contents A are rather uniform throughout the profile: although at greater depth the lighter soil texture tends to reduce the moisture capacity, this effect is counterbalanced by the increasing proximity of the ground-water table.

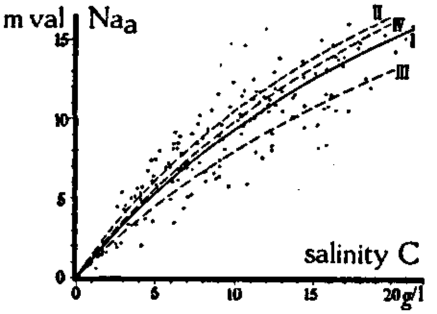
During the penetration of the sea water into the soil part of its Na ions have been exchanged against Ca ions. Therefore a gradual decrease in the fraction of Na amongst the ions in solution, ν, is found at greater depths. Finally also the total ionic concentration of the soil moisture, Σc, will fall as the penetrating water has mixed with the non-saline soil moisture initially present.

The decrease of S_s and ν will tend to decrease the value of φ_{Na}, but this effect appears to be roughly compensated by the simultaneous decrease in Σc. Hence, in the profiles examined, φ_{Na} is rather uniformly distributed; only in WP 29 a slight increase with depth was observed.

4.5. RELATIONS BETWEEN EXCHANGEABLE NA AND SALINITY

Hitherto the distributions of the Na and Cl ions have been mainly examined on their own merits. In this section, the mutual relations between adsorbed Na and Cl will be more closely studied.

In the topsoil a correlation has been found between the Cl concentration in the soil moisture and the amounts of exchangeable Na immediately after an inundation (VAN DEN BERG & WESTERHOF, 1954). This correlation is of great practical importance as measurements of Cl-ion concentrations may be easily and rapidly made by means of electrometric methods (VERHOEVEN, 1953), whereas determination of exchangeable Na in flooded soils, even with modern equipment, requires much more effort. Moreover, after an inundation large numbers of soil samples use to be analysed for Cl concentration to choose suitable crops. Thanks to the correlation mentioned above, these salinity data may be used for estimating the content of exchangeable Na, from which the gypsum requirement of the soils in question may be calculated (section 6.63).



I: observed average
II–IV: calculated from eq. (*4.11*) and (*4.07*)
II: light soil with A = 25; S_a = 65; q = 19; δ = 1.2
III: heavy soil with A = 40; S_a = 65; q = 48; δ = 1.2
IV: like III, but with δ = 1.4.

FIG. 33. Relation between salinity C and exchangeable Na (mval per 100 g of active matter) in the topsoils of flooded soils immediately after their drainage. Soils flooded in 1953, 0–20 cm depth

For the inundations of 1944–'45 only a few data are available, but after the inundations of 1953 the correlation between salinity and exchangeable Na has been extensively investigated. In fig. 33 an example is given of the correlation between salinity and Na content for the topsoils in the northern part of the area flooded in 1953, and for the subsoils the same correlation is represented in fig. 34.

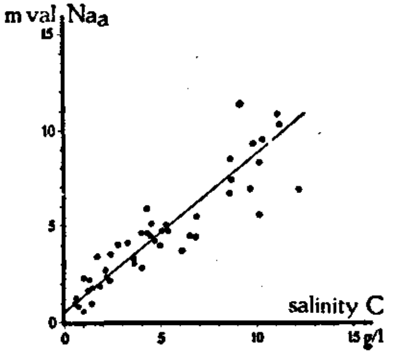
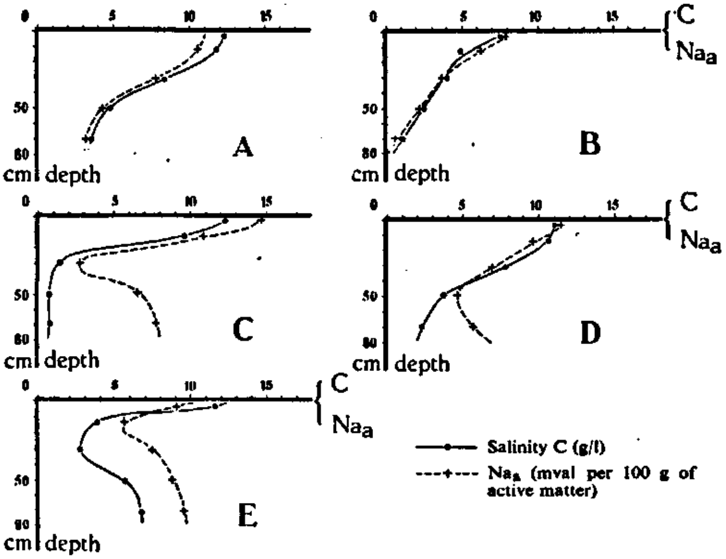


FIG. 34. Relation between salinity C and exchangeable Na (mval per 100 g of active matter) in the subsoils of flooded soils immediately after drainage. Soils flooded in 1953, 40–60 cm depth. Soils flooded earlier in this century and pool soils with permanently saline subsoils not included

In these figures the salinity is, in the usual way, denoted as Cl concentration in the soil moisture, expressed as g/l of NaCl (C-figures). The Na content of the soil is expressed as mval of exchangeable Na per 100 g of active matter (Na$_a$). For $C < 10$ both quantities are approximately equal; above this value the exchangeable Na content lags behind the salinity-figure.

Remarkably enough nearly the same relation as found in the topsoil, appears to be valid for the subsoil (fig. 34), so that, in a given soil profile there exists a striking parallelism between the salinity-depth and Na$_a$-depth curves (fig. 35, A, B). An exception to this rule is found in soils which have been flooded twice; in such soils part of the exchangeable Na left behind by the first inundation may still be present in the subsoil at the moment of the second inundation (fig. 35, C, D). Finally, many old-land pool soils have permanently saline subsoils; in these cases high Na contents may be present in deeper layers, which are not caused by any inundation, but by *permanent salinity. In these cases, however, also a certain parallelism between salt* content and Na$_a$ may be observed (fig. 35, E).



A, B: normal soils

C, D: soils, also subjected to inundation in 1944–'45

E: old pool soil with permanently saline subsoil

FIG. 35. Relations of salinity C and exchangeable Na with depth immediately after the floods of 1953

As follows from the preceding sections the correlations mentioned above cannot be caused by a simple and directly working mechanism, as the adsorption of Na ions is dependent upon several factors. But the combined effects of these factors in the soils investigated are such that a useful relation is obtained.

Theoretically the Na adsorption isotherms, given by equation (*4.03*) should be obeyed. In order to obtain the amount of exchangeable Na in mval per 100 g of active matter (Na$_a$) the sum of metal cations adsorbed should be also expressed in the same unit (S$_a$).

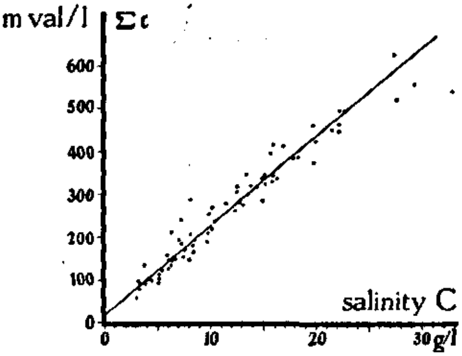


FIG. 36. Relation between salinity C and total ionic concentration of the soil moisture Σc in flooded soils

Hence: $$Na_a = 0.22\, S_s \,.\, \nu^2 \,.\, \log \Sigma c \qquad (4.07)$$

In this equation S_a is approximately 65 for the topsoil of calcareous profiles, becoming slightly higher at greater depth (section 3.4). In flooded soils the value of the total ionic concentration of the soil solution – Σc – is highly correlated with soil salinity C, as appears from fig. 36. This narrow relation is caused by the predominant position of the Cl ion among the anions of the solution, the former usually making up more than 75 per cent of the total.

The only quantity still unknown is ν, the fraction of Na ions among the cations in the soil solution [1]. However, this quantity may be derived by using equation (*4.05*), which may be regarded as a quadratic in ν:

$$0.22\, S_s \,.\, \log \Sigma c \,.\, \nu^2 + \frac{A \,.\, \Sigma c}{1000}\,\nu - \Sigma Na = 0 \qquad (4.08)$$

Of the quantities occurring in this equation Σc is known from its correlation with C whereas S_s may be estimated from the active matter percentage of the soil – q – and the adsorptive capacity of the active matter S_a:

$$S_s = \frac{q}{100}\, S_a$$

Finally Σ Na may be evaluated from:

$$\Sigma Na = \delta \,.\, \Sigma Cl = \delta \,.\, \frac{AC}{58.5} \qquad (4.10)$$

in which, according to table 30, δ is approximately 1.2 for the topsoil and 0.8 for the subsoil. Hence, equation (*4.08*) may be written as:

$$0.0022\, q \,.\, S_a \,.\, \log \Sigma c \,.\, \nu^2 + \frac{A \,.\, \Sigma c}{1000}\,\nu - \frac{\delta\, AC}{58.5} = 0 \qquad (4.11)$$

from which ν – and consequently, by means of equation (*4.07*), also Na_a – may be calculated. Of course many uncertainties are involved in estimating different constants and especially the ratio δ, for which only a few reliable observations are available.

Using the equations (*4.11*) and (*4.07*) the relation between Na_a and C has been calculated for the following topsoils:

1. A light topsoil with A = 25 and q = 19%.
2. A heavy topsoil with A = 40 and q = 48%.

In both cases S_a was estimated at 65 mval, δ at 1.2. The relations obtained in both cases have been indicated in fig. 33 by curves II and III. Both appear to be in general accordance with the observations, though the curve for the heavy soil is somewhat low.

The difference between light and heavy soils suggested by the calculated curves II and III in fig. 33 is not found in practice: upon closer examination of the data represented in fig. 33 no systematic variations of the Na_a-C relation with soil texture appear to exist. This divergence between theory and observations may be easily accounted for by assuming that the value of the ratio δ will be higher for the topsoil of heavy soils. If, for instance, the value of δ for the heavy soil is raised from 1.2 to 1.4 curve IV is obtained, which nearly coincides with the curve for the light soil with δ = 1.2. Though no reliable values for δ are available for heavy soils, it may be reasonably supposed that this quantity, which is differing from unity through exchange processes, will be larger for the topsoils of heavy profiles, where these processes will be more pronounced than in the light soils mentioned in table 30.

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[1] Direct observation of ν is possible by analysis of the expressed fluid. After the inundations of 1953, however, all samples were analyzed by the alcohol method.

The same theory may be used for calculating the values of Na_a in a profile with known salinity C, moisture content A and content of active matter q. In this case, however, the systematic changes in S_a and δ with depth should be taken into consideration. As both are not determined in the ordinary analyses on exchangeable Na and salinity[1] estimation of these quantities will be necessary. As a matter of fact this estimation of S_a and δ at various depths will introduce new errors, which will increase the uncertainty of the results.

A few results of such calculation are shown in table 32.

TABLE 32. Calculated and observed values for Na_a, immediately after inundation with sea water (1953).

Sampling spot	Depth cm	A ml/100 g	Salinity C g/l	Active matter q %	Σc mval/l	S_a mval per 100 g of active matter	δ	ν	Na_a mval per 100 g of active matter	
		obs.	obs.	obs.	est. [1]	est.	est.	calc. [2]	calc [3]	obs.
St 5	0–20	35.1	12.0	36.5	265	65	1.2	0.54	10.3	10.6
	20–40	32.9	8.3	35.0	190	67	1.1	0.45	6.7	7.9
	40–60	32.5	4.7	28.8	115	70	0.9	0.34	3.7	4.2
	60–80	35.1	3.6	24.8	95	75	0.8	0.30	3.0	3.3
St 14	0– 5	38.4	10.0	31.8	225	65	1.3	0.58	11.3	10.3
	5–20	40.9	4.9	32.5	120	65	1.2	0.45	5.9	7.4
	20–40	33.1	2.3	21.1	65	67	1.0	0.33	2.8	4.1
	40–60	31.1	1.0	16.7	40	70	0.9	0.22	1.2	2.3
	60–80	32.0	0.5	17.3	35	75	0.8	0.13	0.4	1.0

[1] Estimated from the relation given in fig. 36.

[2] Calculated by equation (*4.11*).

[3] Calculated by equation (*4.07*).

As is apparent from table 32 the values for Na_a rapidly decrease with depth. Although the calculated values are slightly too low in general, they predict the order of magnitude of the exchangeable Na contents. Moreover the calculations give a qualitative if not quantitative explanation of the remarkable parallelism between Na_a and C mentioned earlier in this section (c.f. fig. 35).

Thus, the ionic distributions occurring immediately after an inundation, have been treated both from an experimental and from a theoretical point of view. Although a rigid theoretical treatment of the processes involved appeared impossible, the rules, established from the observations, could qualitatively at least be explained by the theory. The ionic distributions occurring after different types of inundations with waters of different salinity have been investigated (fig. 30, table 29); the distributions of the Cl and Na ions and their mutual relationships have been treated in more detail. Especially the correlation between the amounts of exchangeable Na – Na_a – and salinity C in the topsoil is of practical importance (fig. 33).

After drainage of flooded soils changes in the ionic distributions occur, resulting in a slow natural recovery. These changes will be treated in the next chapter.

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[1] Recently determination of the adsorptive capacity of the soil, S_a, has been introduced as routine analysis, replacing the former determinations of active matter content.

5. NATURAL REGENERATION

After the drainage of a flooded polder the saline soils, which possess large amounts of soluble salts and high percentages of exchangeable Na, K and Mg, will become exposed to climatic influences. In the moist Dutch climate annual precipitation averages about 700 mm, of which some 200 mm will actually pass through well-drained soils, almost exclusively during the winter months (VERHOEVEN, 1952).

Under these conditions the soluble salts are readily washed out by the percolating water. But the excess amounts of exchangeable Na, K and Mg are only slowly removed. Of these ions Na especially may be regarded as responsible for the breakdown of soil structure which occurs after removal of the bulk of the soluble salts.

In the first observations on the behaviour of flooded soils, mentioned in section 1.1, it was already noticed that bad soil structure may persist for many years. Nevertheless, natural recovery, though slow, does take place, as slow changes in ionic composition of the soil occur after drainage. Such changes have been extensively investigated after the inundations of 1939–'40, 1943, 1944–'45 and 1953. Similar changes in ionic composition were found by KELLEY (1951) after leaching a black alkali soil with irrigation water.

In the following sections some theoretical aspects of this regeneration – including the different reactions involved – will be treated first. These theoretical aspects will be followed by a general and qualitative review of the observed changes in ionic composition, after which the regeneration processes will be treated more thoroughly and from a more quantitative point of view.

5.1. THEORETICAL CONSIDERATIONS

The changes in ionic composition, occurring after drainage, may be caused by the following processes:

1. Concentration-changes in the soil solution.
2. Hydrolysis.
3. Reaction with water containing carbon dioxide.
4. Reaction with dissolved calcium carbonate.
5. Reaction with dissolved gypsum.
6. Reaction with other dissolving Ca compounds.
7. Uptake of ions by plant roots.

Contrary to newly embanked slik soils, gypsum is no natural constituent of flooded polder soils [1]. Therefore the discussion of process 5 will be postponed until chapter 6, where it will be treated in more detail.

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[1] An exception is formed by soils which are covered by young mud during the inundation. After drainage oxidation of this mud will result in gypsum-formation.

As will be shown in section 5.3, process 4 is the main cause of natural regeneration of calcareous flooded soils.

On closer examination of the reactions mentioned above it becomes clear that they will only lead to slight shifts in the ionic composition of the soil unless discharge of the reaction products is possible (c.f. section 5.3). In other words, none of these processes is able to bring about noticeable results by local action alone; only in combination with water passage are further changes possible.

It stands to reason that under these circumstances column effects will play a prominent part. Application of the column theory will be more satisfactory than in the case of a sudden inundation with sea water treated in chapter 4, as the flow rate during the regeneration period will be much lower – at most of the order of 2 cu.cm per sq.cm per 24 hrs. or 20 cu.cm per sq.cm annually. Consequently streaming irregularities will be less pronounced [1].

Application of the column theory to the removal of Cl ions from saline soils has shown that it gives a fair description of the phenomena observed (VAN DER MOLEN, 1956). The theoretical plate thickness – 2 k – was found to be of the order of 5 cm, a value about twice as low as that found for the penetration of sea water during an inundation (section 4.4). This lower value for 2 k indicates a better column performance during the regeneration-period.

In heavy soils the presence of fissures acts as a disturbing factor. As part of the water is rapidly passing through these fissures without reaching equilibrium with the bypassed layers, the efficiency of the leaching process is reduced.

During the regeneration-period the Na, K and Mg ions are replaced by the more strongly adsorbed Ca ions. Hence the adsorption isotherms of the former – and especially those for Na – will be concave. As has been pointed out in section 2.31 this will result in a rear boundary of constant shape, travelling through the column at a rate, proportional to the streaming velocity (c.f. equations *2.75* and *2.78*, section 2.31).

Due to the self-sharpening tendency of these rear boundaries the latter will become sharper than those for ions possessing a linear isotherm – e.g. the Cl ions. Some evidence of this fundamental difference in shape between Na and Cl boundaries has been found in the field (fig. 42, section 5.2).

In the soil profile a separation of different kinds of ions occurs which is analogous to the separation in an exchange column. Ions which are not adsorbed – e.g. Cl. – will be readily washed out, whereas ions held by adsorption may be expected to leave the column in the order of their adsorption affinity, when the column is leached with a dilute solution of foreign ions.

Such separations may be easily demonstrated by laboratory experiments. As an example the following model experiment was carried out: The lower half of a percolation tube was filled with a Ca-saturated clay, and the upper half with a flooded clay soil containing high amounts of exchangeable Na, K and Mg, but from which the soluble salts had been washed out with alcohol. To promote water passage both clays were mixed with quartz sand, in a ratio of 1 : 7.

The column, thus prepared, was percolated with a dilute solution of $CaCl_2$ (0.02 n); the effluent was collected in 10 ml aliquots, which were analyzed for Na and K by means of a flame

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[1] The existence of such irregularities has been demonstrated by VERHOEVEN (1953). Their effects may be largely eliminated by an adequate technique of sampling, including the composition of soil samples from many (usually 16) separate borings.

photometer. The analytical methods for Mg are much less sensitive than those for Na and K, but semi-quantitative estimation of Mg with eriochrome black – after precipitation of Ca as oxalate – allowed discrimination of the classes: absent, trace, distinct and maximal. Assuming the Mg-ratios in these classes to be as 0 : 1 : 2 : 3 and bearing in mind that the total amount of Mg found in the effluent should be equal to the amount of exchangeable Mg originally present in the flooded soil, these data could be transformed into semi-quantitative results.

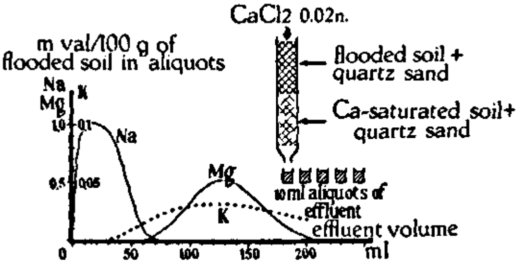


FIG. 37. Ionic separation in a soil column

The break-through curves of Na, K and Mg found in this way are shown in fig. 37. The maxima of these curves appear in the order Na-K-Mg, and the separation of Na from Mg is virtually complete.

Some such ionic separations have been observed in the field, though full development of ionic boundaries in the topsoil is prevented by tillage operations, and the period of observation has not been long enough to establish such boundaries in the subsoil. Moreover, in the subsoil the usual decrease of clay content with depth will act as a disturbing factor. So the possibilities for testing the theory of column operation by comparison with field data are only limited. Nevertheless this theory, and especially equations (*2.77*) and (*2.78*), section 2.31, may serve as a means of estimating the velocity of the different processes occurring during the regeneration period. Before discussing this quantitative aspect of these processes, the general aspects of regeneration as observed in the field, will be shortly reviewed.

5.2. GENERAL ASPECTS

After the floodings of 1943, 1944–'45 and 1953 fixed sampling spots and plots of gypsum trial fields have been periodically sampled for analysis on exchangeable cations. Some of these spots – especially the controls of gypsum trial fields – did not receive any special treatment for improving soil structure, and for this reason they are particularly suited for studying natural regeneration.

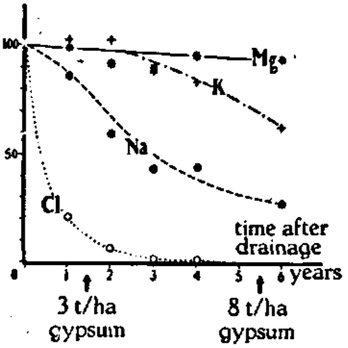
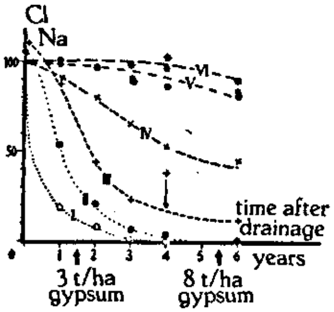


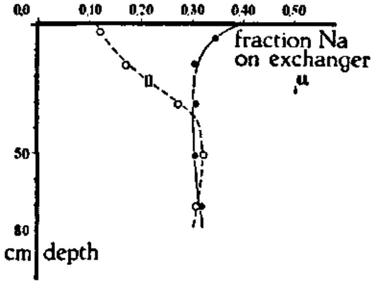
FIG. 38. Relative decrements of Cl and exchangeable Na, K and Mg in the upper 20 cm of a heavy soil. Sampling spot OB 13, polder Oost Beveland. Initial amounts put at 100



I: Cl 0–10 cm
II: Cl 60–80 cm
III: Na 0–10 cm
IV: Na 10–20 cm
V: Na 20–40 cm
VI: Na 40–80 cm

FIG. 39. Relative decrements of Cl and exchangeable Na at different depths. Sampling spot OB 13, polder Oost Beveland.
Average initial Cl content and average initial Na percentage put at 100

As had already been stated in section 5.1, this natural regeneration is characterized by a rapid decrease in soluble salts, a slow decrease in exchangeable Na and a still slower reduction of exchangeable K and Mg. In the soil profile all these processes proceed from top to bottom. As an example of these changes the relative decrements of Cl and of exchangeable Na, K and Mg ions on the sampling spot OB 13 have been represented in figs. 38, 39, and 40.



I: 1946, immediately after drainage
II: 1950

FIG. 40. Relation between exchangeable Na fraction μ and depth. Sampling spot OB 13, Polder Oost Beveland

The sampling spot OB 13, lying in the polder Oost Beveland, had been subjected to natural percolation with sea water for about 16 months. Consequently, during this period, salinity and ionic composition of the soil have become uniformly distributed over the soil profile (c.f. fig. 30 D, section 4.3). Therefore this spot is especially suited for studying the changes in ionic composition during the regeneration period.

Its only drawback is that it received a small dressing of gypsum – 3 t/ha of $CaSO_4 . 2\,H_2O$ – in 1947 and a large dressing – 8 t/ha of $CaSO_4 . 2\,H_2O$ – in 1951. Nevertheless the data for OB 13 may be assumed to be fairly representative for natural regeneration – at least qualitatively – up to 1951. In fig. 38 the relative decrements of Cl and exchangeable Na, K and Mg in the upper 20 cm of the soil are given; the initial amounts of these ions in this layer have been put at 100. In fig. 39, representing the changes in Cl concentration and exchangeable Na percentage in the different layers sampled, the mean initial Cl concentrations and Na percentages, averaged over the entire soil profile, have been put at 100. Finally, in fig. 40, the relationships between exchangeable Na fraction μ and depth, have been given for the period immediately after the inundation, and also four years later.

As appears from these figures the different ions decrease in the order Cl > Na > K > Mg. The changes in K and Mg are very slight, even in the topsoil, and they are quite imperceptible in the subsoil. On the other hand exchangeable Na has been substantially reduced in the topsoil, and in the course of four years its reduction extended to a depth of about 40 cm (fig. 40, II).

On soils which received no gypsum at all – e.g. on the controls of gypsum trial fields – the changes in ionic composition may be expected to be still less. As an example the relative changes in exchangeable Na, K and Mg on the control of trial field GT 18 have been reproduced in table 33. Within the limits of observational errors, no decrease in exchangeable K and Mg could be detected in the course of about six years. On the other hand the amounts of exchangeable Na have been greatly reduced during this period.

TABLE 33. Relative natural decrements in exchangeable Na, K and Mg in the topsoil of a heavy new-land soil [1].
Control of gypsum trial field GT 18, polder Johanna Maria, Tholen; 0–20 cm depth.

Years after drainage	1	1½	2	2½	3	3½	4½	6½	7½
Na	100	101	88	81	83	71	61	49	36
K	100	104	102	100	108	115	96	121	104
Mg	100	102	104	105	97	105	97	106	94

[1] Active matter content 42%.

The reductions in exchangeable Na, K and Mg are compensated by a corresponding increase in exchangeable Ca. Hence, during the regeneration process, the sum of exchangeable metal cations, S_a, will remain constant, at least within the range of experimental errors (table 34). This rule is valid not only for soils containing calcium carbonate, like the new-land and creek-ridge soils, but probably also for non-calcareous and acid pool soils, though for the latter the evidence is too scarce to draw a definite conclusion.

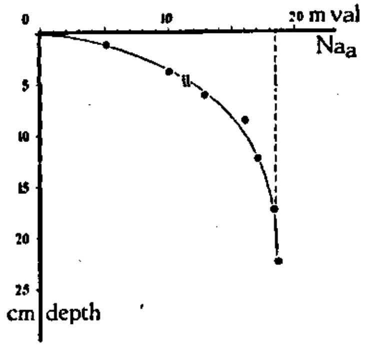
TABLE 34. Ionic composition of soils during the regeneration period.

Sampling spot	Depth	Active matter %	$CaCO_3$ %	Years after drainage	mval per 100 g of active matter				
					Na_a	K_a	Mg_a	Ca_a	S_a
AG 3 [1]	0–20	20.1	4.1	½	12.9	3.6	17.7	33.8	68.0
				4	2.0	2.1	17.5	45.7	67.3
GT 18 [1]	0–20	41.2	4.2	1	10.9	2.8	12.6	32.8	59.1
				6½	4.2	3.1	12.6	43.2	63.1
PP 1 [2]	0–10	±62	0.0	1	6.9	1.6	8.1	13.4	30.0
				3½	2.9	1.6	7.6	15.9	28.0
Sch 1 [2]	0–20	41.2	0.0	1	5.6	2.6	13.3	20.8	42.3
				6½	1.6	1.7	13.0	27.3	43.6

[1] Controls of gypsum trial fields on new-land soils.
[2] Fixed sampling spots on old pool soils; no gypsum applied.

As may be seen from table 34, the sum of exchangeable metal cations S_a is much lower in the acid pool soils PP 1 and Sch 1 than in the calcareous soils AG 3 and GT 18 (c.f. fig. 12, section 3.4). But in each case this sum remained approximately constant during the regeneration period. So in all soils observed, the regeneration mainly consists of a replacement of exchangeable Na by Ca and, to a much less extent, of K and Mg by Ca.

Theoretically such an exchange should lead to the development of a fairly sharp rear boundary of Na ions, which in any case should be sharper than the rear boundary of the Cl ions (section 5.1) (c.f. fig. 40, II). In the topsoil such boundaries will already be set up soon after drainage. Thus fig. 41 gives the distribution of exchangeable Na in the topsoil of the sampling spot VB 4.



I: Hypothetical Na content in summer 1945
II: Na content in February 1946

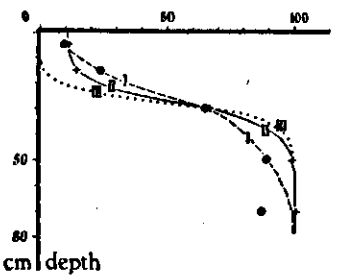
FIG. 41. Natural decrease of exchangeable Na in the topsoil.
Sampling spot VB 4, polder Vierbannen, Duiveland. Untilled soil; no gypsum applied

Since its drainage this field had been neither cropped nor tilled, and no gypsum had been applied. At the moment of drainage – in summer 1945 – the exchangeable Na ions were most probably evenly distributed over the soil profile (fig. 41, I). At the moment of sampling, however, about half a year later, a marked decrease in exchangeable Na has already taken place near the soil surface, whereas at a depth of about 15 cm the initial Na content has still been preserved.

From these and similar observations it becomes clear that the regenerative processes proceed only slowly downward through the soil profile. If therefore, by ploughing, the soil is turned up, layers with a higher Na content will be brought to the surface. For practical reasons, it is hardly possible to reduce the depth of ploughing to less than 8–10 cm; so even in cases where the soil has been very cautiously tilled, the Na boundaries will be subject to periodic disturbance.

Therefore it is not easy to compare the shape of the Na boundaries with those of the much faster running Cl ions. Moreover, for such a comparison, data should be available for the Cl boundaries in the initial stages of desalinization, as well as data about the exchangeable Na many years later. Among the observations made evidence of this kind is extremely scarce; one of the few examples available has been reproduced in fig. 42. These data indeed suggest the presence of a self-sharpening tendency in the Na boundaries; but without theoretical support, the existence of such effects would be doubtful.

The theoretical plate thickness – 2 k – may be derived from the shape of the Cl boundary by employing equation (*2.68*), section 2.31. By applying this equation to the boundary represented in fig. 42 I, the value for 2 k was found to be about 8 cm. By introducing the value $k = 4$ into equation (*2.75*), section 2.31, theoretical values for exchangeable Na could be calculated, which are represented in fig. 42, III. It may be observed that this theoretical Na boundary possesses a still steeper gradient with depth than the observed one, and especially in the topsoil large deviations occur.



I: Cl boundary 9-10-1946
II: Na boundary 23-3-1949
III: Theoretical Na boundary for 2 k = 8 cm

FIG. 42. Rear boundaries of Cl and exchangeable Na. Control of gypsum trial field AG 3, polder Nieuw-Bommenede, Schouwen. Initial contents put at 100

The fact that ploughing will bring Na-rich subsoil to the surface has considerable practical interest. On becoming exposed to climatic influences, especially to the impact of raindrops, the structure of this Na-rich soil may easily collapse. In this way the disadvantages of soil tillage, especially of deep ploughing, already emphasized in the earliest observations on flooded soils (section 1.1), find their explanation. Therefore, if ploughing is unavoidable, the farmers are always recommended to plough as seldom, and as shallow as possible.

Hitherto only general and qualitative aspects of the regeneration have been mentioned. One of its most important features, its velocity, and the different circumstances which may exert a retarding or promoting effect, have been left out of consideration. These subjects, however, will be treated in section 5.4. But first – in the next section – the effects of the different regenerative processes mentioned in section 5.1 will be reviewed in more detail.

5.3. REGENERATIVE PROCESSES

The regenerative processes mentioned already in section 5.1 may be considered either with regard to their local effects (equilibria) or with regard to their effects in combination with water passage (column performance).

Both aspects will be dealt with from a theoretical as well as from an experimental point of view, and most stress will be laid upon the behaviour of the Na ions.

5.31. *Concentration changes in the soil moisture*

As follows from theory (section 2.1) as well as from the observations (section 3.52), dilution of the equilibrium solution will result in an increase in exchangeable bivalent ions at the cost of the monovalent ones; concentration of the solution will have the opposite effect. During the desalinization of flooded soils the salt concentration will fall considerably; consequently an increase in exchangeable Ca and Mg, accompanied by a corresponding decrease in Na and K, may be expected. During summer, when evaporation predominates, the reverse will occur.

In nature, changes of concentration in the soil moisture seldom occur without water movements. Dilution of the soil solution – e.g. by rainfall – is usually followed by drainage, whereas evaporation is generally accompanied by capillary rise. Nevertheless, for simplicity, the local effects of concentration changes will be treated first. In this discussion only the behaviour of the Na ions will be considered.

For the calculation of these effects, the empirical Na adsorption isotherms may be used, already given in section 3.7 by equation (3.23):

$$\mu = 0.22\,\nu^2 \log \Sigma \mathrm{c} \qquad (5.01)$$

In local processes the total amount of any kind of ions must remain constant. Per 100 g of dry matter the total amount of cations present in the soil may be expressed by:

$$\text{Total cations} = \mathrm{S_s} + \frac{\mathrm{A} \,.\, \Sigma \mathrm{c}}{1000} = \text{constant} \qquad (5.02)$$

Of these, the amount of exchangeable metal cations S_s may be considered as being independent of concentration changes in the soil moisture. Hence:

$$\mathrm{A} \,.\, \Sigma \mathrm{c} = \mathrm{A_o} \,.\, (\Sigma \mathrm{c})_\mathrm{o} \qquad (5.03)$$

in which the index o refers to the initial stage.

Further the constancy of the total amount of Na ions requires that:

$$\Sigma\,\mathrm{Na} = (\Sigma\,\mathrm{Na})_\mathrm{o} \qquad (5.04)$$

in which:

$$\Sigma\,\mathrm{Na} = \mu \,.\, \mathrm{S_s} + \nu \frac{\mathrm{A} \,.\, \Sigma \mathrm{c}}{1000} \qquad (5.05)$$

Introducing (*5.01*) into (*5.05*) and rearranging gives:

$$0.22\,\nu^2 \,.\, \mathrm{S_s} \,.\, \log \Sigma \mathrm{c} + \nu \frac{\mathrm{A} \,.\, \Sigma \mathrm{c}}{1000} - \Sigma\,\mathrm{Na} = 0 \qquad (5.06)$$

which, according to (*5.03*) and (*5.04*) may be written as:

$$0.22\,\nu^2 \,.\, \mathrm{S_s} \log \Sigma \mathrm{c} + \nu \frac{\mathrm{A_o}\,(\Sigma \mathrm{c})_\mathrm{o}}{1000} - (\Sigma\,\mathrm{Na})_\mathrm{o} = 0 \qquad (5.07)$$

From this equation ν – and consequently also μ – may be calculated if the other quantities are known. Of these, $(\Sigma\,\mathrm{Na})_\mathrm{o}$ may be evaluated from:

$$(\Sigma\,\mathrm{Na})_\mathrm{o} = \mu_\mathrm{o}\, \mathrm{S_s} + \nu_\mathrm{o} \frac{\mathrm{A_o}\,(\Sigma \mathrm{c})_\mathrm{o}}{1000} \qquad (5.08)$$

Applying these equations to flooded soils it appears that the changes in ionic composition, caused by changes in soil moisture concentration, will be usually relatively small.

As an example the following case will be considered:

A new-land soil with 24% clay ($< 2\,\mu$) and 31% of active matter, possessing an adsorptive capacity $S_s = 20$ has been subject to inundation. After drainage its moisture content was found to be $A_o = 30$, whereas its salinity was $C_o = 23$, corresponding with a total concentration of the soil moisture of $(\Sigma\,c)_o = 500$ (c.f. fig. 36, section 4.5). The exchangeable Na fraction in this soil is assumed to be $\mu_o = 0.20$. As follows from equation (5.01) the fraction of Na among the ions in solution will be $\nu_0 = 0.58$. Hence, the initial situation in this soil is completely defined; the total amount of Na ions present appears to be $\Sigma\,\mathrm{Na} = 12.7$ (table 35).

During the summer following drainage the moisture content of the topsoil is lowered to $A = 7.5$. Consequently, if no capillary rise has occurred, the concentration of the soil moisture would have risen to $\Sigma c = 2000$. Supposing equation (5.01) to be still valid at these high concentrations – in fact it has been derived empirically from data in the range $10 < \Sigma c < 500$ – the final value of ν may be calculated by equation (5.07). It is found that $\nu = 0.55$, corresponding with a value $\mu = 0.22$. In this way the final situation, represented in table 35 may be calculated. Thus, as appears from this table, a fourfold increase in concentration only leads to an increase in exchangeable Na of approximately 10%.

TABLE 35. Calculated changes in ionic composition, caused by a fourfold increase in soil moisture concentration.

		Total concentration of soil moisture Σc mval/l	per 100 g of dry matter			
			Moisture A ml	Total metal cations mval	Fraction of Na ions	Na mval
Initial situation	Adsorbed	—	—	20	0.20	4.0
	Solution	500	30	15	0.58	8.7
	Total	—	—	35	—	12.7
Final situation	Adsorbed	—	—	20	0.22	4.4
	Solution	2000	7.5	15	0.55	8.3
	Total	—	—	35	—	12.7

In a similar way the effects of dilution may be calculated: a summary of the results found for the soil mentioned above has been given in table 36. As appears from this table, a 200-fold change in concentration will lead to a 50% change in exchangeable Na.

TABLE 36. Calculated changes in ionic composition, caused by changes in soil moisture concentration.
Adsorptive capacity of soil: $S_s = 20$ mval/100 g.

Change	Total concentration of soil moisture Σc mval/l	Moisture content A ml/100 g	Salinity C	Fraction Na	
				among adsorbed ions μ	among ions in solution ν
Fourfold concentration	2000	7.5	92	0.22	0.55
INITIAL SITUATION	*500*	*30*	*23*	*0.20*	*0.58*
Fivefold dilution	100	150	4.6	0.17	0.62
Tenfold dilution	50	300	2.3	0.15	0.64
Twentyfold dilution	25	600	1.2	0.14	0.66
Fiftyfold dilution	10	1500	0.5	0.11	0.70

It may be concluded from these examples that changes in soil moisture concentration, as such, will exert relatively little influence on the ionic composition of the soil

In the field, however, substantial changes in moisture concentration are always combined either with capillary rise or with drainage. Due to this moisture transport, the total amounts of any kind of ions present in a given volume of soil will change. As in this case the equations (*5.03*) and (*5.04*) are no longer valid, only equation (*5.06*) may be used for calculating the final Na equilibria. The final values of A, Σc and Σ Na occurring in this equation may be derived from the nature of the processes causing the changes in salt concentration.

On closer examination of these processes and of their effects on ionic composition, it appears that capillary rise of the magnitude usually met with in Dutch soils, will exert little influence. Dilution of the soil solution, combined with drainage will cause the changes to be even smaller than in pure dilution, as the bivalent Mg and Ca ions, which should replace the exchangeable Na on dilution, will also be removed. Therefore the entire process will finally come to a standstill for lack of complementary ions.

As an example the flooded soil mentioned earlier in this section will be supposed to reach a fourfold increase in total salt concentration during the summer following drainage, half of which is caused by capillary rise, half by desiccation. The composition of the moisture risen from deeper layers is supposed to be equal to that of the moisture initially present in the soil. Desiccation will reduce the moisture content from A = 30 to A = 15.

As may be seen from table 35 a capillary rise of 30 ml will add 8.7 mval of Na to the amount already present, thus increasing Σ Na from 12.7 to 21.4. Using equation (*5.06*) with $S_a = 20$, $\Sigma c = 2000$, $A = 15$, $\Sigma \text{Na} = 21.4$ it is found that $\nu = 0.56$. This value corresponds with $\mu = 0.23$, which only slightly differs from that found after a fourfold increase in salt concentration without capillary rise ($\mu = 0.22$).

The effects of dilution, if accompanied by drainage, may be calculated in a similar way.

As an example it may be assumed that the saline soil already used in former computations, will be leached by rainfall. This leaching process is imagined to consist of a twofold dilution of the soil solution, followed by drainage of the excess moisture. Hence, during this imaginary process the moisture content of the soil will first be raised from A = 30 to A = 60, after which it will be reduced again to A = 30 by drainage.

The calculated effects of a repeated action of this process have been represented in table 37. As appears from this table the exchangeable Na fraction μ will approach a limit for infinite dilution. This limit is not far below the initial value of μ.

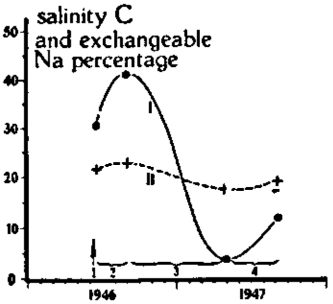
As in the field drainage will start long before a twofold dilution has been reached it may be expected that the actual changes in exchangeable Na during the desalinization period will be still less.

TABLE 37. Calculated effects of repeated twofold dilution, followed by drainage.
Adsorptive capacity of soil: S_a = 20 mval/100 g of dry matter.
Moisture content after drainage: A = 30 ml/100 g of dry matter.

Cycle number	Dilution	Total concentration of soil moisture Σc mval/l	Salinity C	Fraction Na	
				among adsorbed ions μ	among ions in solution ν
0	none	500	23	0.200	0.580
1	2-fold	250	12	0.188	0.595
2	4-fold	125	6	0.178	0.623
3	8-fold	62	3	0.172	0.655
4	16-fold	31	1.5	0.167	0.710
5	32-fold	16	0.7	0.164	0.794
∞	∞	0	0.0	$\cong$ 0.160	—

Hence it may be concluded that even in combination with either capillary rise or drainage, concentration changes will not have large effects on the ionic composition. Consequently the large reduction in soluble salts occurring during the desalinization of flooded soils will make only a small contribution to the regeneration of the soil.

This conclusion is entirely confirmed by the observations made in the field. Although during the first summer after drainage the salt concentration in the topsoil may rise considerably due to capillary action and desiccation, only small variations in exchangeable Na are observed. During the next winter the bulk of the soluble salts will be removed from the topsoil, but this large reduction in soil moisture concentration will be of little influence to the amounts of adsorbed Na. An example of such field data, in which large variations in salt concentration are only feebly reflected by the adsorbed Na ions, has been given in fig. 43.



I: salinity C
II: exchangeable Na percentage
1: date of drainage
2: capillary rise and desiccation; wet summer
3: desalinization in winter
4: capillary rise and desiccation; dry summer

FIG. 43. Changes in salt concentration and exchangeable Na in the topsoil.
Sampling spot OB 13, polder Oost Beveland, 1946–1947, 0–10 cm depth

5.32. *Hydrolysis and reaction with water containing carbon dioxide*

Hydrolysis of Na-clay will result in an exchange of adsorbed Na ions against H_3O ions originating from auto-protolysis of water:

$$H_2O + H_2O \rightleftarrows H_3O^{\cdot} + OH'$$

$$\text{Na-clay} + H_3O^{\cdot} \rightleftarrows H_3O\text{-clay} + Na^{\cdot}$$

The free OH ions resulting from this process will increase pH considerably, even if only a small part of the adsorbed Na ions are released. Consequently this process will soon come to a standstill due to lack of free H_3O ions and to the presence of free Na ions in the equilibrium solution.

The high alkalinity resulting from hydrolysis may cause a breakdown of organic matter and even of clay minerals into small diffusable fragments (c.f. GEDROIZ, 1927). In some of our experiments on hydrolysis of a Na-saturated, non-calcareous soil, diffusion of humates and silicates through a cellophane membrane was indeed observed. This complication makes a study of hydrolysis phenomena extremely difficult.

In the presence of CO_2 the following reactions will occur:

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

$$H_2CO_3 + H_2O \rightleftarrows H_3O^{\cdot} + HCO_3'$$

$$\text{Na-clay} + H_3O^{\cdot} \rightleftarrows H_3O\text{-clay} + Na^{\cdot}$$

Finally, if hydrolysis and reaction with CO_2 are occurring simultaneously, noticeable amounts of carbonate ions may be formed according to:

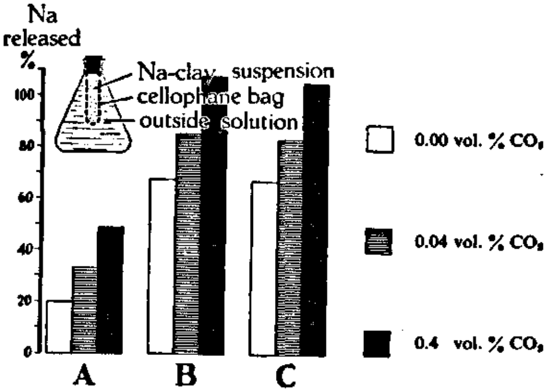
$$HCO_3' + OH' \rightleftarrows H_2O + CO_3''$$

As in this case OH ions will be removed from the solution, the presence of carbon dioxide will reduce pH, increase the amounts of free H_3O ions and consequently also increase the release of adsorbed Na ions.

In the laboratory the effects of hydrolysis on a Na-saturated, non-calcareous Dutch clay soil have been studied by SMEDING & HAASJES (1948). In these experiments the effects of CO_2 and $CaCO_3$ were studied as well.

In the experiments a cellophane bag containing an amount of 12.5 g of this clay[1] suspended in 50 ml of solution was subjected to dialysis against 450 ml of solution by rotating for 8 days. At different intervals the outside solution was analysed for Na, using a flame photometer.

By hydrolysis alone about 20% of the exchangeable Na present in this clay could be released under these conditions, whereas the presence of carbon dioxide increased the amounts liberated considerably (fig. 44, A).



A: no $CaCO_3$ added
B: $CaCO_3$ added to soil suspension
C: $CaCO_3$ added to outside solution

FIG. 44. Amounts of Na released from a Na-saturated clay by dialysis for 8 days. After SMEDING & HAASJES (1948)

Addition of calcium carbonate to the system, however, resulted in a still higher release of Na, and in the presence of carbon dioxide the exchange was virtually complete (fig. 44, B, C). This pronounced effect of $CaCO_3$ indicates that in calcareous soils reaction with this compound will greatly predominate over hydrolysis and reaction with H_2CO_3.

The conditions in the laboratory experiment differed greatly from those in actual soils; therefore a direct comparison is impossible. Whereas in the experiments the

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[1] In these experiments Na-saturation has been achieved by repeated shaking with a normal Na-acetate solution of pH 8.2. After the soil has settled the supernatant liquid was siphoned off and renewed; this process was continued until no Ca ions could be detected in the supernatant liquid. Than the soil was rinsed with alcohol to remove the Na-acetate solution and dried.

soil-water ratio was as low as 1 : 40, it is of the order of 3 : 1 in actual soils. Moreover the Na-saturation of the clay in the hydrolysis- and CO_2-experiments is much higher – even after 8 days of reaction – than is ever observed in flooded soils. In the field the changes may therefore be expected to be much less. As will be seen on closer examination they are quite negligible, unless discharge of reaction products is possible.

After 8 days of hydrolysis the Na concentration in the outside solution had become 1.4 mval/l, and the Na-saturation of the clay had been decreased from $\mu = 1.0$ to $\mu = 0.8$. Assuming that in a flooded soil with $A = 30$, $S_s = 20$ and $\mu_0 = 0.20$ hydrolysis is able to raise the Na-concentration in the soil moisture from zero to this value of 1.4 mval/l, calculation shows that μ will be lowered from 0.200 to 0.198 by local action. Under these circumstances a water passage of 125 mm a year – being a fair average for recently flooded soils – will remove 40 kg/ha of Na annually, which is negligible against the annual Na losses of 390 kg/ha observed in untreated calcareous flooded soils (c.f. table 46, section 5.4).

In the presence of 0.4% of CO_2 the Na concentration in the outside solution had become 3.45 mval/l after 8 days of reaction, and the Na-saturation of the clay had been decreased from $\mu = 1.0$ to $\mu = 0.5$. Again assuming that in a flooded soil the same Na-concentration will be reached, local action will decrease the Na-saturation from $\mu_0 = 0.200$ to $\mu = 0.195$. The annual Na losses may be calculated at 100 kg/ha, which is still far too low to explain the observed losses of 390 kg/ha.

Hence it may be concluded that hydrolysis and reaction with dissolved CO_2 are unable to produce noticeable changes by local action. In combination with water passage small amounts of exchangeable Na may be removed, but in calcareous soils the reaction with dissolving $CaCO_3$ will greatly predominate. This conclusion is confirmed by the observations already mentioned in table 34, section 5.2, which indicate that in calcareous soils Na is replaced by Ca rather than by H_3O.

In non-calcareous soils the situation is less clear. Exchanges with H_3O ions may be expected to play a more prominent part, but this expectation is not confirmed by the few observations available (table 34, section 5.2), possibly because the soils in question have received lime dressings, possible also because Ca has been liberated from other sources, e.g. from other Ca-containing minerals (section 5.34).

But, although no major changes in ionic composition are involved, even a slight degree of hydrolysis will have a marked increasing effect on soil pH, due to the free OH ions. This increased pH is one of the most marked characteristics of soils rich in exchangeable Na.

In alkali soils found in arid regions a fair correlation between pH and exchangeable Na percentages has been observed (FIREMAN & WADLEIGH, 1951; CHANG, 1953). A similar correlation may also be found in flooded soils after the removal of the soluble salts. As an example the relation between pH (measured in a 1 : 2.5 aqueous suspension) and exchangeable Na in calcareous, flooded soils after their desalinization has been represented in fig. 45.

Although this correlation is rather wide, soils high in exchangeable Na will usually also posses a pH of 8.5 or over (fig. 45). This pH is nearly always found if the amounts of exchangeable Na exceed 10 mval per 100 g of active matter ($Na_a > 10$), corresponding with an exchangeable Na percentage above 15 ($\mu > 0.15$). According to RICHARDS *et al* (1954) such soils may be classified as alkali soils. But also in many cases where the amounts of exchangeable Na are lower than 15%, pH-values above 8.5 occur.

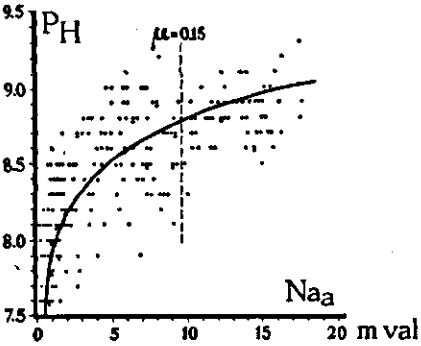


FIG. 45. Relation between exchangeable Na content and pH in calcareous flooded soils after desalinization.
Samples from gypsum trial fields, spring 1948, 0–20 cm.
$C < 1.0$; $CaCO_3 > 0.5$ %

In the old pool soils, where considerable amounts of exchangeable H_3O ions are present, pH is much lower. Even in the presence of much exchangeable Na, pH-values below 6.0 are common. By analogy it may be expected that also in these soils pH has been increased by the inundation and subsequent desalinization, but proof is lacking for want of data.

Thus hydrolysis, though not of much importance to the regeneration of flooded soils, may be regarded as responsible for the alkaline shift found in flooded soils after their desalinization.

5.33. *Reaction with dissolved calcium carbonate*

Calcium carbonate is slightly soluble in water:

$$CaCO_3 \rightleftarrows Ca^{\cdot\cdot} + CO_3''$$

In the presence of even slight amounts of carbon dioxide, this solubility is increased due to bicarbonate formation:

$$CaCO_3 + H_2O + CO_2 \rightleftarrows Ca^{\cdot\cdot} + 2\ HCO_3'$$

The free Ca ions will react with exchangeable Na according to:

$$Na_2\text{-clay} + Ca^{\cdot\cdot} \rightleftarrows Ca\text{-clay} + 2\ Na^{\cdot}$$

Although dissolution of $CaCO_3$ into the soil moisture only gives rise to low Ca concentrations, the process mentioned above appears to be the principal cause of the natural regeneration in calcareous flooded soils.

The importance of this process is already obvious from the laboratory experiments of SMEDING & HAASJES (c.f. fig. 44, B, C), where, at least in the presence of CO_2, virtually complete replacement of the exchangeable Na could be achieved by adding calcium carbonate to the system. In the field, the importance of this process is shown by the predominant replacement of exchangeable Na by Ca (c.f. table 34, section 5.2).

To get more quantitative information about this process we must know the solubility of calcium carbonate in the soil moisture.

Such knowledge, however, is rather scarce, although approximate values may be derived in different ways, viz.:

1. From the well-known solubility of calcite in water containing carbon dioxide (table 38). In normal soils the CO_2-concentration in the soil air is of the order of a few volume per cent (SCHUFFELEN *et al.*, 1954); consequently the solubility of calcium carbonate may be expected to be of the order of 5 mval/l. This solubility, however, is somewhat higher at lower temperatures and moreover it is increased by the presence of Na and K salts. Therefore the Ca concentration in the soil moisture may be expected to be somewhat higher than the values listed in table 38; $c_{Ca} \cong 10$ mval/l seems to be a fair estimate.

TABLE 38. Solubility of calcite in water in the presence of carbon dioxide (after SEIDELL).

Partial pressure of CO_2 atm.	Vol. per cent of CO_2 in soil air	c_{Ca} mval/l	Temperature centigrades
0.01	1	4.4	16°
0.05	5	7.2	25°
0.10	10	8.0	25°

2. From analyses of expressed fluid and drain water from unflooded soils. The few analyses of expressed fluid obtained from unflooded soils show Ca concentrations of approximately 10 mval/l. The expressed fluid from a polder soil, sampled after flooding with fresh water (sampling spot DN 1, 1945 0–20 cm), however, had a Ca concentration of 13.3 mval/l. On the other hand the calcareous slik soils of the Noordoostpolder, after the oxidation of their sulphides and the removal of the sulphates formed, showed Ca concentrations of approximately 6 mval/l. All values mentioned, however, were determined after drying and re-wetting the original soil samples; therefore their reliability is doubtful.
   A sample of drain water from an unflooded, young, calcareous polder soil in the S.W. of the Netherlands, taken in autumn, showed a Ca concentration of 12.7 mval/l (polder Zuid Blankenburg, September 1954). Although more observations are needed, this value is in fair agreement with those mentioned above.
3. From the rate of decalcification. As has been pointed out in section 3.3 the rate of decalcification of the topsoil in the S.W. of the Netherlands corresponds with a loss of 1% of calcium carbonate in about 80 years. Assuming the annual water passage to be of the order of 200 mm (VERHOEVEN, 1953), this loss corresponds with a Ca concentration in the percolating water of 3.5 mval/l.

The value mentioned under 3 appears to be considerably below the earlier estimates, made under 1 and 2. Obviously more elaborate research will be needed to explain this difference. For our purpose, however, in which only the order of magnitude is involved this discrepancy may be left out of further consideration.

In view of the above considerations it seems justified to estimate the Ca concentration in unflooded, calcareous soils at $c_{Ca} = 10$ mval/l. To investigate the maximal effects even the value $c_{Ca} = 15$ mval/l will be used in a few cases. But in calcareous flooded soils the high pH will reduce $CaCO_3$ solubility due to its influence on the HCO_3'–CO_3'' equilibrium; in such soils c_{Ca} was found to be of the order of 4 mval/l (c.f. table 41).

The changes in ionic composition, brought about by the dissolution of calcium carbonate into the soil solution may be calculated in a similar way as those caused by the changes in soil moisture concentration, treated in section 5.31.

Application of the empirical Na adsorption isotherms (*5.01*) to the conditions prevailing in soils will again lead to the quadratic equation (*5.06*):

$$0.22\,\nu^2 \,.\, S_s \,.\, \log \Sigma c + \nu \frac{A \,.\, \Sigma c}{1000} - \Sigma\,\mathrm{Na} = 0 \qquad (5.06)$$

in which in our case ν and Σ c are unknown.

If only Na and Ca ions are taking part in the equilibrium, the fraction of Ca ions among the ions in solution is obviously equal to 1-ν. Consequently the concentration of the Ca ions in the soil solution will be equal to:

$$c_{Ca} = (1-\nu).\ \Sigma c \qquad (5.09)$$

or:

$$\nu = 1 - \frac{c_{Ca}}{\Sigma c} \qquad (5.10)$$

Hence, if the moisture content (A), the adsorptive capacity of the soil (S_s), the total amount of Na present (Σ Na) and the solubility of $CaCO_3$ (c_{Ca}) are known, ν and Σ c may be calculated from the two equations (*5.06*) and (*5.09*). This calculation may be easily accomplished by selecting some tentative values of Σc, calculating the corresponding values of ν by means of equation (*5.10*) and determining which of these values serves (*5.06*), using graphical interpolation if necessary.

In actual cases, however, not only Na and Ca, but also K and Mg are present. If their combined fractions among the ions in solution are assumed to be λ, equation (*5.09*) should read:

$$c_{Ca} = (1 - \lambda - \nu)\ \Sigma c \qquad (5.11)$$

Consequently, equation (*5.10*) should be replaced by:

$$\nu = 1 - \lambda - \frac{c_{Ca}}{\Sigma c} \qquad (5.12)$$

from which, in combination with (*5.06*), ν and Σc may be calculated if the other quantities are known.

For the case that only Na and Ca ions are taking part in the equilibrium an alternative method of computing the equilibria might be followed by making use of the equations (*3.08*), (*3.10*) and (*3.15*) derived for the Na-Ca equilibria on a new-land soil (section 3.52). As however in flooded soils the value of the ionic strength I will fall below the range investigated, equation (*3.15*) should be extrapolated. At I = 0.025 – a value commonly found in desalinized flooded soils – when the activity ratio $\frac{f_{Na}}{\sqrt{f_{Ca}}} = 1.12$, the extrapolated KERR equation for the soil in question may be represented by:

$$\left[\frac{c_{Na}}{\sqrt{c_{Ca}}}\right]_{I} = 0.073 \left[\frac{c_{Na}}{\sqrt{c_{Ca}}}\right]_{II} \qquad (5.13)$$

In this equation $(c_{Na})_I$ and $(c_{Ca})_I$ are expressed as mval per 100 g of soil, whereas $(c_{Na})_{II}$ and $(c_{Ca})_{II}$ are expressed as mval per litre.

Remembering that:

$$(c_{Na})_I = \mu \,.\, S_s;\ (c_{Na})_{II} = \frac{\Sigma\, Na - \mu \,.\, S_s}{A/1000} \qquad (5.14)$$

$$(c_{Ca})_I = (1 - \mu) \,.\, S_s;\ (c_{Ca})_{II} = \text{constant, depending on the solubility of } CaCO_3 \qquad (5.15)$$

equation (*5.13*) may be solved.

The equations mentioned above do not lend themselves to a general discussion about the effects of varying different quantities. Therefore some results of computations are collected in table 39.

TABLE 39. Calculated changes in ionic composition, caused by solution of calcium carbonate.

Number	Method of calculation	Adsorptive capacity S_s mval/100 g	Moisture content A ml/100 g	Solubility of $CaCO_3$ c_{Ca} mval/l	Fraction K+Mg in solution λ	Fraction Na among adsorbed ions		Total concentration of soil moisture mval/l	
						initial μ_o	final μ	initial $(\Sigma c)_o$	final Σc
1	a	20	30	10	—	0.100	0.083	0	21.4
2	b	20	30	10	0.2	0.100	0.077	0	31.6
3	a	20	30	10	—	0.100	0.091	10	22.4
4	a	20	30	15	—	0.100	0.078	0	29.6
5	a	20	30	15	—	0.100	0.086	10	30.8
6	a	30	30	10	—	0.100	0.088	0	22.0
7	c	30	30	10	—	0.100	0.080	0	30.0
8	a	30	30	10	—	0.100	0.094	10	22.8
9	c	30	30	10	—	0.100	0.085	10	31.7
10	a	30	30	10	—	0.200	0.174	0	35.3

[1] a: calculated by means of equations (*5.06*) and (*5.10*).
b: calculated by means of equations (*5.06*) and (*5.12*).
c: calculated by means of equations (*5.13*) and (*5.14*).

Hence, it may be expected theoretically, that:

1. The changes in ionic composition, caused by mere dissolution of $CaCO_3$ into the soil moisture are only slight; in the most favourable case mentioned in table 39 the exchangeable Na percentage decreases from 10.0 to 7.7. Further changes will only take place if removal of reaction products is possible.

2. In the presence of K and Mg ions the changes are slightly larger than in cases where only Na and Ca ions take part in the exchange (c.f. numbers 1 and 2).

3. The solubility of $CaCO_3$ in the soil moisture is of little effect to the changes in exchangeable Na; if this solubility is increased from 10 to 15 mval/l, these changes are becoming only slightly larger (c.f. numbers 1 and 4, 3 and 5).

4. The initial concentration of the soil moisture has a marked effect on the changes in ionic composition. If initially the solution contains soluble salts, these changes are much smaller than in cases that the initial ionic concentration is low (c.f. numbers 1 and 3, 4 and 5, 6 and 8). This implies that reactions with dissolving $CaCO_3$ will be of some importance only at low concentrations of the soil solution, in other words only after desalinization of a flooded soil.

5. It makes little difference whether the equilibria are calculated according to the empirical Na adsorption isotherms (equation *5.01*) or by means of the KERR equation (*5.13*) (c.f. numbers 6 and 7, 8 and 9).
   This is not surprising, as both equations give rather similar adsorption isotherms (c.f. fig. 23, section 3.7).

6. The total concentration of the solution after equilibrium – Σc – is markedly influenced by the solubility of $CaCO_3$ (c.f. numbers 1 and 4, 3 and 5). At the assumed solubilities it may be expected to be of the order of 20–30 mval/l for desalinized, flooded soils. In the presence of large amounts of exchangeable Na even slightly higher values may be expected (c.f. number 10).

The results of SMEDING & HAASJES (1948), in which virtually complete replacement of Na by Ca was observed in systems containing $CaCO_3$ seem to contradict the conclusions mentioned above (c.f. fig. 44, B, C, section 5.32). In these experiments, however, the water: soil ratio was approximately 120 times as high as in natural soils. Calculation of the equilibria established in these experiments by means of equations (*5.06*) and (*5.10*) – using the values $S_a = 30$ mval/100 g, $A = 4000$ ml/100 g, $\mu_o = 1.000$, $(\Sigma c)_o = 0.00$ mval/l, $c_{Ca} = 10$ mval/l – predicts that *in these experiments the* Na *fraction among the adsorbed ions should fall from* $\mu_o = 1.000$ *to* $\mu = 0.048$. Hence the nearly complete replacement of Na by Ca found under these circumstances is in full accordance with the theory outlined above.

These theoretical considerations are confirmed by the observations made in the field. If reaction with $CaCO_3$ could bring about noticeable changes in ionic composition, a quick and easy regeneration might be expected in calcareous flooded soils. This rapid regeneration would not be limited to the topsoil, but also proceed in deeper layers. This is obviously not the case; already in section 5.2 it has been pointed out that during the first years after drainage natural regeneration is almost entirely located in the topsoil (fig. 40). As appears from these data and from those listed in table 40, no substantial changes occur in the subsoil. The changes in the topsoil must be ascribed to removal of reaction products, followed by renewed dissolution of $CaCO_3$, a process which is to be described in more detail in section 5.36.

TABLE 40. Natural regeneration in a calcareous, flooded soil. Control of gypsum trial field AG 17, polder Anna Jacoba, St. Philipsland.

Depth cm	Clay content % < 2 μ	Organic matter %	$CaCO_3$ %	Fraction Na among the adsorbed ions μ	
				12-4-'46	31-3-'48
0–10	28.1	2.0	2.8	0.207	0.093
10–20	27.8	2.0	3.1	0.218	0.155
20–40	21.8	1.4	4.7	0.221	0.208
40–60	9.7	0.5	4.4	0.208	0.210
60–80	4.4	0.3	4.2	0.207	0.226

Another indication of the inefficiency of a local reaction is given by the small effect of lime dressing on the ionic composition of non-calcareous soils; this will be treated in more detail in the next chapter (section 6.3).

Finally, more detailed information about the equilibria of flooded soils with $CaCO_3$ may be derived from analyses of expressed fluid from calcareous, flooded soils after their desalinization. According to the calculated data, mentioned in table 39, the total ionic concentration of such soil solutions — Σc — should be of the order of 20–30 mval/1, at least if the solubility of $CaCO_3$ in the soil moisture is estimated at 10 mval/1. The few available observations, represented in table 41, however, suggest lower values for both, viz. $\Sigma c \lessapprox 20$ mval/1 and $c_{Ca} \lessapprox 4$ mval/1.

TABLE 41. Analyses of expressed fluid from from calcareous, flooded soils after their desalinization.
Polder Wilhelmina, Zuid-Beveland, May 1945.

Sampling spot	Depth cm	Salinity C g/l	Na-fraction among adsorbed ions μ	Composition of expressed fluid mval/l		
				c_{Na}	c_{Ca}	Σc
WP 55	0–10	0.0	0.035	10.3	4.4	19.5
	10–20	0.5	0.104	12.0	2.2	18.3
WP 72	0–10	0.6	0.072	8.0	4.3	17.5
	10–20	0.4	0.091	10.4	4.1	20.6
WP 61	0–10	0.6	0.172	13.9	3.7	21.5
	10–20	0.6	0.179	23.3	2.3	29.5

Only on the sampling spot WP 61, where μ is higher than on the other spots, somewhat higher values for Σc are found; this is in accordance with the theory, which predicts increasing values for Σc at increasing μ (c.f. table 39, number 10 and conclusion 6).

But as most values for c_{Ca} and Σc appear to be considerably below our earlier estimates, the solubility of $CaCO_3$, in the soil moisture has obviously been over-estimated. Probably this divergence is caused by the high pH-values occurring in flooded soils, which reduces the solubility of calcium carbonate to lower values than those occurring in normal soils. As a consequence of this over-estimation also the changes in ionic composition, predicted by table 39 are too high. This however, does not alter our conclusions regarding the slightness of the effects of a direct reaction with $CaCO_3$ and the influence of different factors on the equilibria.

Thus, major changes in ionic composition will occur only if removal of the reaction products takes place by water passage. This combination of solution of $CaCO_3$ and water passage will be treated in more detail in section 5.4. Prior to this, however, the effects of two other regenerative processes of minor importance will be dealt with.

5.34. *Dissolution of other Ca compounds*

As has been pointed out in section 5.2 and especially in table 34 (sampling spots PP 1 and Sch 1), replacement of Na by Ca also occurs in non-calcareous soils. It is not unlikely that in these old pool soils, which are usually strongly acid, a slow dissolution of other Ca compounds – e.g. of Ca-containing feldspars – will occur. Moreover Ca ions may be liberated during the decomposition of organic matter, which is abundantly present in these old pasture soils. As appears from table 42 appreciable amounts of non-exchangeable Ca are found in these acid and non-calcareous soils.

TABLE 42. Amounts of Ca present in a non-calcareous, acid pool soil. Sampling spot Sch 1, polder Schakerloo, Tholen, 0–10 cm depth.

Clay $< 2\mu$ %	Organic matter %	Active matter %	$CaCO_3$ %	pH (H_2O)	Ca (mval per 100 g of active matter)				
					exchange-able	soluble in HCl			total [1]
						0.1 n	5 %	25 %	
23.1	8.4	48.3	0.0	5.4	22.7	23.7	34.7	32.8	36.8

[1] Determined by fusion with Na_2CO_3.

As appears from this table decinormal HCl is able to liberate only the exchangeable Ca from this soil, but at higher concentrations this acid is capable of extracting also part of the non-exchangeable Ca. A comparison between total and exchangeable Ca reveals that in this soil approximately 14 mval/100 g of active matter are present in non-exchangeable form. This non-exchangeable Ca may in any case be considered as a potential source of Ca ions.

But the exact management of the fields on which the two sampling spots on old-land soils (PP 1 and Sch 1) are situated, is unknown. Consequently it is impossible to decide how far the observed replacements of Na by Ca have been caused by mobilization of non-exchangeable Ca or by application of lime amendments. On the other hand it will stand to reason that in calcareous soils this mobilization of Ca from compounds other than $CaCO_3$ will only play a negligible part.

5.35. *Uptake of ions by plant roots*

We may expect that this process will be most important for ions which happen to occur in small quantities and which are adsorbed in appreciable amounts by plant roots.

Consequently this process will probably exert little influence on the amounts of exchangeable Na, Mg, and Ca ions present in flooded soils, whereas on the other hand it may cause a relatively large reduction in exchangeable K.

As has been shown by table 29 (section 4.3) the amounts of exchangeable K are increased by an inundation with salt water, viz. from approximately 3.5% of the adsorptive capacity to about 6.5%.

For the upper 20 cm of the soil this increase in exchangeable K of about 3% corresponds to a supply of 32.8 S_a kg/ha. Consequently a light soil with an exchange capacity $S_a = 15$ mval/100 g will become enriched in its topsoil with approximately 500 kg/ha of K, whereas in a heavy soil with $S_a = 30$ this amount will be twice as high. In soils flooded with brackish water, however, these gains will be substantially less.

Considering the K requirements of crops (e.g. OTTEN & VEENSTRA, 1941), it appears that under normal conditions an amount of 500 kg/ha of K will be consumed during a rotation of 3 crops of small grains and 1 crop of sugar beets. Although these figures might be slightly different for flooded soils, it may reasonably be expected that the excess amounts of K, present in light soils after an inundation, will be exhausted by a few years of cropping. Only on heavy soils these conditions will be somewhat more favourable.

These considerations are in accordance with manuring experiments carried out after the inundations and with the advices given about K dressing (WESTERHOF *et al*, 1951). For heavy soils flooded with salt water it was advised to omit K manuring for some years, whereas for light soils K dressings might be reduced. For soils flooded with brackish water, however, normal K dressings were recommended.

In view of natural regeneration of flooded soils it may therefore be stated that the uptake of K by plant roots may be an important and probably even the principal factor in reducing the excess quantities of exchangeable K.

The amounts of Na taken up by crops growing on flooded soils will on the average be of the same order of magnitude as the amounts of K. Whereas in some crops Na may exceed K (sugar beets, spring barley), in others (spring wheat, flax, peas, horse beans) the reverse will be true (VAN DEN BERG, 1952). But a Na extraction by plants comparable to the extraction of K would – even in light soils – diminish the exchangeable Na percentage in the topsoil from – say – 25 to 22 only. This change is small in comparison with the much larger decrease caused by other processes.

5.4. REGENERATIVE PROCESSES IN COMBINATION WITH REMOVAL OF REACTION PRODUCTS

If the reactions mentioned above are accompanied by removal of reaction products, they may be treated as column processes. Accordingly the changes produced, and especially the shape of the boundaries formed, will greatly depend on the shape of the adsorption isotherm. The consequences for flooded soils have already been mentioned in section 5.2, where it was pointed out that due to this effect the rear boundaries of Na should be sharper than those of Cl.

In this section special reference will be made to the velocity at which the column processes proceed. In these considerations the point at which the amounts of exchangeable ions have been reduced to half their initial value will be regarded as the main characteristic.

According to the GLUECKAUF theory for a linear adsorption isotherm, treated in section 2.31, this point will obey equation (*2.64*):

$$\bar{v} = ax = \frac{f_0}{c_0} x \qquad (5.16)$$

For a quadratic isotherm the theory – and especially equation (*2.77*) – predicts that the adsorbed ions will be reduced by half after passage of a volume $\bar{\bar{v}}$, equal to:

$$\bar{\bar{v}} = \frac{f_0}{c_0} (x - 0.882\ k) \qquad (5.17)$$

which for $x \gg k$ reduces to:

$$\bar{\bar{v}} \backsimeq \frac{f_0}{c_0} x \qquad (5.18)$$

In these equations the amounts of percolating water v should be expressed as cm^3/cm^2, the depth either as g/cm^2 of overlying soil (x) or as cm (d), the initial content of exchangeable ions f_0 as mval/g and the initial concentration in the soil moisture c_0 as mval/cm^3. Finally 2 k denoting the thickness of the theoretical plate, is expressed in g/cm^2, whereas the corresponding value 2 k′ is expressed in cm.

All these equations are only valid at depths which are substantially greater than the theoretical plate thickness.

In desalinized soils the amounts of cations held in the pore spaces are negligible compared with the adsorbed ions. Hence, for Na:

$$f_0 \backsimeq f^*_0 = \frac{\mu_0 . S_8}{100} \text{ and } c_0 = \frac{\nu_0 . \Sigma c}{1000} \qquad (5.19)$$

Moreover, if ϱ denotes the density of the soil in its natural position (g/cm^3):

$$x = \varrho\, d \backsimeq 1.4\ d \text{ and } k = \varrho\, k' \backsimeq 1.4\ k' \qquad (5.20)$$

Hence, by introducing (*5.19*) and (*5.20*) into (*5.17*):

$$\bar{\bar{v}} = \frac{14\, \mu_0 . S_8 . d}{\nu_0 . \Sigma_c} \left\{ 1 - 0.882 \frac{k'}{d} \right\} \qquad (5.21)$$

As, however, μ_0, ν_0 and Σc are mutually related by the empirical Na adsorption isotherm given by equation (*5.01*), equation (*5.21*) may also be written as:

$$\bar{\bar{v}} = 6.56\ S_8 . d . \sqrt{\mu_0} \frac{\sqrt{\log \Sigma c}}{\Sigma c} \left\{ 1 - 0.882 \frac{k'}{d} \right\{ \qquad (5.22)$$

The reduction of the amount of exchangeable Na to half its initial value corresponds with a loss of Na equal to:

$$\triangle\ \text{Na} = \frac{\mu_0}{2} . S_8 \quad \text{mval/100 g of soil} \qquad (5.23)$$

This loss is caused by an amount of passing water $\bar{\bar{v}}$ cm^3/cm^2. Consequently the loss of Na per unit volume of passing water, averaged over the entire period may be written as:

$$\frac{\triangle \mathrm{Na}}{\bar{\bar{v}}} = \frac{\nu_0 \,.\, \Sigma c}{28\, d} \frac{1}{1 - 0.882 \frac{k'}{d}} \tag{5.24}$$

or, according to equation (*5.22*) as:

$$\frac{\triangle \mathrm{Na}}{\bar{\bar{v}}} = \frac{\sqrt{\mu_0}}{13.12\, d} \frac{\Sigma c}{\sqrt{\log \Sigma c}} \frac{1}{1 - 0.882 \frac{k'}{d}} \tag{5.25}$$

The equations (*5.21*) and (*5.22*) obviously denote the volume approximately needed to reduce the initial amount of exchangeable Na by half, whereas (*5.24*) and (*5.25*) describe the average velocity at which the exchangeable Na will be removed from flooded soils.

From these equations the following conclusions may be derived:

1. The volumes $\bar{v}$ and $\bar{\bar{v}}$ needed to reduce the initial amounts of exchangeable cations by half depend on the fraction $\frac{f_0}{c_0}$ (equations *5.17* and *5.18*). For a given soil and a given concentration in the soil moisture, this fraction is proportional to the gradient of the adsorption isotherm. Under the conditions prevailing in flooded soils this gradient increases in the order Na $<$ K $<$ Mg. Consequently the reverse order may be expected for the velocity of regeneration.

2. The volumes $\bar{v}$ and $\bar{\bar{v}}$ needed for reduction by half will increase at increasing depth (x of d), indicating that the process proceeds from top to bottom.

3. All changes will be larger as more water passes through the soil. Consequently water passage will be of fundamental importance for the regeneration.

4. The volume $\bar{\bar{v}}$ needed for reduction by half will increase at increasing adsorptive capacity S_s. Consequently such a reduction will take more passing water – or more time – in heavy soils than in light ones (equations *5.21*, *5.22*). But on the other hand the average absolute losses of exchangeable Na will be independent of the exchange capacity S_s and consequently also independent of soil texture (equations *5.24*, *5.25*).

5. The volume $\bar{\bar{v}}$ needed for reduction by half will – at least for the Na ions – increase at increasing Na fraction μ_0 (equation *5.22*). But also the absolute Na losses will increase at increasing values of μ_0 (equation *5.25*). For testing the effect of μ_0 a consideration of the absolute losses is to be preferred, as in that case the otherwise dominating effect of soil texture has been eliminated.

6. The volume $\bar{v}$ needed for reduction by half will decrease at increasing values of Σc, whereas increase in Σc will likewise increase the absolute losses, as at the concentrations prevailing in flooded soils – $\Sigma c > 10$ mval/l – the changes in Σc will dominate the changes in $\sqrt{\log \Sigma c}$. In untreated calcareous soils Σc is mainly dependent upon the solubility of $CaCO_3$. After addition of gypsum, Σc may become much higher (table 55, section 6.41).

7. In some cases interference of several effects may occur. Thus in the case of regeneration by dissolution of $CaCO_3$ the values of Σc will have a tendency to be higher for high values of μ_0 (c.f. table 39, number 10 and table 41). In such cases prediction of the ultimate effect becomes very difficult.

The different conclusions mentioned above are confirmed by observational data, obtained from the field. The main features of the regeneration process – such as the relative order for the different cations involved and the downward proceeding of the process – have already been discussed (section 5.2). In this section especially the importance of water passage mentioned under 3 and the other conclusions derived above will be confronted with experimental evidence.

The fundamental importance of water passage is already obvious from the observation that no major changes in ionic composition occur during summer, when percolation is negligible. During winter, however, water passage in flooded soils may be seriously hampered by a limited topsoil permeability. Whereas in normal, well-drained new-land soils in the areas considered runoff is negligible, considerable amounts of water may be removed over the surface of flooded soils. As has been shown by Verhoeven (1953) water passage in untreated flooded soils is usually considerably lower than in gypsum treated soils: in untreated soils the annual percolation may be estimated at about half the normal value of 200 mm. Local circumstances, however, may cause large variations.

Due to the latter large differences may be expected between controls of otherwise comparable trial fields. Such differences are indeed observed; an example has been given in table 43.

Table 43. Differences in natural regeneration between two soils of similar composition. Controls of trial fields AG 8 and AG 17, 0–20 cm depth.

Trial field	Clay < 2 μ %	Organic matter %	$CaCO_3$ %	Exchangeable Na in mval per 100 g of active matter					
				1945 Autumn	1946		1947 Spring	1948 Spring	1949 Spring
					Spring	Autumn			
AG 8	24	1.6	3.2	16.4	15.2	16.8	15.2	15.4	13.8
AG 17	28	2.0	3.0	—	13.1	12.0	11.0	7.4	—

As may be seen from table 43 the changes on AG 17 are considerably greater than on AG 8, although in other respects the soils are much slike. On AG 8, where soil structure was bad, water passage has been extremely small. As follows from salinity measurements it amounted to only 180 mm over the entire period 1945–1949, corresponding with an annual average of less than 50 mm. Although water passage on AG 17 is unknown – most of its salt had already been removed before its first sampling – it may be readily assumed that the differences mentioned in table 43 are caused by a difference in water passage.

More direct evidence of this effect may be derived from laboratory leaching experiments carried out in 1941. In these experiments soils flooded in 1939–'40, contained in MITSCHERLICH pots and treated with different amendments were daily sprinkled with tap water. In one series of experiments no amendments were applied. In this control series individual differences in permeability caused large variations in water passage. In some pots the soil structure became so bad that virtually no water could penetrate, whereas in others normal water passage remained possible. As may be seen from the example given in table 44 the decrease in exchangeable Na in the upper 10 cm is closely related to the amount of water which passed through the soil during the period of observation.

TABLE 44. Differences in natural regeneration caused by differences in water passage. Leaching experiments 1941, 0–10 cm depth.

Exp. number	Clay $< 2\mu$ %	Organic matter %	$CaCO_3$ %	Water passage [1] mm	Exchangeable Na mval/100 g of active matter	
					initial	final
2	12	1.6	2.7	18	7.2	6.1
3	13	1.8	0.3	250	6.8	3.3

[1] in about 45 days.

These effects give a satisfactory explanation for the old observation that in cases of total collapse of soil structure the recovery will be extremely slow (PONSE, 1808). In such cases the low topsoil permeability will seriously hamper water passage, and the lack of percolating water will in turn retard the process of regeneration. The control of trial field AG 8, mentioned in table 43, is an example of such an extremely unfavourable case.

The differences in water passage between the individual trial fields make it difficult to prove the other effects (4 to 7 inc.) from field data. Nevertheless the available data suggest their existence. Thus, the effect of the adsorptive capacity of the soil S_s mentioned under 4 may be illustrated by the data listed in table 45. On the light soils AG 7 and AG 3 the exchangeable Na is reduced by half in about 2½ years, but the same reduction has required 5 years in the heavy soil GT 18.

TABLE 45. Differences in natural regeneration, caused by differences in soil texture. Controls of gypsum trial fields, 0–20 cm depth.

Trial field	Active matter %	Sum of exchangeable metal cations [1] mval/100 g	Exchangeable Na (mval per 100 g of active matter)					
			Winters after lay-out of trial field					
			0	1	2	3	4	6
AG 7	20	13	13.3	11.6	7.3	5.6	—	—
AG 3	20	13	14.4	15.2	11.3	5.0	2.0	—
AG 13	30	20	12.4	11.8	9.5	9.2	6.9	—
GT 18	42	27	11.3	12.2	9.8	8.3	7.2	5.4

[1] Estimated from active matter content.

The absolute Na losses from untreated flooded soils are listed in table 46, which covers all available trial fields. As appears from these data, there is a tendency for these losses to increase as active matter content increases, especially above 30%, and with increasing initial Na fraction μ_0. The first effect is not in accordance with the theory outlined above (conclusion 4), but the increasing effect of μ_0 confirms our conclusion 5.

Upon closer examination of the data it appears that the increase in Na losses with active matter content is due to a few trial fields laid out in spring 1946 on rather young, heavy new land soils, normally possessing an excellent soil structure. These trial fields show a high rate of natural regeneration, which is probably caused by a high waterpassage after flooding.

TABLE 46. Average annual Na losses (in kg/ha) from untreated flooded soils. Controls of 36 trial fields, 0–20 cm depth.

Initial Na fraction μ_0 / Active matter%	0.07–0.14	0.14–0.20	0.20–0.25	0.25–0.32	Average 0.19
< 20	270	370	430	—	360
20–30	270	370	320	370	330
< 30	350	530	510	480	470
Average	290	420	420	430	390

From this table, based upon a large observational material, the average annual Na losses from untreated soils appear to be 390 kg/ha at an average initial Na fraction of 0.19.

In untreated soils, Σc is mainly dependent upon the solubility of $CaCO_3$, which may be regarded as rather constant. All efforts to raise this solubility – and consequently to promote regeneration – by adding large amounts of farmyard manure or other organic materials to the soil have not met with much succes (c.f. section 6.2). Therefore the influence of Σc cannot be derived from the observations made on untreated flooded soils.

Hitherto only the qualitative aspects of the regeneration have been considered. *To get more quantitative information the values of* $\bar{v}$ *and* $\bar{\bar{v}}$ *can be calculated by* estimating the other entities occurring in the equations mentioned above. In order to estimate regeneration velocities, however, these values for v should be transformed into a time-scale.

For this conversion we assume that during the first years after drainage bad topsoil structure will restrict water passage in untreated soils to 100 mm annually, except for the first year when the still saline soil may permit the passage of slightly higher amounts. After some years, however, soil structure will improve, so that the annual water passage will gradually approach the normal value of 200 mm. Hence, as a tentative approach, the relation, given by table 47 will be used for transforming the calculated values for $\bar{v}$ or $\bar{\bar{v}}$ into a time-scale.

TABLE 47. Assumed relation between time and water passage in untreated flooded soils.

Years after drainage	Water passage cm^3/cm^2		Years after drainage	Water passage cm^3/cm^2	
	annual	total		annual	total
1	15	15	6	20	90
2	10	25	7	20	110
3	10	35	8	20	130
4	15	50	9	20	150
5	20	70	10	20	170

As an example a calcareous flooded soil will be considered, in which $S_a = 20$ mval/100 g, $A = 30$ ml/100 g and $\mu_0 = 0.20$. After desalinization the total ionic concentration will be assumed to be $\Sigma c = 20$ mval/l. We further assume that the Na ions will follow the quadratic adsorption isotherm given by equation (*5.01*), and we suppose K and Mg to obey linear isotherms with slopes of 0.5 and 1.0 respectively (c.f. figs. 25 and 26, section 3.7).

As only the order of magnitude is involved the simple equations (*5.16*) and (*5.18*) will be used, even for depths as shallow as $d = 10$ cm. Moreover the amounts of ions present in the soil solution are negligible compared with the amounts of adsorbed ions, with the exception of Cl. With these data and by using the conversion-table 47 the times needed to reduce the amounts of Cl and exchangeable Na, K and Mg to half their initial values may be calculated. These calculated times are recorded in table 48; as a matter of fact these values are only a rough approximation.

TABLE 48. Times needed to reduce the excess amounts of Cl, Na, K, and Mg in an untreated calcareous flooded soil to half their initial values.
Calculated for a soil with $S_a = 20$; $A = 30$; $\Sigma c = 20$; $\mu_0 = 0.20$.

Depth cm	Time (years)			
	Cl	Na	K	Mg
10	¼	3	5	8
20	½	5	8	15
30	1	7	12	22
50	2	10	18	35
70	2½	13	26	50

As appears from table 48, Cl will be readily removed from the soil, whereas the reduction of the exchangeable Na will proceed at a much lower rate. In the subsoil the excess amounts of exchangeable Mg will even persist for decades. Therefore it may be expected that former inundations can be easily recognized by the occurrence of high amounts of exchangeable Mg in the subsoil for periods up to half a century. This conclusion is confirmed by the observations: nearly 50 years after an inundation appreciable amounts of exchangeable Mg can still be observed in the subsoil (table 49).

TABLE 49. Ionic composition of a soil flooded half a century ago in comparison with an unflooded soil.

Sampling spot	Polder	Year of sampling	Years after inundation	Depth cm	Exchangeable cations %			
					Na	K	Mg	Ca
WP 17 a	Wilhelmina	1943	unflooded	0–20	0.4	2,9	2.2	94.5
				50–80	0.5	1.0	3.9	94,6
St B 1	Bath	1952	46	0–20	0.9	3.2	9.8	86.1
				60–80	1.5	1.2	19.1	78.2

For the Na ions more accurate estimates are possible, as the Na adsorption isotherms are much better known than those of K and Mg. Experimentally it has been found from observations of 36 controls of trial fields that the annual Na losses from the upper 20 cm averaged 390 kg/ha at an average initial Na fraction $\mu_0 = 0.19$ (table 46).

Theoretically these Na losses may be calculated by using equation (*5.25*). Inserting the values $\mu_0 = 0.19$, $d = 10$ cm, assuming Σc to be 20 mval/l and $2\,k' = 5$ cm, and supposing that during the first few years after drainage the annual water passage averages 125 mm, it may be calculated that the annual Na losses from the upper 20 cm should be approximately 600 kg/ha. Although this theoretical value is of the same order of magnitude as the experimental value of 390 kg/ha, it is obviously far too high. This difference between theory and experiment is probably due to the disturbing effects of soil tillage. Another possibility is that the assumed value of $\Sigma c = 20$ mval/l is still too high. With the value $\Sigma c = 15$ mval/l an annual Na loss of 470 kg/ha is found, but in view of the data listed in table 41, section 5.33 this assumption seems hardly justified.

Therefore it may be concluded that the theory of column operation, though giving a good explanation of the phenomena observed, is unable to predict the exact value of the rate of regeneration in flooded soils.

5.5. REDUCTION IN $CACO_3$ CONTENT DURING THE REGENERATION PERIOD

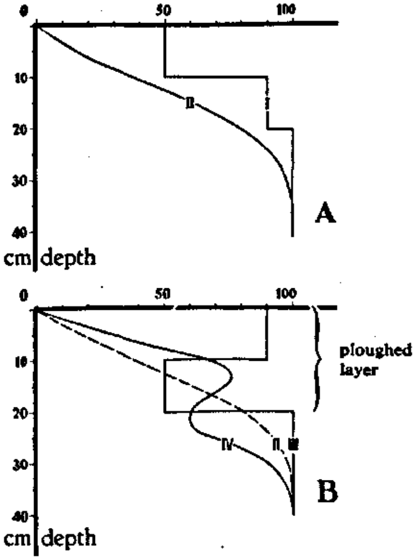
As natural regeneration in flooded soils is mainly caused by dissolution of $CaCO_3$ and subsequent ionic exchange reactions, it will be accompanied by a decrease in $CaCO_3$ content of the soil. As has been shown in table 46 (section 5.4) the average annual Na losses from flooded soils amount to 390 kg/ha, which is equivalent to 850 kg/ha of $CaCO_3$. For the upper 20 cm of the soil these losses correspond with a decrease in $CaCO_3$ content of 1% in 33 years, which is about twice as high as in normal soils (section 3.3). But during the relatively short period of regeneration the $CaCO_3$ losses will be rather small and of the order of 0.1%. Thus, on the controls of 11 trial fields, observed for a period of 5–7 years, the average total $CaCO_3$ losses amounted to 0.11 ± 0.09%. No wonder that such small losses could not be reliably estimated from a comparison between the $CaCO_3$ contents shortly after drainage and those found a few years later.

5.6. EFFECTS OF SOIL TILLAGE

In the foregoing sections the disturbing effects of soil tillage have already been mentioned. Ploughing will seriously interfere with the process of regeneration: soil already improved will be buried by soil still possessing an unfavourable ionic composition.

Although a thorough theoretical treatment is not yet possible for ions adsorbed with a curvilinear adsorption isotherm, it will be clear that regeneration of the topsoil will be delayed by ploughing, as the excess Na brought to the surface must first be removed before further progress can be made. On the other hand it may be expected that the regeneration of the layers underlying the ploughed soil will be slightly accelerated, as these layers will receive soil moisture from the original topsoil, which is relatively low in exchangeable Na.

These phenomena may be investigated theoretically for ions adsorbed with a linear isotherm, as in that case the principle of superposition may be used. In this way both the retarded regeneration of the ploughed layer and the accelerated recovery of the layer immediately underneath may be demonstrated. An example of these phenomena is given by fig. 46.



I: Initial boundary, untilled soil
II: Final boundary, untilled soil
III: Initial boundary, ploughed soil
IV: Final boundary, ploughed soil

A: Untilled soil
B: Ploughed soil

FIG. 46. Theoretical rear boundaries in an untilled soil in comparison with a soil in which the layers 0–10 and 10–20 cm have been reversed by ploughing. Calculated for a linear adsorption isotherm

In practical cases the turning up of Na-rich soil by ploughing may even cause a renewed breakdown of soil structure. This emphasizes the importance of shallow ploughing, as already recommended by PONSE (1808).

As the advice of shallow ploughing was nearly always put into practice by the farmers concerned, ploughing depths on the trial fields were also usually limited to 10–12 cm. As in most cases these fields were sampled in layers of 10 cm thickness, the effects of soil tillage could not be derived from the data obtained in this way. Only on one trial field, which had been flooded with brackish water, a reversal of the normal course of the Na boundary was observed; this reversal was caused by ploughing to a depth of about 20 cm. As the soil in question was low in exchangeable Na this deep tillage had no detrimental effects on soil structure. As appears from table 50 the Na boundary, after being reversed in autumn 1947, had regained its normal course after one winter. During this period the decrease in exchangeable Na has been low in the layer 10–20 cm – the former topsoil – and remarkably high in the underlying unploughed subsoil, in accordance with the views developed above.

TABLE 50. Effect of soil tillage on the regeneration of a flooded soil. Control of trial field AG 10, polder Dirksland, Overflakkee [1].

Depth cm	Exchangeable Na (Na_a) mval per 100 g of active matter			Decrease in winter 1947–1948
	12-4-1947	7-10-1947	17-3-1948	
0–10	2.8	3.9	1.4	2.5
10–20	4.3	3.4	2.2	1.2
20–40	5.5	6.1	4.2	1.9

[1] Active matter content 26%.

Thus it has been shown in the foregoing sections that natural regeneration of calcareous, flooded soils is chiefly caused by dissolution of $CaCO_3$ and subsequent reaction with the exchangeable cations. This reaction, however, will proceed to a measurable extent only if the reaction products are removed by passing water, but even then it is rather slow. From the theory of column operation an estimate of the velocity of the process can be made. This estimate is of the same order as the observed rate of regeneration. Soil tillage has a retarding effect.

6. METHODS OF PROMOTING REGENERATION

Although in the course of time natural regeneration will restore normal soil conditions, its rate, especially in heavy soils, is so slow that agriculture is badly hampered for many years. Therefore promotion of the regeneration-process is of great practical importance. Already PONSE (1808) has proposed several treatments for this purpose; among other things he advised the growing of perennial crops like grass and clovers. In a later paper (PONSE, 1825) he suggested application of slaked lime on a trial scale. Moreover he noticed that organic manuring had only little effect.

As has been mentioned in the first chapter, MAYER (1879 *b*) observed some improvement after application of sulphuric acid, and in the Netherlands the use of gypsum was introduced by HISSINK in 1918.

Most of these treatments, together with some others, have been tested by field trials after the inundations of 1939–'40 and 1944–'45. From these experiments it appeared that growing perennial crops, organic manuring and application of slaked lime were of little practical use, but dressings with more soluble calcium compounds like calcium chloride or gypsum proved quite successful. Moreover excellent results were obtained by adding sulphur to calcareous flooded soils.

In this chapter the effects of these different treatments will be discussed. As gypsum is most commonly used, it will receive most attention. This discussion on the effects of gypsum, however, will be preceded by a short review of the effects of perennial crops, organic manuring and liming, and be followed by a discussion on the effects of other chemicals. Finally the practical aspects of gypsum application will be reviewed; this discussion will mainly concern the technique of application and the amounts to be used.

6.1. EFFECTS OF PERENNIAL CROPS

The use of perennial crops for promoting natural regeneration of flooded soils has been studied on a series of G.V.-trial fields, a diagram of one of which is represented in fig. 2, section 1.2. On these fields the effects of growing grass[1], red clover (*Trifolium pratense* L.) and lucerne (*Medicago sativa* L.) were compared; part of these fields also received a gypsum dressing.

A comparison of the exchangeable Na contents of the plots not treated with gypsum, reveals that in most cases natural regeneration has been highest under grass and lowest under lucerne (table 51). Moreover it appeared from field observations that soil structure was usually much better under grass than under clover or lucerne, which was probably due to the preservation of soil structure by the shallow root system of the grasses. In many cases the clover and lucerne crops sown too late in autumn 1945 were a failure and had to be resown the next spring; probably this complication has contributed to the differences observed.

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[1] The grass plots had been sown with a mixture of *Lolium perenne* (28%), *Phleum pratense* (13%), *Poa pratensis* (19%), *Agrostis stolonifera* (9%), *Festuca rubra* (17%) and *Trifolium repens* (14%).

TABLE 51. Effects of different perennial crops on the exchangeable Na content of flooded soils. Controls of G.V. trial fields, 0–10 cm depth.

Trial field	Time of lay-out	Exchangeable Na Na^1_a in spring 1947			Sequence of Na_a-figures in spring 1947
		G[2]	R[2]	L[2]	
GV 2	autumn 1945	2.7	3.8	3.4	$G < L < R$
GV 5	autumn 1945	4.9	5.6	6.0	$G < R < L$
GV 8	autumn 1945	9.9	10.5	11.4	$G < R < L$
GV 9	autumn 1945	5.1	4.0	5.6	$R < G < L$
GV 11	autumn 1945	4.5	6.1	6.4	$G < R < L$
GV 14	autumn 1945	0.9	1.8	2.4	$G < R < L$
GV 19	summer 1946	2.1	2.3	2.3	$G < R = L$
GV 20	summer 1946	1.0	1.5	0.9	$L < G < R$

[1] mval per 100 g of active matter.
[2] G = grass; R = red clover; L = lucerne

The differences in exchangeable Na content mentioned in table 51 may either result from or be the cause of differences in soil structure. Measurements of soil salinity on trial field G.V.11 however, suggest that the observed differences in natural regeneration have primarily been caused by differences during the first winter in water passage; these have in turn arisen from differences in soil structure. As appears from table 52 salt content (B) and salt concentration (C) were markedly lower on the grass-grown plots than on those carrying clover or lucerne.

TABLE 52. Differences in soil salinity under different perennial crops. Controls of trial field G.V. 11, Herenpolder, Overflakkee; 1-10-1946.

Crop	Depth cm	A[1] ml/100 g	B[2] g/100 g	C[3] g/l
Grass	0–10	21.6	0.01	0.9
	10–20	23.3	0.04	1.7
Red clover	0–10	23.1	0.02	1.1
	10–20	22.8	0.07	3.1
Lucerne	0–10	22.8	0.02	1.1
	10–20	22.1	0.06	2.9

[1] Moisture content of soil.
[2] Cl content of soil, expressed as NaCl.
[3] Cl concentration in the soil moisture, expressed as NaCl.

A direct comparison between the effects of perennial crops on the one hand and annuals on the other is not possible as no annual crops were included in the G.V. trials. Therefore such inquiry must be carried out by comparing the rates of regeneration between the untreated plots of the G.V. fields and the controls of other trial fields. With the exception of G.V.11, however, the period of observation of the fields from the G.V.-series has been too short to make a reliable estimate of the regeneration rate under perennial crops.

On the trial field G.V.11, which has been observed for five years, the decrease in exchangeable Na caused by natural regeneration is equivalent to an annual loss of Na from the upper 20 cm of 520 kg/ha. As appears from fig. 47 the mutual differences between grass, clover and lucerne chiefly originated during the first winter after drainage. The nearly parallel course of the lines in fig. 47 proves that afterwards the water passage under these crops has been virtually the same.

The losses of exchangeable Na on G.V.11 are of the same order of magnitude as the average Na losses from the controls of other series of trial fields, which amounted to 390 kg/ha (c.f. table 46, section 5.4). The slightly larger rate of regeneration on G.V.11 might be due to the absence of the disturbing effects of soil tillage on this field or to a somewhat higher water passage.

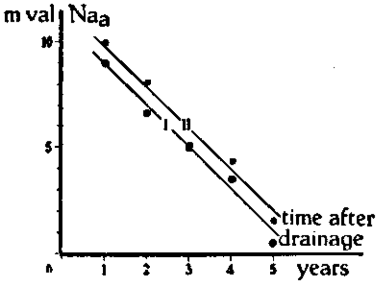

FIG. 47. Effects of different perennial crops on the natural regeneration of a flooded soil.
Trial field GV 11, Heerenpolder. No gypsum added

From the foregoing it is concluded that under perennial crops the rate of regeneration may be expected to be slightly higher, though the difference is by no means a spectacular one. Therefore it may be stated that PONSE's advice is not justified by a substantial promotion of regeneration, but that its main advantage lies in avoiding the troubles attached to soil tillage for a couple of years. In the meantime natural regeneration will be able to bring about a considerable improvement in soil conditions.

After the 1945 inundations perennial crops, especially lucerne, were grown on a fairly large scale. But, as in the G.V. experiments, the results were disappointing, especially in comparison with the much better results of gypsum. Thus, after the floodings of 1953, this method of treating flooded soils was no longer applied on any scale.

6.2. EFFECTS OF ORGANIC MANURING

Application of organic matter to flooded soils, even in excessive quantities, has never met with much succes (PONSE, 1808; RAPPORT, 1945; HARMSEN).

After the floodings of 1939–'40 and 1944–'45 field experiments were laid out, including heavy dressings with farmyard manure or crop residues. Although these experiments have been elaborately discussed elsewhere (RAPPORT, 1945; HARMSEN) a short review of the results will be given here.

As has been observed by HARMSEN addition of organic substances to flooded soils resulted in a marked increase in CO_2 production. It might be expected that this increase would promote the solution of $CaCO_3$, resulting in a more rapid regeneration. From the field experiments, however, it appeared that organic manuring could only bring about minor improvements in soil structure, which were quite negligible against those observed after gypsum or sulphur dressings. Although no determinations were made of the exchangeable Na contents on these trial fields, the relation between soil structure and ionic composition is close enough to draw the same conclusion with respect to exchangeable Na.

In soils with good and even moderate structure the gaseous exchange between the soil air and the atmosphere is obviously efficient enough to prevent high CO_2 concentrations, even at high production levels. In soils with collapsed structure, gaseous exchange will be impeded – as is reveiled by signs of reduction in such soils – but at the same time water passage also will be badly hampered, so that the increased Ca concentration in the soil moisture will have little effect. Moreover, as appears from table 38, section 5.33, a tenfold increase in CO_2 concentration – viz. from 1 to 10% – will only result in a twofold increase in $CaCO_3$ solubility. Finally CO_2 production will be low in winter, when water passage is maximal [1].

6.3. EFFECTS OF MARL AND SLAKED LIME

Slaked lime, $Ca(OH)_2$, will readily change into the carbonate if applied to soils of high pH. Although the finer division of the $CaCO_3$ precipitated in this way might be an advantage, its effects in these soils may be expected to be similar to those of marl, $CaCO_3$. Therefore it stands to reason that application of these lime amendments is of little use for soils already containing natural $CaCO_3$. Consequently most experiments with lime amendments have been carried out on non-calcareous soils, though slaked lime has also been included in a few trials on calcareous soils (c.f. section 6.5).

On *non-calcareous soils* the Na reducing effects of slaked lime and marl, although unmistakable, are only slight and in any case much less pronounced than the effects of a comparable weight of gypsum (table 53).

This difference is the more striking as a given weight of pure slaked lime will contain more than twice as much Ca as an equal amount of pure gypsum. On the trial fields, where crude products were used, the difference in purity – with gypsum possessing the lowest grade – accentuates the difference.

As a matter of fact addition of lime raises pH values in cases that the treated soils were distinctly acid (table 54).

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[1] In India good results are reported from green manuring followed by rice (JOACHIM, 1941). Under these conditions the organic matter will decay under anaerobic conditions and the carbon dioxide liberated cannot escape into the atmosphere. In combination with some water passage, regeneration may proceed at noticeable speed.

TABLE 53. Effects of slaked lime, marl and gypsum on the amounts of exchangeable Na in non-calcareous flooded soils.
G.T. and S.M. trial fields, 0–20 cm depth.

Trial field	Time of sampling	Winters after lay-out	Amendment used	Amount t/ha	Exchangeable Na Na_a [1]	Remarks
GT 15	spring 1947	2	none slaked lime gypsum	— 8 6½	6.5 5.0 3.8	Arable land on creek ridge [2]
GT 30	spring 1948	3	none slaked lime gypsum gypsum	— 8 4 10	6.0 5.6 3.4 2.5	Arable land on creek ridge [2]
SM 4	spring 1948	2	none slaked lime marl gypsum gypsum	— 6 8 4½ 9	5.4 5.2 5.1 4.3 4.1	Pasture on slightly acid pool soil [3]

[1] mval per 100 g of active matter.
[2] Non-calcareous; pH between 6.5 and 7.0.
[3] C.f. table 54.

TABLE 54. Effects of slaked lime, marl and gypsum on pH of a slightly acid pool soil, two years after their application.
Trial field SM 4, polder Walcheren, spring 1948, 0–10 cm depth.

Amendment	none	gypsum		marl		slaked lime	
tons/ha	—	4½	9	4	8	3	6
pH	*5.6*	*5.6*	*5.2*	*6.9*	*7.0*	*6.9*	*7.3*

On calcareous soils the Na-reducing effects of slaked lime were almost imperceptible (c.f. table 63, section 6.5).

The low efficiency of lime dressings for reducing the amounts of exchangeable Na in flooded soils is in accordance with the observations on soil structure on the trial fields mentioned. Application of lime amendments never resulted in any noteworthy improvement in soil structure (WESTERHOF).

6.4. EFFECTS OF GYPSUM

From a practical point of view gypsum application is of outstanding importance as a means of promoting the regeneration of flooded soils. Gypsum may occur naturally in newly drained *slik* soils (ZUUR, 1952), it may be formed in the soil after addition of elementary sulphur, or it may be added as such.

In the discussion of the effects of gypsum distinction will be made between local reactions and reactions occurring in combination with water passage. As will be shown in the next sections it makes a great difference whether gypsum is applied as a top-dressing – like after the treatment of flooded soils – or whether it is formed in the soil itself, like in newly drained slik soils. Moreover it is of importance whether gypsum is present in excess quantities or not. Though from a theoretical point of view the former case, in which a saturated solution is formed, is the most interesting one, the amounts usually applied to flooded soils are insufficient to maintain this condition for more than 1–2 years. They are generally even too small to replace all exchangeable Na from the upper 20 cm of the soil. Under these conditions, it is of considerable practical importance to know the efficiency with which the added gypsum replaces these Na ions.

The subjects mentioned above will be treated in more detail in the following sections. A review of the practical sides of gypsum application will be postponed until section 6.7.

6.41. *Local effects*

In soils containing an excess of solid gypsum the solubility of this compound will determine the Ca concentration in the soil moisture and ultimately the rate of changes in ionic composition. To calculate these changes the same equations may be used as for the reaction of a flooded soil with dissolving $CaCO_3$, viz. equations (*5.06*) to (*5.12*) for the local effects and (*5.16*) to (*5.25*) for column processes.

For drawing quantitative conclusions it is necessary to estimate the solubility of gypsum in the soil moisture of flooded soils. As for $CaCO_3$, different methods of approach are available.

The solubility of gypsum may be estimated in the following ways:

1. From the well-known solubility of $CaSO_4$ in the presence of $CaCO_3$ in water containing carbon dioxide. This solubility will give rise to a Ca concentration of 35.0 mval/l at a partial pressure of CO_2 of 0.121 atm. and at 25° C (SEIDELL).
2. From the maximal Ca concentrations in the expressed fluid of calcareous, newly embanked slik soils. In such soils gypsum will usually be formed in such abundance that its crystals appear in the soil. From analysis of such soils the maximal Ca concentrations in the soil moisture were found to be approximately 40 mval/l (table 55). Furthermore, SO_4 concentrations are still considerably higher, as exchange reactions result in the formation of the highly soluble salts Na_2SO_4 and $MgSO_4$.

TABLE 55. Maximal Ca concentrations, simultaneously observed SO_4, and total ionic concentrations in the expressed fluid of a newly drained slik soil.
Sampling spot M 21, Noordoostpolder, drained 1941.

Depth cm	Ca_{max} mval/l	SO_4 mval/l	Σc mval/l	Time at which Ca_{max} was observed
0– 5	39.7	71.5	129.6	spring 1943
5–10	33.8	54.8	82.2	spring 1943
10–20	36.3	63.4	90.9	spring 1943
20–50	32.3	50.0	62.0	spring 1946
50–80	40.2	88.6	114.2	spring 1946

3. From the maximal Ca concentrations observed in the expressed fluid of flooded soils treated with heavy gypsum or sulphur dressings. In such soils the maximal Ca concentration observed amounted to 39.0 mval/l (trial field De Koeyer, polder Nieuw Olzende, summer 1942).

Thus, the concentration of Ca ions in soils containing solid gypsum may be estimated at approximately 40 mval/l.

As an example the local effects of gypsum will be calculated for a calcareous flooded soil after its desalinization. Prior to the gypsum dressing such a soil will be in equilibrium with $CaCO_3$. After addition of gypsum a new equilibrium will be set up, which may be calculated according to equations *(5.06)* and *(5.12)*. The results of such a computation, starting from an observed equilibrium, are given in table 56.

A difficulty in these calculations is the value of the fraction K + Mg in the soil solution, λ. As a first approximation λ is assumed to remain constant. There is some experimental evidence in favour of this supposition, rather than for the alternative assumption that the absolute amounts of K and Mg in solution would remain the same.

TABLE 56. Calculated changes in ionic composition, caused by local action of gypsum. Initial state: Sampling spot W.P. 61, polder Wilhelmina, May 1945 [1].

Depth cm	State	Adsorptive capacity S_a mval/100 g	Moisture content A ml/100 g	c_{Ca} mval/l	Fraction K+Mg in solution λ	Fraction Na among the ions		Total concentration of soil solution Σc mval/l
						adsorbed μ	in solution ν	
0–10	Initial [2]	14.1	26.3	3.7	0.177	0.172	0.646	21.5
	Final [3]	14.1	26.3	40.0	0.177 [4]	0.099	0.468	113.–
10–20	Initial [2]	13.7	23.6	2.3	0.129	0.179	0.790	29.5
	Final [3]	13.7	23.6	40.0	0.129 [4]	0.119	0.514	112.–

[1] C.f. table 41, section 5.33.
[2] Before addition of gypsum; observed.
[3] After addition of gypsum; calculated.
[4] Estimated.

As appears from table 56 application of gypsum may be expected to result in a marked decrease in exchangeable Na. Naturally the local effects of gypsum will be more pronounced than those of the less soluble $CaCO_3$. But on the other hand the bulk of the exchangeable Na still remains; these ions may only be removed in combination with water passage.

Another consequence of the addition of gypsum is a large increase in total ionic concentration of the soil solution, viz. from approximately 25 to over 100. These calculated values for Σc are in accordance with those observed in soils containing solid gypsum (c.f. table 57).

In the field addition or formation of gypsum in excess quantities appears to produce only minor changes in ionic composition. The best examples of these local effects of gypsum are found in newly drained, calcareous slik soils, where large amounts of gypsum are formed. An example of the changes caused by this oxidation process is to be found in table 57.

TABLE 57. Changes in ionic composition caused by formation of gypsum in a newly drained slik soil.
Trial field Kraggenburg, Noordoostpolder, summer 1939, 10–20 cm depth[1].

Group of analyses	Analyses	11-4-1939	16-8-1939
Salinity	A[2] ml/100 g	46.4	36.6
	B[3] g/100 g	0.08	0.08
	C[4] g/l	1.7	2.2
Expressed fluid	Na mval/l	29.3	53.5
	K mval/l	1.1	3.7
	Mg mval/l	11.8	43.2
	Ca mval/l	10.2	44,4
	Σc mval/l	52.4	144.8
Sulphates	in soil moisture g/100 g	0.04	0.16
	soluble in excess H_2O g/100 g	0.06	0.30
Exchangeable cations %	Na	11.1	9.7
	K	7.2	6.7
	Mg	42.6	35.6
	Ca	39.1	48.0

[1] Drained in autumn 1938.
[2] Moisture content of soil.
[3] Cl content of soil, expressed as NaCl.
[4] Cl concentration of soil moisture, expressed as NaCl.

As appears from the salinity data, especially from the constancy of the amount of Cl ions present in the soil – B –, neither water passage nor capillary rise was important between the two dates of sampling. But on the other hand the composition of the soil moisture was fundamentally changed. In the spring of 1939 the soil – which was drained in autumn 1938 – was still in a reduced state. During the summer of 1939 oxidation of ferrous sulphides resulted in the formation of large amounts of gypsum. Consequently large increases in the ionic concentrations were observed. Initially only minute quantities of SO_4 were present in the soil. At the second sampling date, however, the soil contained 0.30% of water-soluble sulphates, of which only half was actually in solution. Consequently the soil solution must have been saturated with gypsum.

But the effects of the considerable changes in the composition of the soil moisture on the ionic composition of the soil, though unmistakable, were not very large. Remarkably enough, the changes did not only include an exchange of Na against Ca, but also a marked replacement of K and Mg ions by Ca.

In the treatment of flooded soils the gypsum is usually applied as a surface-dressing; in fact it proved to be highly undesirable to work it into the soil. Such a dressing does not exert great influence on the ionic composition of the soil, unless in combination with water passage. This is confirmed by observations on AG trial fields, from which it appeared that spring application of gypsum did not much change the ionic composition of the upper 10 cm during the next summer. Some examples of these observations have been given in table 58. As appears from these data spring application of gypsum caused some decrease in exchangeable Na during the summer of 1946, but it had virtually no effect during the summer of 1947. This difference must be ascribed to a slight water passage in the wet summer of 1946, whereas in the dry summer of 1947 no water passage occurred.

TABLE 58. Effects of spring gypsum dressings on the amounts of exchangeable Na observed next autumn.
A.G. trial fields. 0–10 cm depth.

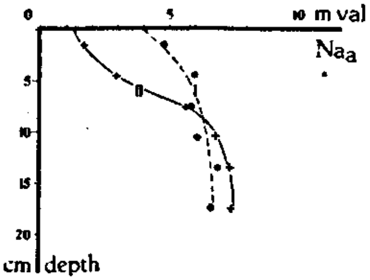
Trial field	Difference in Na_a [1] found in autumn between control and spring application of 12 t/ha of gypsum	
	1946	1947
AG 3	+ 3.4	— 0.3
AG 7	+ 2.0	+ 0.5
AG 8	+ 2.5	— 0.2
AG 10	+ 0.9	— 0.3
AG 12	+ 2.3	+ 0.3
AG 13	+ 4.1	+ 0.3
AG 14	+ 2.0	— 0.2

[1] mval per 100 g of active matter.

These conclusions about the inefficiency of spring gypsum dressings for reducing exchangeable Na during the next summer are at first sight in contradiction with the great practical importance of such dressings for preventing structural breakdown of the seed-bed during showers. But for this purpose an improvement of the upper few cm only will be sufficient. For improving soil conditions in deeper layers, however, water passage is indispensable.

6.42. *Effects of excess amounts of gypsum in combination with water passage*

Except for their higher rate the processes caused by gypsum application in combination with water passage resemble those observed during natural regeneration (section 5.4). Thus the improvements will proceed downward through the soil profile (fig. 48), and their velocity will depend on factors like water passage and soil texture.



I: control
II: 4 t/ha of crude gypsum, applied in autumn 1953

FIG. 48. Effects of gypsum application to the relation between exchangeable Na and depth. Trial field GT 58, polder Middelland, Tholen, spring 1954

The same equations (*5.16*) to (*5.25*), derived for natural regeneration, may be employed for calculating the effects of gypsum in combination with water passage, at least as long as excess solid gypsum is present.

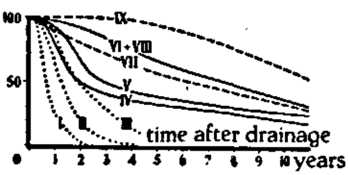
In evaluating these effects distinction should be drawn between soils containing excess solid gypsum throughout and soils which had received a top-dressing. In the presence of solid gypsum the total ionic concentration of the soil moisture will be of the order of 100 mval/l (c.f. table 57, section 6.41), whereas a top dressing will cause the soil to be leached with a saturated solution, containing approximately 40 mval/l of ions.

In gypsum-dressed soils runoff is minimal; consequently water passage will be considerably higher than in untreated soils: for well drained, gypsum-treated soils it may be estimated at 200 mm annually. Therefore gypsum does not only accelerate the regeneration by removing the Na, K and Mg ions from their adsorption seats, but also by improving water passage.

As an example of the rate of regeneration in a gypsum-saturated soil the changes in ionic composition in the trial field Kraggenburg will be calculated according to the principles mentioned above, after which these calculated changes will be compared with the actually observed ones.

In this example the following values will be used:
$S_s = 16.8$ mval/100 g; $A = 35$ ml/100 g; $\Sigma c = 100$ mval/l, which values are based upon experimental data. A difficulty is that the moisture content A in this newly drained soil is considerably decreasing during the regeneration period; the value chosen must be considered as a fair average. Also Σc is subject to considerable changes; the assumed value is a first approximation.

For Na, equation (*5.22*) has been used with $\mu_0 = 0.10$, $2\ k' = 5$ cm, whereas K and Mg were supposed to possess linear adsorption isotherms with a slope of 1.5 (c.f. fig. 25 and 26, section 3.7). As only the order of magnitude is involved in these calculations, the simple equation (*5.16*) has been employed for K and Mg. Water passage was assumed to amount to 200 mm annually. In this way theoretical values for $\bar{v}$ and $\bar{t}$ were obtained. In table 59 these values are compared to the observed times of halving, found from curves in which the amounts of exchangeable cations had been plotted against time (fig. 49).



I: Na 0—20 cm
II: Na 20—50 cm
III: Na 50—80 cm
IV: Mg 0—20 cm
V: Mg 20—50 cm
VI: Mg 50—80 cm
VII: K 0—20 cm
VIII: K 20—50 cm
XI: K 50—80 cm

FIG. 49. Relative decrements of exchangeable Na, K and Mg in a newly drained slik soil.
Trial field Kraggenburg, Noordoostpolder, 1938-1949.
Initial contents put at 100

TABLE 59. Volumes of passing water and times needed to reduce the amounts of exchangeable Na, K, and Mg in a newly drained slik soil to half their initial values. Calculated and observed for trial field Kraggenburg, Noordoostpolder, with $S_s = 16.8$; $A = 35$; $\Sigma c = 100$; $\mu_0 = 0.10$; $2\ k' = 5$.

Depth cm	Average depth d cm	$\bar{v}$ (cm)			$\bar{t}$ (years)					
		Na	K	Mg	Na		K		Mg	
		calc.	calc.	calc.	calc.	obs.	calc.	obs.	calc.	obs.
0–20	10	3.8	35	35	0.2	0.7	1.8	6	1.8	2
20–50	35	16.2	125	125	0.8	1.3	6	7.5	6	3
50–80	65	31.0	230	230	1.5	2.0	11	11	11	8

As appears from table 59 the changes in ionic composition were extremely rapid in comparison to those occurring in untreated flooded soils (c.f. table 48, section 5.4). The calculated values are of the right order of magnitude, but they do not predict the observed difference between K and Mg. The reduction in exchangeable Mg was larger than in K, so that under these circumstances the sequence of the adsorption affinities was obviously Na $<$ Mg $<$ K. Probably the difference with natural regeneration of flooded soils, in which this sequence is as Na $<$ K $<$ Mg, is caused by the valency effect. According to this effect the bivalent Mg ion will be less strongly adsorbed in equilibria with more concentrated solutions.

As has already been mentioned, the ionic concentrations Σ c will be considerably lower in soils which had received a heavy top-dressing with gypsum. It may therefore be expected that top-dressing, even in excessive amounts, will not cause such rapid changes in ionic composition as those observed in soils containing excess solid gypsum throughout. On the trial fields on flooded soils, however, the gypsum dressings given were usually far from excessive and in most cases not even sufficient to replace all exchangeable Na present in the upper 20 cm. Only in a few cases on light soils gypsum has been given in excess. The following example will refer to such a case, viz. to the trial field AG 3, treated with 12 t/ha of crude gypsum.

In this example the following values will be used: $S_s = 14.5$; $A = 23.4$; $\Sigma c = 40$ mval/l; $\mu_0 = 0.20$; $2\ k' = 5$ cm; $d = 10$ cm. Hence $\bar{v}$ may be calculated according to equation (*5.22*).

In table 60 the calculated value of $\bar{t}$ as derived from $\bar{v}$ has been compared with the observed time of halving, obtained by plotting exchangeable Na content against time (fig. 50).

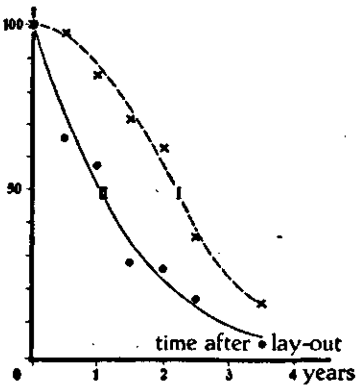


FIG. 50. Relative decrements of exchangeable Na in a calcareous flooded soil dressed with excess gypsum.
Trial field AG 3, polder Nieuw Bommenede, Schouwen, 0–20 cm depth.
Initial content put at 100

TABLE 60. Volume of passing water and time needed to reduce exchangeable Na in a gypsum-treated flooded soil to half its initial value. Calculated and observed for trial field AG 3, polder Nieuw-Bommenede, Schouwen. Treated with 12 t/ha of crude gypsum [1].

Depth	Average depth d cm	$\bar{v}$ (cm) Na	$\bar{t}$ (years) Na	
		calc.	calc.	obs.
0–20	10	10.5	0.5	1.3

[1] Containing approximately 6.5 t/ha of $CaSO_4 . 2\ H_2O$.

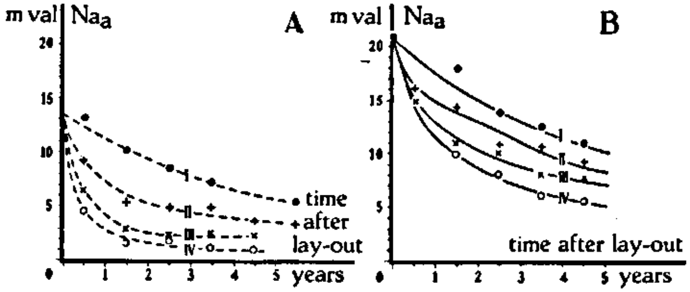
It is clear that in this case the changes have been less rapid than in a newly drained slik soil (c.f. table 59, although the cases are not quite comparable). Nevertheless the changes in ionic composition have been much accelerated by the treatment employed (fig. 50).

The difference between the calculated and the observed values for $\bar{t}$ is possibly due to irregularities in the distribution of gypsum, through which complete saturation of the percolating water was not reached always or everywhere.

6.43. *Effects of smaller amounts of gypsum*

As a rule the gypsum dressings applied on the trial fields and in practice were much smaller than those treated in the foregoing section. Usually the amounts given were insufficient to replace all exchangeable Na present in the upper 20 cm of the soil.

Consequently, in such cases the gypsum given is only able to cause a partial regeneration. Usually application of relatively small amounts of gypsum is followed by a rapid decrease in exchangeable Na, but after 1–2 winters the effects of gypsum will cease, so that further progress is rather slow (fig. 51; c.f. also fig. 53, section 6.61).



I: control
II: 6½ t/ha of crude gypsum
III: 13 t/ha of crude gypsum
IV: 19½ t/ha of crude gypsum

I: control
II: 5 t/ha of crude gypsum
III: 10 t/ha of crude gypsum
IV: 15 t/ha of crude gypsum

A: Trial field GT 18, polder Joanna Maria, Tholen, 0–20 cm depth
B: Trial field GT 46, polder Walcheren, 0–20 cm depth.

FIG. 51. Effects of gypsum dressings upon the regeneration of a calcareous flooded soil

Moreover it appears from the observations that the excess amounts of exchangeable K and Mg are only slightly affected by the usual gypsum dressings, even in the topsoil (c.f. table 64, section 6.5). The same conclusion may be drawn with regard to the amounts of exchangeable Na below 20 cm depth during the first years after gypsum application. The latter will only be notably reduced after the bulk of the exchangeable Na has disappeared from the topsoil.

Besides the effects on ionic composition, and especially on the exchangeable Na content of the topsoil, gypsum usually lowers soil pH. As has already been mentioned in section 5.32 there exists a correlation between pH and exchangeable Na. For individual trial fields this relation is usually much closer than the widely scattered general correlation shown in fig. 45, section 5.32. An example of the effects of gypsum on exchangeable Na content and pH of a calcareous flooded soil has been given in table 61, and for a non-calcareous soil a similar pH-reducing effect may be seen in table 54, section 6.3.

TABLE 61. Effects of gypsum dressings on the amounts of exchangeable Na and on soil pH in a calcareous flooded soil.
Trial field G.T. 11, polder Oude Kijkuit, Tholen, spring 1948.

Amounts of gypsum applied [1] t/ha	Depth cm	Exchangeable Na Na_a [2]	pH [3]
0	0–10	5.9	8.6
	10–20	11.1	9.0
9	0–10	2.4	8.4
	10–20	6.1	8.9
18	0–10	1.7	8.3
	10–20	4.4	8.7
27	0–10	0.8	8.2
	10–20	3.1	8.7

[1] Applied in autumn 1945.
[2] mval per 100 g of active matter.
[3] pH of 1 : 2.5 aqueous suspension.

6.44. *Efficiency of gypsum dressings*

For practical purposes, especially for a calculation of the amounts of gypsum needed in particular cases, it is necessary to know the efficiency of gypsum dressings for reducing the amounts of exchangeable Na in the topsoil. This efficiency may be calculated from the difference in exchangeable Na content between the controls and the gypsum-treated plots of gypsum trial fields. As may be seen from fig. 51 A this difference sometimes reaches a maximum a few years after gypsum application. In other cases – especially if the gypsum is only able to replace a relatively small part of the excess Na ions – a more constant difference is observed (c.f. fig. 51 B).

The efficiency of gypsum dressings may be calculated by comparing the gypsum equivalents of the differences in exchangeable Na with the amounts of gypsum actually given.

Putting, for the upper 20 cm of the soil:

ΔNa_a: difference in exchangeable Na between treated and untreated plots (mval per 100 g of active matter)

q: active matter percentage of soil

G: gypsum equivalent of ΔNa_a

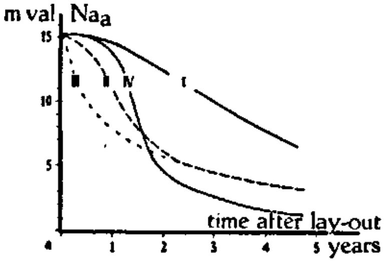
it is found that

$$G = 0.024 \,.\, \Delta Na_a \,.\, q \qquad \text{t/ha of } CaSO_4 \,.\, 2\,H_2O \qquad (6.01)$$

Ca concentration in the soil moisture. This increase will occur most rapidly after application of the highly soluble Ca chloride; after heavy gypsum dressings it will be restricted by the limited solubility of this compound (c.f. section 6.61).

For sulphur an increase in Ca concentration is only possible after its oxidation and after the subsequent reaction of the sulphuric acid formed with $CaCO_3$. The oxidation of sulphur, however, is a microbiological process, which therefore requires time, especially if the vital conditions for the bacteria involved are unfavourable.

Therefore it is to be expected that Ca chloride will act more quickly than gypsum, and the effects of sulphur will only become perceptible after a certain lapse of time. These expectations agree with the observations (fig. 52).



I: control, humus & slaked lime
II: gypsum, 15 t/ha
III: Ca chloride, 6 t/ha
IV: sulphur, 3 t/ha

FIG. 52. Effects of different chemicals on the amounts of exchangeable Na in calcareous flooded soils.
Trial fields SM 1 + SM 2, Walcheren, 0–20 cm depth

The time-lag after sulphur dressings on SM 1 and SM 2 (fig. 52) is accentuated by the fact that the dressings were given in autumn. Due to the low temperatures in winter the oxidation of sulphur probably did not occur before the next summer. As however the local effects of the gypsum formed are negligible, a decrease in exchangeable Na was not observed before the second winter after application.

If, therefore, the use of sulphur is contemplated, early application is necessary.

The efficiency of the different chemicals for reducing exchangeable Na in the topsoil may be calculated in the same way as the efficiency of gypsum dressings. As an example the efficiencies observed on one of the S.M. trial fields calculated at the moment of their maximum are listed in table 65.

This table illustrates the negligible effects of slaked lime, whereas the efficiency of gypsum is quite near the average value of 52%, mentioned in section 6.44. On equivalent base, the effects of Ca chloride are approximately the same as those of gypsum; the slightly higher efficiency suggested by the data of table 65 is not confirmed by observations on other trial fields. On the other hand 3 t/ha of sulphur had a relatively slight effect on the exchangeable Na content of the topsoil. This is probably due to the relatively high amount used, which has also caused a marked reduction in exchangeable K and Mg in the upper 20 cm (c.f. table 64) and of exchangeable Na in deeper layers.

For practical purposes only gypsum is attractive as a means of improving soil conditions. Under Dutch circumstances the price of sulphur is prohibitive, whereas the use of Ca chloride is prevented by its pronounced hygroscopicity. The comparisons made above are therefore mainly of academic interest.

TABLE 65. Efficiency of different chemicals for reducing the amounts of exchangeable Na in the topsoil of a calcareous flooded soil.
Trial field SM 1, polder Walcheren, spring 1949 [1], 0–20 cm depth.

Amendment	Amount of crude substance applied t/ha	Pure gypsum equivalent of amount applied t/ha	Pure gypsum equivalent of improvement t/ha	Efficiency of dressings %
Slaked lime	5½	10.4	0.44	4
Gypsum	5	3.5	1.87	53
Gypsum	10	7.0	3.76	54
Gypsum	15	10.5	5.37	53
Ca chloride	2	2.3	1.43	62
Ca chloride	4	4.7	3.30	70
Ca chloride	6	7.0	3.82	55
Sulphur	3	15.8	5.68	36

[1] 3 years after application; maximal efficiency.

6.6. GYPSUM APPLICATION IN PRACTICE

In practice several questions arise regarding the technique of gypsum application and the amounts to be used.

6.61. *Technique of gypsum application*

Regarding the technique of dressing, different problems had to be solved concerning time and ways of application. Thus, it was believed at first that it was desirable to postpone gypsum dressing until the soils had lost most of their soluble salts, as in that case the efficiency of gypsum was expected to be higher. For the investigation of this problem a series of AG trial fields were laid out after the inundations of 1944–'45, on which varying amounts of gypsum applied in different seasons were compared.

Contrary to the initial expectations, it soon appeared from these trials that gypsum should in any case be applied before the first winter after drainage, in order to prevent a collapse of topsoil structure. Moreover no reliable differences in ultimate efficiency could be detected between different seasons of application, even if the gypsum dressing was carried out in the saline stage.

As an example a synopsis of the results obtained on one of the A.G. trial fields is represented in fig. 53, from which it is clear that whenever gypsum was given, the final result was the same. But of course early dressings are to be preferred from a practical point of view.

These observations may be explained in the following way: As long as the soil is saline gypsum will certainly cause less improvement than in desalinized soils. But if gypsum – as usual – is given as a top-dressing it will not dissolve until water passage occurs. This water-passage will at the same time reduce the salinity of the topmost layers, so that the gypsum will only act on layers which have already lost most of their soluble salts. Moreover the large difference in downward velocity between the fastly running Cl boundary and the slowly proceeding rear boundary of Na will add to the difference.

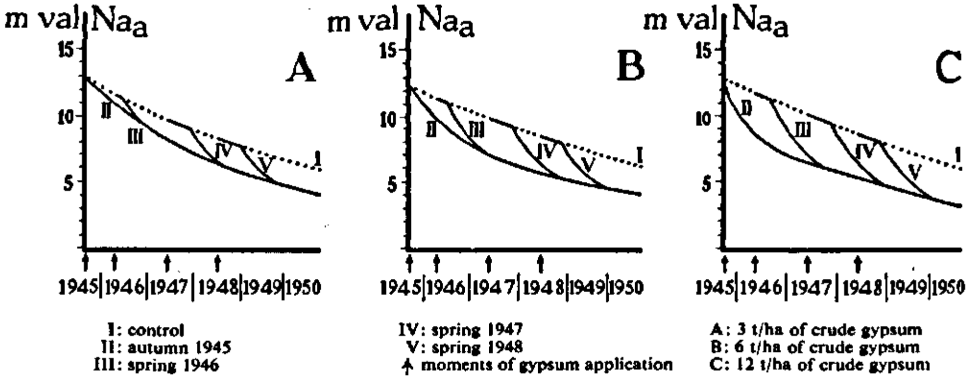


FIG. 53. Effects of gypsum, applied at different moments and in different quantities. Trial field AG 13, polder Oude Tonge, Flakkee, 0–20 cm depth

Thus, in order to prevent a collapse of soil structure gypsum should be added as soon as possible. Usually soils flooded in winter can be drained in late winter or early spring, and it is often possible to grow salt-tolerant crops – like barley or sugar beet – in the same year. In that case a small gypsum dressing – e.g. 1 t/ha – should be given immediately after sowing to prevent a collapse of the seed-bed. As, however, very little water-passage may be expected in summer, this small amount will suffice. During the next winter, however, much higher amounts will be needed.

It is unnecessary and even harmful to give these high amounts in the first spring after drainage. This gypsum would remain largely undissolved and would be buried by ploughing in autumn, thus exposing fresh, Na-rich soil to the impact of the winter rains. Therefore, after the small spring-dressing mentioned application of more gypsum should be postponed until after ploughing, so that it may protect the structure of the topmost layers during winter (VAN BEEKOM c.s., 1953)[1].

Concerning the method of application it has been found in practice that the best protection of soil structure is obtained by top-dressing. In this case the gypsum will readily regenerate the upper few cm of the soil, making them much less sensitive to the impact of raindrops. If, on the other hand, gypsum is mixed with the topsoil or worked under – e.g. by subsequent harrowing or ploughing – the topsoil structure is apt to break down, resulting in the formation of a compact crust (VAN BEEKOM c.s. 1953; WESTERHOF). As all spots which are not covered by gypsum will remain sensitive to collapse, the dressing should be carried out as evenly as possible.

Another problem, which is closely connected with those already mentioned is

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[1] If sulphur is to be used as an amendment, it should already be applied in spring as only during summer its oxidation is proceeding at a noticeable rate (c.f. section 6.5).

whether heavy gypsum dressings should be applied all at once or in divided portions. On the trial fields laid out after the inundations of 1944–'45 this problem was not investigated, but after the floods of 1953 some comparisons were made between application made at one time and applications spread over two subsequent years. The latter method of dressing was in concordance with current practice, as – due the large amounts of gypsum needed – it was impossible to deliver all gypsum as early as autumn 1953. Therefore, supplementary amounts were put at the disposal of farmers for application in autumn 1954, and in some cases a third gypsum dressing was applied in autumn 1955.

Although the trials mentioned above have not given definite conclusions, the observations made on soil structure are slightly in favour of application in two different portions.

This practice of divided application of gypsum seems also entirely justified from a theoretical point of view. Early gypsum dressing, as recommended above, will result in a rapid regeneration of the topsoil the first winter after drainage. But this regeneration will be mainly located near the soil surface (c.f. fig. 48, section 6.42). If, therefore, the soil is turned up again by ploughing next autumn, layers still containing considerable amounts of exchangeable Na will be brought to the surface, and layers already considerably improved will be buried. After this tillage, therefore, an additional gypsum dressing would again reduce the risk of crust-formation during the winter. As a matter of fact this additional dressing will be the more urgent as the depth of ploughing is greater.

A second justification of divided application is the limited solubility of gypsum, which prevents complete solution of large dressings during one winter. Estimating the solubility of gypsum at 40 mval/l and the water passage at 200 mm, the latter will only be able to dissolve approximately 7 t/ha of $CaSO_4 . 2 H_2O$. Gypsum dressings in excess of this quantity will therefore remain undissolved on the soil surface and will be turned under next autumn. This limited solution was clearly demonstrated on a number of trial fields laid out after the floodings of 1953, which had received gypsum in the autumn of that year. In the spring of 1954 undissolved gypsum might be seen lying on the surface of plots which had received over 10 t/ha of crude gypsum (± 90% purity). Analytically the presence of undissolved gypsum was demonstrated by the high values for water-soluble sulphates found in samples from such plots (table 66).

TABLE 66. Amounts of water-soluble sulphates found in spring 1954 in soils dressed with gypsum in autumn 1953.
Trial field GT 54, Molen-polder, Hoekse Waard.

Amount of gypsum (applied autumn 1953) , t/ha	0	7	14	21	28
Water-soluble sulphates, spring 1954, 0–10 cm, % [1]	0.01	0.43	0.49	2.24	2.51
Water-soluble sulphates, spring 1954, 10–20 cm, % [1]	0.02	0.15	0.19	0.65	0.58

[1] g of SO_4 per 100 g of dry matter.

Due to sampling errors it is impossible to derive quantitative conclusions from these data, but it is clear that especially on the plots treated with 21 and 28 t/ha large amounts of water-soluble sulphates in the form of undissolved gypsum were found, especially in the upper 10 cm of the soil.

Thus for soils drained late in winter or in early spring it is desirable to give a small gypsum dressing over the seed bed in the first spring, and more gypsum should be given next autum after soil tillage; to get full profit it should be left on the surface. It is desirable to divide gypsum application over more than one year, and in any case gypsum dressings should not exceed 7 t/ha of $CaSO_4 . 2\,H_2O$ per annum.

6.62. *Amounts of gypsum required by flooded soils*

All observations indicate that on *former meadows*, even if broken up after the inundation, gypsum requirements are nil, as a collapse of structure has never been observed on such soils.

For estimating the gypsum requirements of *arable land* two different methods may be followed. The first and most simple one is to review the observations made on gypsum trial fields with regard to soil structure and crop response. In this way the amounts of gypsum required for securing normal yields and a reasonable soil structure may be evaluated for each trial field. Then, it may be attempted to collect these separate results into one empirical relation. In this way DOMINGO (1944), using the observations made after the inundations of 1939–'40 and 1943, made recommendations for the amounts of gypsum to be used on soils flooded with salt water (table 67).

TABLE 67. Recommended amounts of gypsum for application on arable land flooded with salt water.
After DOMINGO (1944).

Clay content ($< 2\,\mu$)	%	< 5	5–12	12–17	17–25	> 25
Active matter content [1]	%	$\backsimeq 10$	$\backsimeq 15$	$\backsimeq 20$	$\backsimeq 30$	$\backsimeq 40$
Amounts of $CaSO_4 . 2\,H_2O$	t/ha	*0*	*2.5*	*5.7*	*8.9*	*10.0*

[1] Approximate values.

From extensive material, WESTERHOF (1953) derived the following empirical equation:

$$R = 2.2\,[Na_{s(0-10)} - 1] \quad \text{t/ha} \qquad (6.02)$$

in which R denotes gypsum requirement — in t/ha of pure $CaSO_4 . 2\,H_2O$ – and $Na_{s(0-10)}$ the exchangeable Na content – in mval per 100 g of dry matter – in the upper 10 cm of the soil immediately after drainage.

As:

$$Na_{s(0-10)} = Na_{a(0-10)} \cdot \frac{q}{100} \qquad (6.03)$$

equation (*6.02*) may be also written as:

$$R = 2.2 \left[Na_{a(0-10)} \cdot \frac{q}{100} - 1 \right] \text{ t/ha} \qquad (6.04)$$

in which q denotes the active matter percentage (clay $< 2\mu + 3 \times$ humus) and $Na_{a\,(0-10)}$ the amount of exchangeable Na – in mval per 100 g of active matter – observed shortly after drainage in the upper 10 cm of the soil.

After the 1953 floods, however, these values proved to be too low. Therefore, after studying the results of trial fields laid out in 1953, equation (*6.04*) was changed by WESTERHOF (1956) into:

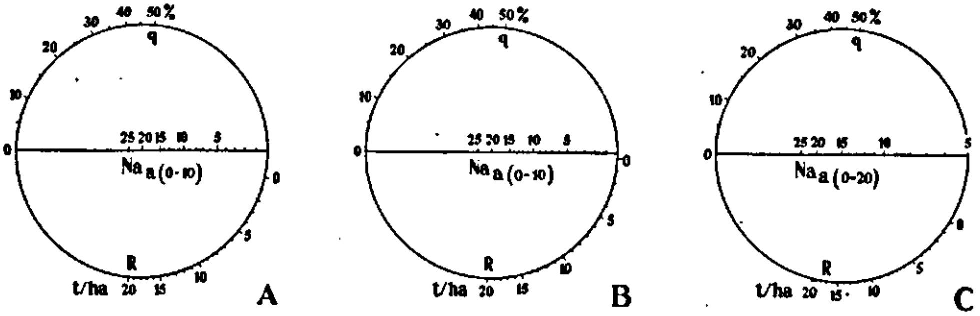
$$R = 2.25 \left[Na_{a\,(0-10)} \cdot \frac{q}{100} - 0.25 \right] \text{ t/ha} \qquad (6.05)$$

A second method for estimating the required amounts of gypsum consists of the following steps:

1. Formulating the standards for permissible Na contents of the soil. In practice no serious collapse of soil structure occurs if in the upper 20 cm Na_a falls below 5 within two years after drainage.
2. Estimating the velocity of natural regeneration. As appears from table 46, section 5.4 the annual loss of exchangeable Na from the upper 20 cm of a calcareous soil amounts to 390 kg/ha, which is equivalent to 1.45 t/ha of $CaSO_4 . 2\ H_2O$.
3. Estimating the efficiency of gypsum dressings in reducing exchangeable Na. This efficiency, however, is dependent upon the amounts applied. Therefore it should be calculated for amounts satisfying condition 1. At such dressings the average efficiency was found to be approximately 52% (section 6.44).

Assuming the density of the soil in its natural position to be $\varrho = 1.4$ these considerations will lead to the following equation for gypsum requirement:

$$R = 0.046 \,.\, q \,.\, Na_{a\,(0-20)} - 0.23\, q - 5.6 \quad \text{t/ha} \qquad (6.06)$$



q: active matter percentage
Na_a (0–10): exchangeable Na, 0–10 cm depth (mval per 100 g of active matter)
Na_a (0–20): ibidem, 0–20 cm depth
R: gypsum requirement, t/ha of $CaSO_4 . 2\ H_2O$
A: equation (*6.04*) B: equation (*6.05*) C: equation (*6.06*)

FIG. 54. Theoretical gypsum requirements of flooded soils

Nomograms for the equations (*6.04*), (*6.05*), and (*6.06*) have been reproduced in fig. 54. A comparison between these equations becomes possible if the relation between $Na_{a\,(0-10)}$ and $Na_{a\,(0-20)}$ is known.

After inundations of short duration, like most of those occuring in 1953, $Na_{a\,(0-10)}$ is usually somewhat higher than $Na_{a\,(0-20)}$ (c.f. fig. 35, section 4.5). But the equations (*6.04*) and (*6.06*) have both been derived from data obtained after the much more prolonged military inundations of 1944–'45, for which it may be assumed that:

$$Na_{a\,(0-10)} \cong Na_{a\,(0-20)} \qquad (6.07)$$

Therefore a direct comparison between equations (*6.04*) and (*6.06*) is possible. This comparison is represented in table 68.

TABLE 68. Comparison between gypsum requirements in t/ha, calculated according to equations (*6.04*) and (*6.06*).

$Na_{a\,(0-10)}$ $Na_{a\,(0-20)}$	Method of calculation[1]	Active matter percentage q				
		10	20	30	40	50%
5	1	0	0	1.1	2.2	3.3
	2	0	0	0	0	0
10	1	0	2.2	4.4	6.6	8.8
	2	0	0	1.3	3.6	5.9
15	1	1.1	4.4	7.7	11.0	14.3
	2	0	3.6	8.2	12.8	17.4
20	1	2.2	6.6	11.0	15.4	19.8
	2	1.3	8.2	15.1	22.0	28.9

[1] 1: according to equation (*6.04*)).
2: according to equation (*6.06*).

As appears from table 68, equation (*6.04*) predicts higher requirements for light soils and for soils flooded with brackish water, in which Na_a is low. For heavy soils, especially if inundated with water of high salinity the reverse is true. In the majority of cases, however, Na_a did not exceed 15 mval/100 g, whereas in the areas flooded in 1944–'45 q is usually below 40%. In this range the results of both methods of calculation agree well enough for practical purposes. Moreover the figures listed for $Na_a = 15$ agree fairly well with DOMINGO's earlier estimates for soils flooded with salt water (c.f. table 67).

In practice the Na_a values of flooded soils have usually not been directly determined. Instead use has been made of the correlation between salinity C and exchangeable Na – Na_a – observed shortly after the inundation (fig. 33, section 4.5). Neither were the gypsum requirements calculated for each separate field, but usually for entire polders and in some cases for parts of them. The active matter content of the arable land in these polders was estimated from their clay content, which was either known from former soil analyses, or estimated. For practical reasons soil salinity and soil texture were grouped into classes, after which the gypsum requirements were determined for each class (c.f. table 70).

6.63. *Amounts of gypsum applied in practice*

Since 1940 it has become a rule that damage caused by military inundations or by stormfloods of extraordinary magnitude is repaired at government expense. Under this scheme, gypsum is supplied free to the farmers.

Initially little was known about the amounts to be applied. After the 1939–'40 inundations 3–4 t/ha of crude gypsum were delivered to the farmers (VAN VLIET, 1945). This gypsum was a residual product of the super-phosphate industries; its content of pure $CaSO_4 . 2 H_2O$ was rather low (approximately 65%) and its high moisture content hampered its application. Though these dressings met with good results, the general opinion was that the quantities applied had been too low. This was in accordance with the observations made on a few trial fields.

After the extensive military inundations of 1944–'45 large amounts of gypsum had to be applied. Due to transport difficulties shortly after World War II most of this gypsum could not be delivered before 1946 and 1947. The amounts needed for regeneration had already been estimated by DOMINGO (table 67). The delay in distributing gypsum enabled the amounts finally supplied to be correlated – if necessary – with the results of trial fields laid out immediately after drainage. Thus the amounts actually supplied show some discrepancies from those listed in table 67 (table 69).

TABLE 69. Amounts of crude gypsum [1] applied on arable land after the inundations of 1944–'45.

Salinity of flooding water C g/l	$CaCO_3$-content of soil %	Clay content				
		$<16 \mu : <10$ $< 2 \mu : < 7$	10–20 7–24	20–30 14–20	30–40 20–27	>40% >27%
<15	<2.0	0	4	6	8	10
	>2.0	0	3	5	7	8
>15	<2.0	0	4	6	10	12
	>2.0	0	3	5	10	12

[1] With 70% $CaSO_4 . 2 H_2O$.

[2] Approximately.

As the variations in salinity of the flood water were not sufficiently allowed for, the amounts of gypsum administered proved too low in very saline soils, such as occurred in the island of Walcheren, but they were probably too high in soils flooded with brackish water.

In general, however, these dressings have secured a fairly good soil structure and reduced damage to arable crops considerably. Unfortunately they were applied late – in many cases not before autumn 1946 – which was a serious drawback, as in the winter of 1945–'46 deterioration of soil structure occurred in many areas.

After the floods of 1953 it was decided to supply immediately 1 t/ha of gypsum for all soils flooded with salt or brackish water, in order to prevent a breakdown of seed-bed structure during the first year of cultivation.

The total quantities to be given were derived from the observations made after the 1944–'45 inundations. Though different methods of approach gave different results, their mutual accordance was fair enough to estimate the amounts needed. These were so large – in total more than 500,000 tons – that delivery in one year was quite impossible. Therefore it was decided to distribute about one half of the amounts needed in 1953, part of the remainder in 1954 and – if necessary – an additional amount in 1955. In the meantime the results obtained from newly laid-out trial fields could be used for guidance. The total amounts ultimately given after the 1953 floodings have been listed in table 70.

TABLE 70. Amounts of crude gypsum [1] applied on arable land after the inundations of 1953.

Salinity of topsoil immediately after drainage C g/l	Clay content						
	$<16\mu$: 0–10 $<2\mu$ [2] : 0– 7	11–20 7–14	21–30 14–20	31–40 20–27	41–50 27–34	51–60 34–40	$>60\%$ $>40\%$
<3	0	0	0	0	0	0	0
3– 6	0	1	2	4	5	5	6
6–10	0	1	4	6	8	9	11
10–15	0	4	7	10	12	15	17
>15	0	5	9	12	14	18	20

[1] With 90% $CaSO_4 . 2 H_2O$.
[2] Approximately.

As far as may be judged at the present moment, these amounts, if applied in time and if combined with a careful treatment of the flooded soils, have been sufficient to secure a fair soil structure and to prevent much reduction in crop yields.

A final comparison between the amounts given after different inundations and the theoretically calculated requirements is given in table 71.

The divergence between theoretically calculated requirements and the amounts given in practice results from two causes. Firstly, the manipulation of data involves errors in grouping and rounding-off. Apart from these accidental deviations, it appears from table 71 that in general the amounts applied in 1945 were too high for soils flooded with brackish water and too low for soils inundated with water of high salinity. On the whole the amounts given in 1953 were considerably higher, except for soils flooded with brackish water. Nevertheless, for these soils, they were still higher than those required by theory.

The main reason for these high gifts after brackish-water floodings is that in such cases it was possible to grow valuable, fine-seeded crops – like flax – already in the first year after drainage. To avoid all risks with these sensitive crops some excess gypsum has been given.

For very saline, heavy soils the amounts distributed in 1953 might be still too low. This combination, frequently met with in Walcheren in 1945 and also occurring in the polder Oost Beveland in 1946, was only seldom found after the 1953 floods.

As a matter of fact no gypsum was supplied for old pastures.

Thus, by adding adequate amounts of sulphur, gypsum or other highly soluble Ca compounds the natural regeneration of flooded arable land may be promoted to such an extent that serious troubles with soil structure are avoided. Under Dutch circumstances only gypsum – preferably applied as a top dressing and in an early stage – is attractive from a practical point of view.

Some effects of gypsum on soil structure and on crop growth are illustrated by figs. 55–58. These effects will be extensively dealt with in another paper in this series, to be published by WESTERHOF.

TABLE 71. Comparison between theoretical gypsum requirements and amounts of gypsum applied after different inundations.
Amounts of gypsum, expressed as t/ha $CaSO_4 . 2 H_2O$.

Salinity of soil after drainage C g/l	Exchangeable Na-content Na_e mval	Method or period	Clay- and active matter content			
			<16 μ: 15 < 2 μ: 10 q: 16	24 16 22	36 24 31	45% 30% 39%
5	5	Westerhof [1]	0.0	0.2	1.2	2.1
		Westerhof [2]	1.2	1.9	2.9	3.8
		v. d. Molen [3]	0.0	0.0	0.0	0.0
		1945 [4]	2.1	3.5	4.9	5.6
		1953 [5]	0.9	1.8	3.6	4.5
8	8	Westerhof [1]	0.6	1.7	3.3	4.6
		Westerhof [2]	2.3	3.4	5.0	6.5
		v. d. Molen [3]	0.0	0.0	0.0	0.0
		1945 [4]	2.1	3.5	4.9	5.6
		1953 [6]	0.9	3.6	5.4	7.2
14	12	Westerhof [1]	2.0	3.6	6.0	8.1
		Westerhof [2]	3.8	5.4	7.8	10.0
		v. d. Molen [3]	0.0	1.5	4.4	6.9
		1945 [4]	2.1	3.5	4.9	5.6
		1953 [5]	3.6	6.3	9.0	10.8
20	15	Domingo [6]	2.5	5.7	8.9	10.0
		Westerhof [1]	3.1	5.1	8.0	10.6
		Westerhof [2]	4.8	6.9	9.9	12.6
		v. d. Molen [3]	1.7	4.5	8.6	10.3
		1945 [4]	2.1	3.5	7.0	8.4
		1953 [5]	4.5	8.1	10.8	12.6
25–30 [7]	20	Westerhof [1]	4.8	7.5	11.4	15.0
		Westerhof [2]	6.6	9.3	13.4	17.0
		v. d. Molen [3]	5.4	9.6	15.8	21.2
		1945 [4]	2.1	3.5	7.0	8.4
		1953 [5]	4.5	8.1	10.8	12.6

[1] Equation *(6.04)*
[2] Equation *(6.05)*
[3] Equation *(6.06)*
[4] Table 69; $CaCO_3 > 2\%$
[5] Table 70
[6] Table 67
[7] Inundations of long duration

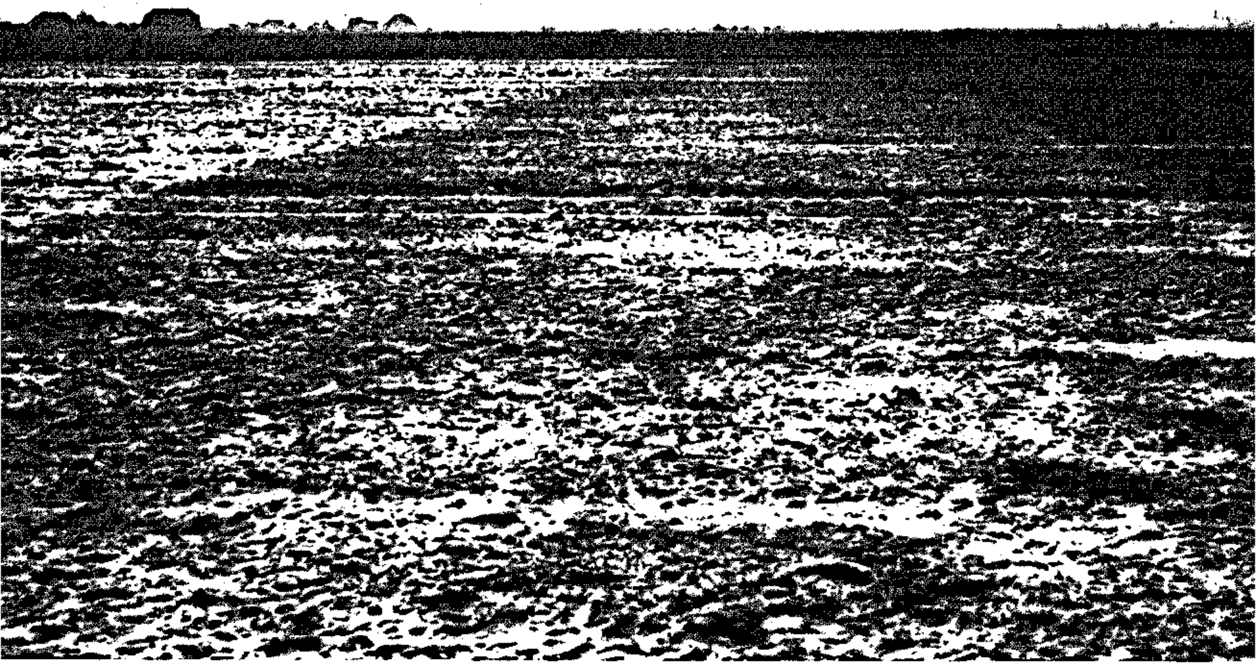


FIG. 55. Effect of gypsum on the structure of a light soil flooded in 1953.
Trial field GS 3, Polder Nieuwe Hei, W.-Brabant, 26-2-1954

Left: no gypsum, soil covered with pools
Middle: 1½ t/ha, structure rather bad
Right: 6 t/ha, structure rather good

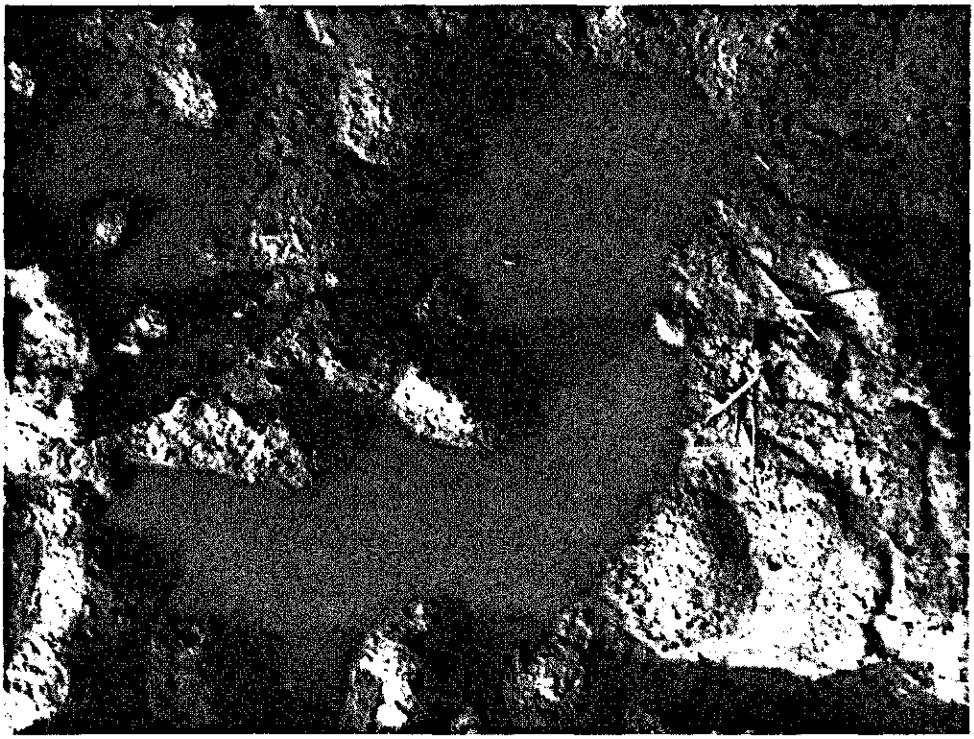


FIG. 56. Effect of gypsum on the structure of a heavy soil flooded in 1953.
Trial field GT 54, Molenpolder, Hoekse Waard, 26-2-1954
Top: no gypsum, soil impermeable
Bottom: 28 t/ha; normal structure with undissolved gypsum on the surface

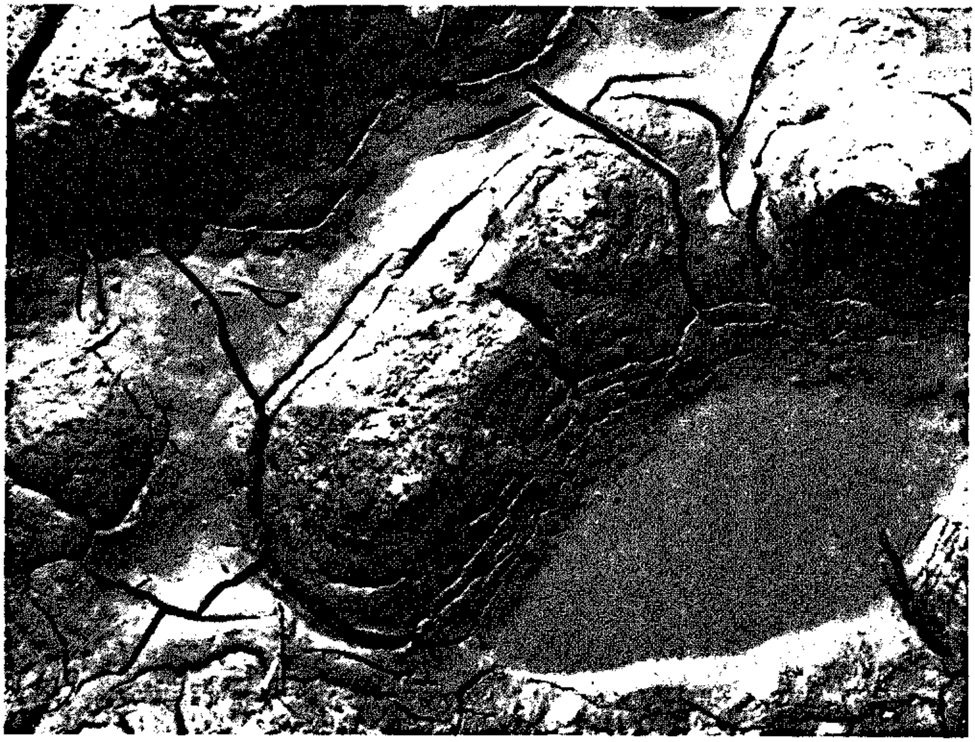


FIG. 57. Effect of gypsum on the structure of a heavy soil flooded in 1953.
Trial field GT 54, Molenpolder, Hoekse Waard, 17-3-1954
Top: no gypsum; water still on the surface
Bottom: 28 t/ha; normal structure with undissolved gypsum on the surface

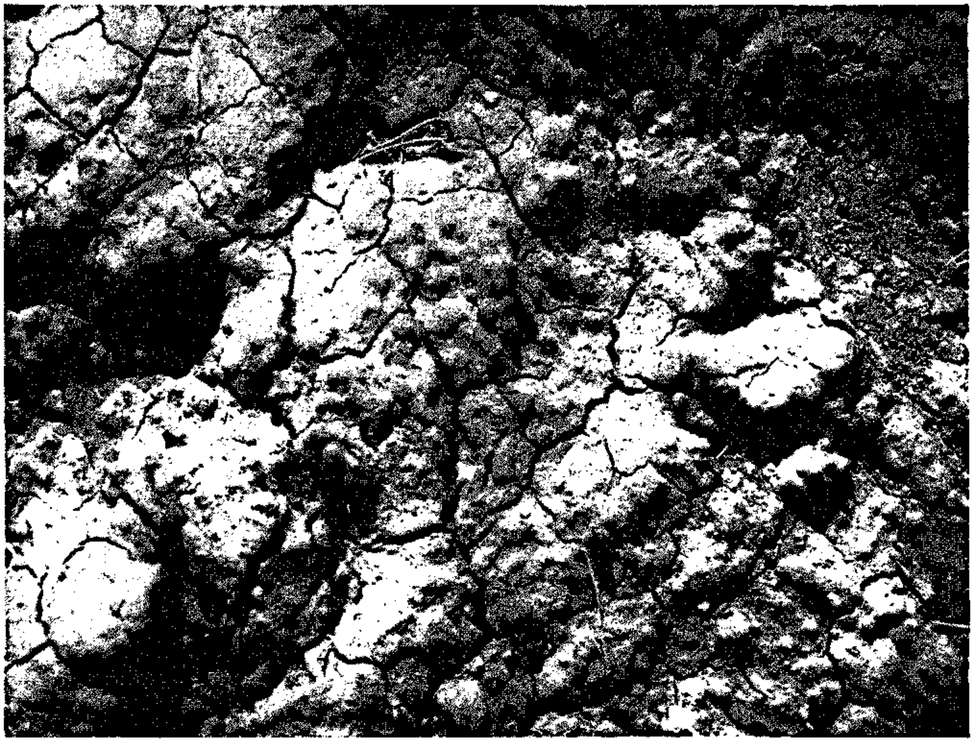


FIG. 58. Effect of gypsum on the germination of spring barley.
Trial field GT 54, Molenpolder, Hoekse Waard, 4-6-1956.
On the control soil structure was so bad that the crop failed to germinate. In the surroundings, where different amounts of gypsum were applied, growth was near to normal

SUMMARY

1. In the first chapter an introduction is given into the problems of flooded soils in general and especially into those arising after the extensive inundations in the S.W. of the Netherlands during the period 1939–1953. The general problems of flooded soils, mainly concerning the harmful effects of salinity and unfavourable soil structure, have been regarded from a historical point of view. Although the phenomena were already known for a long time and their first elaborate description was published as early as about 1800, their explanation was not given before the beginning of the 20th century. Gypsum application was introduced on a trial scale by HISSINK in 1918.

In the period 1939–1953 large areas in the S.W. of the Netherlands were flooded with salt or brackish water. A review of these inundations has been given in fig. 1. Especially after the military inundations of 1944–'45 extensive investigations were carried out, including the lay-out of numerous gypsum trial fields and their investigation for exchangeable cations, soil structure and crop response (fig. 2, tables 1 and 2). In these investigations most attention was given to the exchangeable Na ions, which may be regarded as the main cause of bad structure in flooded soils.

2. The treatment of the subject-matter has been mainly deductive in nature. Therefore a rather elaborate review of the theoretical principles involved in ion exchange precedes a more detailed account of the phenomena occurring in flooded soils. These theoretical considerations involve ion exchange equilibria, exchange kinetics and column effects. The former may be either based on the DONNAN equilibrium (fig. 3) or on model considerations (fig. 5).

For homovalent ion exchange all theoretically derived equations become identical with those proposed by KERR (eq. *2.27* and *2.29*). But the STERN theory of the electric double layer (fig. 5) predicts that specific differences in the adsorption of ions of equal valency will become less at increasing dilution of the equilibrium solution (STERN effect). This implies that the exchange constant K occurring in the equations may be expected to approach unity at infinite dilution.

For heterovalent exchange different equations have been proposed, i.a. by KERR (*2.28*), VANSELOW (*2.38*), KRISNAMOORTHY & OVERSTREET (*2.42*) and GAPON (*2.46*). All of these predict an increased adsorption of the ions possessing the highest valency at increasing dilution of the equilibrium solution (valency effect).

In many cases, however, these equations are inadequate. Therefore empirical relations are often to be preferred. Of these, the relations proposed by ROTHMUND & KORNFELD (*2.48*, *2.49*) are frequently employed.

In soil profiles the exchange processes bear complete analogy to the reactions occurring in an ion exchange column (figs. 6, 7, 8). The theory of the latter is therefore of fundamental importance for the understanding of the exchange processes in soils. This theory predicts diffuse rear boundaries for ions adsorbed with a convex or linear adsorption isotherm and much sharper rear boundaries for ions possessing a concave isotherm. For front boundaries the reverse will be true. Diffusion and streaming irregularities will have disturbing effects, but these may be comprised into one single entity, the theoretical plate thickness. If this thickness is known, the behaviour of the column, especially with regard to the velocity of the elution process, may be predicted, except for the case that the ions leaving the column possess a convex adsorption isotherm.

3. After these general theoretical considerations the properties of the soils occurring in the investigated area have been more closely examined. A review has been given about their genesis and morphology, followed by a short description of their texture (table 4). One of the most marked processes in these soils is their gradual decalcification under the influence of the humid Dutch climate. By this process the topsoil is deprived of its $CaCO_3$, so that the difference in $CaCO_3$ content between topsoil and subsoil increases at increasing age. From these data the annual $CaCO_3$ losses from the upper 20 cm of the soils in the S.W. of the Netherlands may be estimated at approximately 350 kg/ha, corresponding with a loss of 1% of soil weight in 80 years. This implies that these soils will be percolated with a solution containing about 3.5 mval/l of Ca ions.

The adsorptive properties of the soils are closely related with their content of active matter (figs. 9, 10). This active matter is defined as the sum of clay content ($< 2\,\mu$) and three times humus content (eq. *3.01*). At pH 8.0 the adsorptive capacity of the active matter for Ca ions is approximately 70 mval per 100 g in the topsoil (fig. 11) and slightly higher in the subsoil (table 5). In calcareous soils the available adsorption seats are almost entirely occupied by the metal cations Na, K, Mg and Ca (table 6, fig. 11). But in non-calcareous soils the total of these ions may be considerably lower than the adsorptive capacity due to the presence of H_3O-ions. Therefore a narrow correlation exists between the sum of exchangeable metal cations and soil pH (fig. 12).

The behaviour of the soils against binary salt solutions has been studied by percolating two typical soils from the area (table 7) with mixed solutions of $NaCl + KCl$, $NaCl + CaCl_2$ and $MgCl_2 + CaCl_2$. The results of these experiments have been represented as adsorption isotherms (figs. 13, 15, 17), whereas the different laws proposed for ion exchange have been tested (figs. 14, 16, 18). For the homovalent exchanges Na-K and Mg-Ca the specific differences between the ions involved appeared to decrease at increasing dilution of the equilibrium solution (figs. 13, 17), in accordance with the STERN theory. For these exchanges only the empirical equations of ROTHMUND & KORNFELD were able to give an adequate description of the phenomena observed, though the constants K and p occurring in these equations varied considerably with the ionic concentration of the solution (tables 11, 17).

For the heterovalent Na-Ca exchange the valency effect caused an increased adsorption of Ca at increasing dilution (fig. 15). Of the exchange equations to be tested only that of GAPON was obviously inadequate, whereas those of KERR, KRISNAMOORTHY & OVERSTREET and VANSELOW all gave an excellent description of the experimental evidence (fig. 16), at least within the limits set by experimental errors.

But also in these equations the value of the exchange constant K varied with the ionic concentration of the equilibrium solution (table 14).

In the equilibria occurring in flooded soils four major ionic species are taking part instead of two. Due to mutual interference of these ions extension of the laws derived for binary equilibria becomes impossible, except for groups of equilibria with *solutions of kindred ionic composition.* Thus an extension of KERR's equation gives a fair account of the equilibria with excess amounts of diluted sea water and brackish water (table 21). In more complicated cases, like equilibria with limited amounts of sea water, this extended KERR equation fails completely (fig. 21).

The equilibria with sea water at different dilutions, obtained by percolating soils with excess liquid, reveal that at increasing dilution the amounts of exchangeable Mg and Ca will increase at the cost of Na and K (figs. 19, 20). This phenomenon is obviously caused by the valency effect. In equilibria with brackish water more Ca will be adsorbed than in equilibria with diluted sea water of equal salinity, which difference is caused by the relatively higher Ca content of brackish water (fig. 20). As has been mentioned before, an extended KERR equation appears to give a satisfactory explanation of the observations (table 21). But on the other hand the ionic ratios observed in these four-ion equilibria do not agree with those calculated from the equations for binary exchange (table 23), as the counter ions obviously interfere with them.

This mutual interference of different ionic species is still more obvious from the experiments on equilibria with limited amounts of sea water, for which calculation according to the extended KERR equation mentioned above appears to be impossible (fig. 21). Therefore equilibria of this kind – which are common in flooded soils – may only be described by means of empirical rules, e.g. by empirical adsorption isotherms (figs. 22–27). For Na these empirical isotherms may be represented by a rather simple, quadratic equation (*3.23*). The results of this empirical equation appear to be nearly identical with those obtained from the equations for the binary Na-Ca equilibrium (fig. 23, C). Especially for K and Mg the kind of complementary ions exerts great influence on the adsorption isotherms (figs. 25, 26): the adsorption of these ions is much stronger in cases that Na is the predominating complementary ion than in cases that Ca dominates.

Finally the ionic composition of unflooded soils has been shortly reviewed. In these soils Ca is always the leading metal cation, whereas Na is only present in minute quantities. The amounts of exchangeable Mg appear to increase with age (fig. 28).

4. During inundations with sea water the ionic composition of the soil will undergo considerable changes due to exchange reactions. Usually the amounts of water penetrating into the soil are limited, so that complete equilibrium with the flooding water is not reached by far. An exception is formed by soils subjected to natural percolation, which may be due to alternated flooding at high tide and drainage at low tide. In such cases the ionic composition of the soil will approach the complete equilibrium with sea water found in laboratory percolation experiments (fig. 29). Usually, however, the changes are much less, especially in the subsoil (fig. 30).

Complete equilibria with brackish water were not reached in the flooded areas, but they may be studied by analysis of estuary bottom soils. These soils will contain more exchangeable Ca and in some cases also more Mg as the salinity of the water is lower (table 28), which is in accordance with laboratory percolation experiments (c.f. fig. 20). After brackish water inundations, however, such complete equilibria were not reached by far (table 29). Thus the typical increase in exchangeable Mg at decreasing salinity was never observed after brackish-water inundations, whereas also the amounts of exchangeable Na and K remained far below the values observed in laboratory percolation experiments. Due to column effects the changes in ionic composition were large in the topsoil and much smaller in the subsoil (fig. 31).

The column effects may be studied by observing the distribution of Cl ions shortly after an inundation: after inundations of short duration the concentration of these ions is strongly decreasing with depth. This distribution may be explained from the theory of column operation. For light soils the agreement between theory and observations is excellent, but for heavy soils percolation of flood water through existing cracks results in higher salt concentrations in the subsoil than expected (fig. 32). In recently flooded soils a fair correlation was observed between Cl concentration and exchangeable Na, not only for the topsoils (fig. 33), but also for the subsoils (fig. 34). As a consequence a close parallelism existed between the distributions of Cl and of exchangeable Na throughout the soil profile (fig.. 35, A, B), at least for soils which were not flooded twice within a short period or for soils with permanently saline subsoils.

Starting from the empirical Na adsorption isotherms it was possible to give a qualitative if not quantitative explanation of the relations between Cl and exchangeable Na mentioned above (fig. 33, table 32).

5. After the drainage of flooded soils a slow but distinct natural regeneration occurs. The soluble salts are readily leached by percolating rain water, i.a. causing a rapid decrease of Cl content. But also the amounts of exchangeable Na – and to a much less extent also the excess amounts of exchangeable Mg and K – will decrease in the course of time (fig. 38).

From model experiments (fig. 37) as well as from field observations (fig. 38) it appears that the cations leave the soil in the order Na $>$ K $>$ Mg and that the changes proceed from top to bottom through the soil profile (fig. 39, 40, 41). In accordance with the theory of column operation the boundary of the Na ions has a steeper gradient than the boundary of Cl (fig. 42). From field observations it appears that the main process during the regeneration is a replacement of exchangeable Na by Ca (table 34).

Considering the different regeneration processes it appears that *concentration-changes in the soil moisture* will result in a shift in the equilibrium between dissolved cations and cations in solution. Theoretically this shift cannot result in large changes in composition of the adsorbed cations (table 37), a conclusion which is confirmed by field observations (fig. 43).

Hydrolysis and reaction with water containing carbon dioxide will result in a replacement of exchangeable Na ions by H_3O ions and in an increase in pH due to free OH ions in the soil solution. The high pH of soils rich in exchangeable Na is well-known; it was observed that a high content of exchangeable Na is usually combined with a high pH (fig. 45). For the removal of exchangeable Na, however, these processes are of little importance, at least in calcareous soils, where replacement of exchangeable Na by Ca ions liberated from dissolving calcium carbonate strongly predominates over hydrolysis. In non-calcareous soils hydrolysis may be of more importance, but the number of observations on these soils has been too small to draw a definite conclusion.

Dissolution of Ca from dissolving $CaCO_3$ and subsequent replacement of exchangeable Na by Ca is the principal natural regeneration process in calcareous flooded soils. Theoretical considerations show that the process soon comes to a standstill (table 39) unless the Na ions liberated from exchange positions are removed by leaching. Therefore the leaching of these Na ions will act as the limiting factor in natural regeneration.

In non-calcareous soils *dissolution of Ca from other Ca-containing minerals* – e.g. from feldspars – may be of some importance. Finally, *uptake by plant roots* may contribute to the reduction of the excess exchangeable K ions; for Na and Mg this process is of little importance.

It has been mentioned that in the regeneration of calcareous flooded soils the replacement of exchangeable Na – and to a much less extent of K and Mg – by Ca is the principal process. The limiting factor in this process is the removal of these replaced ions by leaching.

As a consequence the velocity of regeneration is strongly dependent on water-passage (table 43, 44). Moreover it appears to be faster in light soils than in heavy ones (table 45).

The average annual Na losses from flooded soils during their natural regeneration amount to 390 kg/ha, this figure being slightly higher for soils rich in exchangeable Na (table 46).

From the theory of column operation estimates can be made about the velocity of the regeneration processes, using the empirical adsorption isotherms as a base. It is found that Cl is readily washed out, that Na is slowly removed and that K and especially Mg are remaining in excess for a long time, especially in the subsoil (table 48). As a consequence soils flooded long ago are still characterized by high Mg contents in the subsoil (table 49). From the theory the average annual Na losses may be estimated at 600 kg/ha, a value obviously higher than the observed losses (390 kg/ha). This difference may be caused by the disturbances caused by soil tillage (fig. 46), which have a retarding effect.

6. In the course of time natural regeneration will restore normal conditions in flooded soils, but its velocity is so low that agriculture will be hampered for many years. Different treatments, however, may accelerate the recovery.

Growing perennial crops is an old method. In a series of field trials grass proved to be more effective than clover or lucerne (table 51). Under perennial crops the unfavourable effects of soil tillage are avoided, so that the rate of regeneration will probably be somewhat higher than under annuals. But this difference is by no means spectacular.

Organic manuring, even if applied in excessive quantities, is ineffective.

Of the different chemicals tested *marl*, *slaked lime*, and a *humus preparation* appeared to be of little use. On the other hand favourable effects were obtained by application of *gypsum*, *calcium chloride* and *sulphur* (tables 53, 63, 64). Of these, calcium chloride acted most rapidly, followed by gypsum. Sulphur, which has first to be oxidized to sulphuric acid before being able to react with the exchangeable cations, was very effective, but only after a certain lapse of time (fig. 52). Calcium chloride, however, was too cumbersome to handle, whereas the price of sulphur was prohibitive. So only gypsum has been used on a large scale.

The most rapid regeneration by gypsum was observed in soils in which this compound was present in excess throughout the soil profile. This is the case in newly drained sea-bottom soils, where this compound is formed by natural processes, viz. by oxidation of ferrous sulphides to sulphuric acid and subsequent reaction of this acid with calcium carbonate. But even in such cases the direct reaction of the gypsum with the exchangeable cations only resulted in a fairly slight shift in the equilibrium (table 57). Only in combination with water passage – which will remove the Na, K and Mg ions liberated from the exchange positions – rapid changes are possible (fig. 49, table 59).

In flooded soils gypsum was given as a top-dressing and usually the quantities applied were insufficient to replace all exchangeable Na from the top-layers. In such cases the regeneration was less fast (fig. 50, table 60) and usually only a partial regeneration was obtained (fig. 51). Moreover the usual gypsum dressings only removed part of the exchangeable Na, but left the exchangeable K and Mg practically unchanged (table 64). Nevertheless such dressings were valuable from a practical point of view: exchangeable Na and pH were lowered (table 61), soil structure improved (fig. 54–57) and crop growth promoted (fig. 58).

The efficiency of gypsum for removing exchangeable Na was highest for low gifts (table 62). For practical gifts approximately 50% of the gypsum added was able to replace exchangeable Na ions from the upper 20 cm of the soil. In practice the best results were observed after early application of gypsum. If the soil is drained in winter a low gift in spring is to be recommended in order to avoid collapse of seed-bed structure during showers. Application of large quantities in spring, however, is of little use, as practically no water passage occurs during summer and consequently no regeneration wil take place.

In autumn, after ploughing, larger quantities of gypsum must be given to avoid collapse of the ploughed layer during winter. To give full protection, the gypsum should be left on the surface.

It is of little use, however, to apply more than about 7 t/ha, as the excess quantity will remain undissolved and will be ploughed under next year. If larger quantities are needed it is better to apply the remainder in the next autumn, again after ploughing.

The amounts of gypsum required by flooded arable soils increase at increasing clay content and at increasing initial salinity of the soils. They have been calculated in two ways, viz. from direct observation of a large number of trial fields (eq. *6.05*) and by means of a calculation involving the velocity of natural regeneration and the efficiency of gypsum dressing (eq. *6.06*). The results of these calculations have been reproduced as nomograms (fig. 54). A comparison between the amounts calculated by both methods and the amounts actually given in practice has been listed in table 71.

On former meadows no gypsum is needed: on these soils a decline of soil structure was never observed.

In an appendix the analytical methods used are shortly described. In the estimation of exchangeable cations two methods have been employed: the expressed fluid method and the alcohol method. Within the limits of experimental errors both methods appear to yield the same results (table 72, figs. 59–62).

SAMENVATTING

UITWISSELBARE KATIONEN IN GRONDEN NA OVERSTROMING DOOR ZEEWATER

1. Het eerste hoofdstuk omvat een algemeen overzicht van het gedrag van gronden, die met zeewater overstroomd zijn geweest. De moeilijkheden met dergelijke gronden worden deels veroorzaakt door een hoog zoutgehalte, deels door een ongunstige bodemstructuur.

Ofschoon deze moeilijkheden reeds in de middeleeuwen bekend waren en zij omstreeks 1800 uitvoerig werden beschreven, duurde het toch tot het begin van de twintigste eeuw, voordat een bevredigende verklaring van de verschijnselen kon worden gegeven. Proeven met gipsbemesting op overstroomde gronden werden in Nederland het eerst door HISSINK in 1918 genomen.

In de periode 1939–1953 werden grote gebieden in het zuidwesten van Nederland met zout of brak water overstroomd, ten dele door militaire inundaties gedurende de Tweede Wereldoorlog, ten dele door natuurlijke oorzaken (dijkvallen, stormvloed van 1 februari 1953). Een overzicht van de overstroomde gebieden is weergegeven in fig. 1. Vooral na de militaire inundaties van 1944–'45 werden uitvoerige onderzoekingen verricht; deze omvatten o.a. de aanleg en de waarneming van talrijke gipsproefvelden. Op deze proefvelden werden het gehalte van de grond aan uitwisselbare kationen, de bodemstructuur en de reactie van het gewas nagegaan (fig. 2, tabel 1 en 2). Bij deze onderzoekingen werd vooral aandacht besteed aan het gehalte aan uitwisselbaar natrium, omdat het natrium beschouwd mag worden als de voornaamste factor bij het ontstaan van de slechte structuur van overstroomde gronden.

2. Bij de behandeling van de processen welke in overstroomde gronden optreden is voornamelijk de deductieve methode gevolgd; daarom is eerst een overzicht gegeven van de theoretische grondslagen van de ionen-uitwisseling. Dit omvat beschouwingen over uitwisselings-evenwichten, over de snelheid, waarmede deze evenwichten tot stand komen en over de analogie van de bodem met een kolom van een ionen-uitwisselende stof. Bij de beschouwingen over de uitwisselings-evenwichten kan men hetzij uitgaan van het DONNAN-evenwicht (fig. 3), hetzij van model-beschouwingen (fig. 5).

Voor uitwisseling van ionen met gelijke waardigheid leiden beide beschouwingen tot de vergelijking van KERR (vergelijking *2.27* en *2.29*). De theorie van STERN over de elektrische dubbellaag (fig. 5) leidt echter tot de gevolgtrekking, dat de specifieke verschillen in adsorptie van verschillende gelijkwaardige ionen moeten verminderen bij toenemende verdunning van de evenwichtsvloeistof (STERN effect). Dit houdt in, dat de uitwisselingsconstante K in de vergelijking van KERR bij toenemde verdunning tot één zal moeten naderen.

Voor uitwisseling van ionen met ongelijke waardigheid zijn vergelijkingen opgesteld door KERR (*2.28*). VANSELOW (*2.38*), KRISNAMOORTHY & OVERSTREET (*2.42*) en GAPON (*2.46*). Al deze vergelijkingen voorspellen een toenemende adsorptie van het ion met de hoogste waardigheid bij toenemende verdunning van de evenwichtsvloeistof (valentie-effect).

In vele gevallen blijken de genoemde vergelijkingen echter niet te voldoen. Daarom verdient het dikwijls de voorkeur gebruik te maken van empirische betrekkingen. In vele gevallen voldoet de empirische betrekking van ROTHMUND & KORNFELD (*2.48*, *2.49*) zeer goed.

In een bodemprofiel zijn de optredende uitwisselingsprocessen analoog met de reacties in een kolom van een ionen-uitwisselaar (fig. 6, 7, 8). Daardoor kan ook de theorie van de ionen-uitwisseling in kolommen worden toegepast op de uitwisselingsprocessen in de bodem. Deze theorie voorspelt, dat de begrenzing van de ionen, die de kolom verlaten, diffuus zal zijn als deze ionen een lineaire of convexe adsorptie-isotherm bezitten, maar dat voor ionen met een concave adsorptie-isotherm deze begrenzing veel scherper zal zijn. Voor de voorste begrenzing van de intredende ionen geldt het omgekeerde.

Volgens GLUECKAUF kunnen storende invloeden als diffusie en onregelmatigheden in de stroming door de kolom worden samengevat in één grootheid: de dikte van de theoretische uitwisselings-eenheid. Als deze dikte bekend is, kan het gedrag van de kolom kwantitatief worden voorspeld, behalve voor het geval dat de uittredende ionen een convexe adsorptie-isotherm bezitten.

3. Na deze algemene theoretische beschouwingen worden de eigenschappen van de betreffende gronden nader uiteengezet. Na een kort overzicht van de wordingsgeschiedenis van het gebied volgt een korte beschrijving van de korrelgrootte-verdeling en de gehalten aan koolzure kalk en organische stof van de gronden in de overstroomde gebieden (tabel 4). Een van de meest opvallende processen in deze gronden is een langzame ontkalking onder invloed van het vochtige klimaat. Hierdoor wordt het gehalte aan koolzure kalk in de bovengrond steeds geringer, zodat het verschil in kalkgehalte tussen onder- en bovengrond toeneemt met de ouderdom van deze gronden. Uit de toeneming van dit verschil met de ouderdom van de inpoldering valt af te leiden, dat de gronden in Zuidwest-Nederland uit hun bovenste 20 cm jaarlijks ongeveer 350 kg/ha kalk verliezen, hetgeen overeenkomt met een teruggang in het gehalte aan koolzure kalk van 1 % in 80 jaar. Dit houdt tevens in, dat de concentratie aan calcium-ionen in het bodemvocht omstreeks 3,5 mval/l zal bedragen en dat de gronden voortdurend met een oplossing van deze sterkte zullen worden gepercoleerd.

De adsorptieve eigenschappen van de gronden hangen zeer nauw samen met hun gehalte aan actief materiaal (fig. 9, 10), waaronder wordt verstaan de som van het lutumgehalte (deeltjes $< 2\mu$) en drie maal het gehalte aan organische stof (*3.01*). Bij pH 8,0 is de adsorptiecapaciteit van dit actieve materiaal in de bovengrond ongeveer 70 mval per 100 g (fig. 11) en nog enigszins hoger in de ondergrond (tabel 5). In kalkhoudende gronden worden deze beschikbare adsorptieplekken vrijwel geheel ingenomen door de ionen Na, K, Mg en Ca (tabel 6, fig. 11). Slechts in gronden, die geen koolzure kalk bevatten is het totaal van deze metaal-kationen soms aanmerkelijk lager dan de adsorptie-capaciteit, doordat ook H_3O-ionen zijn geadsorbeerd. In deze gronden bestaat er dan ook een duidelijk verband tussen de som van de metaal-kationen en de pH van de grond (fig. 12).

Voor de studie van binaire uitwisselings-evenwichten werden twee typische gronden (tabel 7) gepercoleerd met een overmaat aan gemengde oplossingen van $NaCl + KCl$, $NaCl + CaCl_2$ en $MgCl_2 + CaCl_2$. De uitkomsten van deze proefnemingen zijn weergegeven als adsorptie-isothermen (fig. 13, 15, 17), terwijl de verschillende theoretische betrekkingen voor deze evenwichten aan de waarnemingen werden getoetst (fig. 14, 16, 18). Van de homovalente evenwichten Na-K en Mg-Ca bleken de specifieke verschillen in adsorptie tussen de ionen af te nemen bij teonemende verdunning van de evenwichtsvloeistof (fig. 13, 17), hetgeen in overeenstemming is met de theorie van STERN. Slechts de empirische vergelijkingen van ROTHMUND en KORNFELD bleken een bevredigende beschrijving van de evenwichten te geven, hoewel ook in deze vergelijkingen de parameters K en p afhankelijk bleken te zijn van de concentratie van de oplossing (tabel 11, 17).

Voor het heterovalente evenwicht Na-Ca bleek de adsorptie van calcium toe te nemen bij verdunning, in overeenstemming met het valentie-effect (fig. 15). De vergelijking van GAPON bleek niet bruikbaar te zijn voor een beschrijving van het evenwicht, maar de vergelijkingen van KERR, KRISNAMOORTHY & OVERSTREET en VANSELOW gaven goede uitkomsten, althans binnen de grenzen van de waarnemingsfouten. Toch was ook in deze vergelijkingen de waarde van de uitwisselingsconstante K nog afhankelijk van de concentratie van de evenwichtsoplossing (tabel 14).

In overstroomde gronden treden echter evenwichten op tussen vier soorten van ionen in plaats van twee. Doordat deze ionen elkaar onderling beïnvloeden, stuit een uitbreiding van de wetten voor binaire evenwichten op moeilijkheden. Slechts voor een groep van evenwichten met oplossingen van verwante samenstellingen zou een dergelijke uitbreiding kans van slagen bieden. Zo geeft een uitbreiding van de vergelijking van KERR tot vier soorten ionen een bevredigende beschrijving van de evenwichten van de twee typische gronden met een overmaat zeewater, verdund zeewater en brak water (tabel 21). In meer ingewikkelde gevallen, zoals evenwichten met beperkte hoeveelheden zeewater, is ook deze uitgebreide vergelijking niet meer bruikbaar (fig. 21).

Uit de waargenomen evenwichten met verdund zeewater – die werden bereikt door percolatie van de grond met een overmaat vloeistof – blijkt, dat bij toenemende verdunning de hoeveelheden uitwisselbaar Mg en Ca toenemen ten koste van Na en K (fig. 19, 20). Dit verschijnsel wordt veroorzaakt door het valentie-effect. Voorts wordt bij evenwichten met brak water meer Ca geadsorbeerd dan bij evenwichten met verdund zeewater van hetzelfde zoutgehalte, omdat brak water naar verhouding rijker is aan Ca dan zeewater (fig. 20). Zoals reeds is vermeld blijkt een uitbreiding van de vergelijking van KERR tot vier ionen een redelijke beschrijving te geven van de waargenomen evenwichten (tabel 21). Maar anderzijds wijken de onderlinge verhoudingen van de geadsorbeerde ionen soms sterk af van de verhoudingen, die zouden volgen uit de vergelijkingen van een binair evenwicht (tabel 23). Hieruit blijkt duidelijk dat de verschillende soorten van ionen elkander onderling sterk beïnvloeden. Door deze storingen is een algemene beschrijving van evenwichten met vier ionen voorshands nog niet mogelijk.

Evenwichten van deze aard komen echter in overstroomde gronden zeer algemeen voor; daarom is getracht deze evenwichten te beschrijven met empirische adsorptie-isothermen (fig. 22–27). Voor Na kunnen deze empirische adsorptie-isothermen worden beschreven met een eenvoudige, kwadratische vergelijking (*3.23*). De uitkomsten van deze vergelijking blijken eveneens redelijk goed overeen te komen met de uitkomsten van de vergelijkingen voor het binaire evenwicht Na-Ca (fig. 23, C). Vooral voor Mg blijken de tegenionen Na en Ca grote invloed uit te oefenen op de adsorptie-isothermen (fig. 26): de adsorptie van dit ion blijkt sterk te zijn indien Na het meest voorkomende tegenion is en zwak indien Ca overweegt.

Tenslotte is de ionenbezetting van niet-overstroomde gronden in het kort besproken. In deze gronden is Ca steeds het voornaamste geadsorbeerde metaal-kation, terwijl slechts sporen uitwisselbaar Na aanwezig zijn. De hoeveelheden geadsorbeerd Mg nemen toe met toenemende ouderdom van de gronden (fig. 28).

4. Gedurende een overstroming met zout water zal de ionenbezetting van de grond sterk veranderen. In de regel dringt slechts een beperkte hoeveelheid overstromingswater in de bodem, zodat een volledig evenwicht met zeewater meestal lang niet wordt bereikt. Een uitzondering vormen gronden, die tijdens de overstroming door het overstromingswater worden gepercoleerd, bijvoorbeeld door een afwisselende overstroming bij hoog water, gevolgd door een drooglegging bij laag water. In dergelijke gevallen kan de ionenbezetting van de grond naderen tot het volledige evenwicht met zwwater, zoals dit bij laboratoriumproeven is gevonden (fig. 29). Meestal echter zijn de veranderingen in de ionenbezetting veel kleiner, vooral in de ondergrond (fig. 30).

Volledige evenwichten met brak water werden bij de bestudeerde overstromingen niet bereikt, maar zij kunnen worden nagegaan door een analyse van de bodems van brakke estuaria. Dergelijke gronden bevatten meer uitwisselbaar calcium en soms ook meer uitwisselbaar magnesium naarmate het zoutgehalte van het bovenstaande water geringer is (tabel 28); dit is in overeenstemming met laboratoriumproeven (vgl. fig. 20). Bij de overstromingen met brak water in de periode 1939–'53 werden deze volledige evenwichten evenwel lang niet bereikt (tabel 29). Zo werd de kenmerkende stijging van het gehalte aan uitwisselbaar magnesium bij dalend zoutgehalte van het overstromingswater nimmer aangetroffen bij overstroomde gronden. Ook de gehalten aan uitwisselbaar Na en K van dergelijke gronden lagen ver beneden de gehalten, die in het laboratorium na percolatie met overmaat brak water werden gevonden.

Doordat de grond tijdens de overstroming gewerkt heeft als een uitwisselingskolom waren de veranderingen in de bovengrond steeds veel groter dan in de ondergrond (fig. 31). Dit kolomeffect kan goed worden bestudeerd door de verdeling van de Cl-ionen onmiddellijk na de overstroming te onderzoeken: na overstromingen van geringe tijdsduur neemt de concentratie van deze ionen sterk af met de diepte. Vergelijkt men de gevonden verdeling met de theorie van de kolomwerking, dan blijkt voor lichte gronden de overeenstemming zeer goed te zijn. Voor zware gronden treden echter afwijkingen op, die veroorzaakt worden door de aanwezigheid van scheuren; hierdoor wordt in de ondergrond de Cl-concentratie hoger dan volgens de theorie van de kolomwerking te verwachten is.

Dadelijk na een overstroming bleek er een vrij goede samenhang te bestaan tussen de Cl-concentratie in het bodemvocht en het gehalte aan uitwisselbaar Na, niet slechts in de bovengrond (fig. 33), maar ook in de ondergrond (fig. 34). Daarbij bleek er in het bodemprofiel tevens een sterke gelijkenis te bestaan tussen de verdeling van Cl-ionen in het bodemvocht en de verdeling van het uitwisselbare natrium (fig. 35, A, B). Uitzonderingen hierop vormden gronden, die binnen korte tijd tweemaal werden overstroomd en gronden met een permanent verzilte ondergrond.

Uitgaande van de empirische Na adsorptie-isotherm bleek het mogelijk te zijn een semi-kwantitatieve verklaring te geven voor de gevonden betrekkingen tussen het gehalte aan Cl-ionen in het bodemvocht en het gehalte aan uitwisselbaar Na onmiddellijk na een overstroming (fig. 33, tabel 32).

5. Nadat overstroomde gronden wederom zijn drooggelegd, treedt van nature een langzaam doch onmiskenbaar natuurlijk herstel op. De opgeloste zouten worden door het percolerende regenwater uitgewassen, waardoor o.a. het gehalte aan Cl in het bodemvocht snel daalt. Maar ook het gehalte aan uitwisselbaar Na – en in veel mindere mate ook de gehalten aan uitwisselbaar K en Mg – vertonen in de loop van enige jaren een daling (fig. 38).

Uit modelproeven (fig. 37) en uit veldwaarnemingen (fig. 38) blijkt, dat de geadsorbeerde kationen de grond verlaten in de volgorde Na — K — Mg en dat deze veranderingen in het bodemprofiel van boven naar beneden voortschrijden (fig. 39, 40, 41). In overeenstemming met de theorie van een uitwisselings-kolom is daarbij de begrenzing van de Na-ionen scherper dan de overeenkomstige begrenzing van de Cl-ionen (fig. 42). Uit waarnemingen van proefplekken blijkt, dat na een overstroming het voornaamste uitwisselingsproces bestaat uit het vervangen van uitwisselbaar Na door uitwisselbaar Ca (tabel 34).

Het natuurlijke herstel van overstroomde gronden wordt door verschillende processen bewerkstelligd. Zo zullen veranderingen in de *concentratie van het bodemvocht* leiden tot een verschuiving in de verdeling tussen ionen in oplossing en geadsorbeerde ionen. Het blijkt echter, dat deze verschuiving niet kan leiden tot sterke veranderingen in de ionenbezetting (tabel 37), een uitkomst, die bevestigd wordt door waarnemingen op proefplekken (fig. 43).

Hydrolyse en reactie met koolzuurhoudend water zullen leiden tot een vervanging van geadsorbeerde Na-ionen door H_3O-ionen en tot een stijging van de pH als gevolg van de vrije OH-ionen, die in de oplossing achterblijven. Gronden, die rijk zijn aan uitwisselbaar Na bezitten dan ook in het algemeen een hoge pH; er bestaat daarbij een zeker verband tussen gehalte aan uitwisselbaar Na en pH (fig. 45). Voor de verwijdering van het uitwisselbare Na uit overstroomde, kalkhoudende gronden is dit proces echter van weinig betekenis, omdat de reactie met H_3O-ionen ver achterblijft bij de vervanging van Na door Ca, afkomstig van de in de grond aanwezige koolzure kalk.

In gronden, die geen koolzure kalk bevatten, is hydrolyse mogelijk van meer betekenis; het aantal waarnemingen op dergelijke gronden was echter te beperkt om hierover een beslissende uitspraak te kunnen geven.

Uitwisseling van Ca-ionen afkomstig van de oplossing van koolzure kalk is het voornaamste proces bij het natuurlijke herstel van kalkhoudende overstroomde gronden. Uit theoretische beschouwingen blijkt echter dat ook dit proces spoedig tot stilstand komt (tabel 39), tenzij de Na-ionen, die vrijgekomen zijn door uitwisseling met Ca, door uitspoeling worden verwijderd. De snelheid van het natuurlijke herstel van overstroomde gronden wordt daarom bepaald door de uitspoeling van deze vrijgekomen Na-ionen. Eerst als deze zijn verwijderd, kunnen wederom geabsorbeerde Na-ionen worden uitgewisseld tegen Ca en kunnen nieuwe Ca-ionen uit het aanwezige carbonaat in oplossing gaan.

In niet-kalkhoudende gronden is mogelijk de *oplossing van Ca uit andere Ca-houdende mineralen* van betekenis voor het natuurlijke herstel. Ten slotte kan ook een *opneming van ionen door de plantenwortels* bijdragen tot een daling van het uitwisselbare K; voor Na en Mg, die in veel grotere hoeveelheden aanwezig zijn, is dit proces van weinig betekenis.

Zoals reeds is vermeld is bij het natuurlijke herstel van kalkhoudende overstroomde gronden de vervanging van uitwisselbaar Na – en in veel mindere mate van uitwisselbaar K en Mg – door Ca het belangrijkste proces. De beperkende factor in dit proces is de verwijdering van de vrijgemaakte ionen door uitspoeling. Als gevolg daarvan is de snelheid van herstel zeer sterk afhankelijk van de waterpassage (tabel 43, 44). Voorts blijkt het herstel bij lichte gronden sneller te verlopen dan bij zware gronden (tabel 45).

De gemiddelde verliezen aan uitwisselbaar Na na een overstroming met zout water bedragen 390 kg per ha per jaar, een cijfer, dat nog enigszins hoger ligt voor gronden die veel uitwisselbaar Na bevatten (tabel 46).

Met behulp van de theorie van de uitwisseling van ionen in kolommen van een adsorberende stof kan een schatting worden gemaakt van de snelheid van het natuurlijke herstel. Hierbij kunnen de empirische adsorptie-isothermen als uitgangspunt worden genomen. Op deze wijze wordt gevonden, dat Cl spoedig wordt uitgewassen, dat Na langzaam wordt verwijderd en dat K en vooral Mg nog lange tijd in overmaat aanwezig blijven, vooral in de ondergrond (tabel 48). Als gevolg daarvan bezitten gronden, die tientallen jaren geleden met zout water overstroomd zijn geweest, nog steeds een hoog gehalte aan uitwisselbaar Mg in de ondergrond (tabel 49). De theorie voorspelt voor de bovengrond een gemiddeld verlies aan uitwisselbaar Na van 600 kg per ha per jaar, een waarde die hoger ligt dan de waargenomen verliezen (390 kg per ha en per jaar). Dit verschil wordt mogelijk veroorzaakt door verstoringen van het profiel als gevolg van de grondbewerking (fig. 46); deze verstoringen vertragen het herstel.

6. Hoewel het natuurlijke herstel op den duur in staat is de grond wederom in een normale toestand te brengen is de snelheid van dit herstel zo langzaam, dat de landbouw gedurende vele jaren moeilijkheden ondervindt van een slechte bodemstructuur. Met behulp van verschillende behandelingen kan echter het herstel aanzienlijk worden bespoedigd.

Verbouw van overblijvende gewassen is een oude behandelingswijze voor overstroomde gronden. In een reeks proefnemingen bleek gras meer effectief te zijn dan rode klaver of luzerne (tabel 51).

Bij verbouw van overblijvende gewassen vermijdt men de storende invloed van de grondbewerking op het herstel. Toch is de daling van het gehalte aan uitwisselbaar Na slechts weinig groter dan bij verbouw van éénjarige gewassen.

Bemesting met organisch materiaal bleek weinig uitwerking te hebben, zelfs indien zeer grote hoeveelheden werden toegediend.

Van verschillende chemicaliën bleken *kalkmergel*, *gebluste kalk* en een *humuspreparaat* weinig effect te hebben. Anderzijds werde sterke verbeteringen bereikt met toediening van *gips*, *calciumchloride* of *zwavel* (tabel 53, 63, 64). Daarbij vertoonde calciumchloride de snelste werking, gevolgd door gips. Zwavel, dat eerst tot zwavelzuur moet worden geoxydeerd alvorens te kunnen werken, was zeer effectief, maar eerst na verloop van tijd (fig. 52). Doordat calciumchloride zeer moeilijk te hanteren was en doordat de prijs van zwavel te hoog lag, kwam alleen gips in aanmerking voor gebruik op grote schaal.

De snelste regeneratie van de grond door gips werd waargenomen in gronden, waar deze verbinding in het gehele bodemprofiel aanwezig was. Dit is het geval in pas drooggelegde zee-bodems; in dergelijke slikgronden wordt gips gevormd door natuurlijke processen, namelijk door oxydatie van sulfiden. Maar zelfs in deze gronden leidt een plaatselijke reactie van dit gevormde gips met de uitwisselbare kationen van het adsorptie-complex nog slechts tot een vrij kleine verschuiving van het evenwicht (tabel 57). Alleen in combinatie met waterpassage – waardoor de uitgewisselde Na-, K- en Mg-ionen worden verwijderd – zijn snelle veranderingen mogelijk (fig. 49, tabel 59).

Bij oudere gronden werd na een overstroming met zout water gips toegediend door uitstrooien op het maaiveld. Meestal waren de gegeven hoeveelheden nog niet toereikend om alle uitwisselbare Na uit de bouwvoor te verdrijven. In deze gevallen was het herstel minder snel (fig. 50, tabel 60) en meestal werd slechts een gedeeltelijke regeneratie bereikt (fig. 51). Voorts bleek, dat bij gipsbemesting wel een gedeelte van het uitwisselbare Na werd vervangen, maar dat het uitwisselbare K en Mg nagenoeg onveranderd bleven (tabel 64). Toch waren deze gipsbemestingen voor de praktijk van grote betekenis: uitwisselbaar Na en pH werden verlaagd (tabel 61), de structuur van de grond werd aanmerkelijk verbeterd (fig. 55–57) en de schade aan de gewassen werd aanzienlijk beperkt (fig. 58).

Het nuttig effect van gips voor het verwijderen van uitwisselbaar Na was het hoogst voor lage giften (tabel 62). Voor giften, zoals deze in de praktijk werden verstrekt bleek ongeveer 50 % van het gebruikte gips nuttig te werken voor het verdrijven van uitwisselbaar Na uit de bovenste 20 cm van de grond. In de praktijk bleek, dat de beste uitkomsten worden verkregen bij een vroegtijdige aanwending van gips. Wanneer een overstroomde grond nog in de winter of in het vroege voorjaar weer droog valt is het aan te bevelen nog in het voorjaar een kleine hoeveelheid gips toe te dienen om te voorkomen, dat de structuur van het zaaibed bij een zware regenbui verloren gaat. Het heeft echter weinig zin om reeds in het voorjaar grote hoeveelheden gips aan te wenden, omdat er gedurende de zomer vrijwel geen waterpassage optreedt en het gips dus ook slechts weinig zal bijdragen tot de regeneratie van de grond.

In de herfst moeten na het ploegen grote hoeveelheden gips worden toegediend om een verval van de structuur gedurende de winter te voorkomen. Voor een zo goed mogelijke werking dient het gips op de oppervlakte te worden achtergelaten. Het verdient geen aanbeveling per jaar meer dan 7 ton/ha aan gips te geven; grotere hoeveelheden immers zullen door de beperkte oplosbaarheid van gips achterblijven en bij de volgende grondbewerking worden ondergeploegd. Indien grotere hoeveelheden nodig zijn dan 7 ton/ha is het dan ook beter de gipsbemesting over meer dan één jaar te verdelen.

De hoeveelheden gips, benodigd voor het herstel van overstroomd bouwland, zijn afhankelijk van de zwaarte van de grond en van het zoutgehalte onmiddellijk na de overstroming. Deze hoeveelheden zijn op twee manieren bepaald, namelijk op directe wijze door waarneming van de resultaten van een groot aantal proefvelden (*6.05*) en op indirecte wijze door berekening, waarbij rekening werd gehouden met het natuurlijke herstel en met het rendement van een gipsbemesting (*6.06*). De resultaten van deze beide beschouwingswijzen zijn als nomogram weergegeven (fig. 54), terwijl tabel 71 een vergelijking geeft tussen beide berekeningswijzen en de hoeveelheden gips die in de praktijk werden aangewend.

Op overstroomde oude graslanden behoeft geen gips te worden gegeven, aangezien op deze gronden nimmer verval van structuur is waargenomen.

In een aanhangsel is een korte beschrijving gegeven van de toegepaste analytische methoden. Voor de bepaling van de uitwisselbare kationen zijn twee werkwijzen gevolgd, namelijk de perssap-methode en de alcohol-methode. Binnen de grenzen van de waarnemingsfouten geven deze twee methoden dezelfde uitkomsten (tabel 72, fig. 59–62).

APPENDIX

ANALYTICAL METHODS

CLAY CONTENT is determined according to the pipette method (ROBINSON, 1922). In the soil sample organic matter is destroyed by treatment with concentrated H_2O_2; iron compounds, calcium carbonate and soluble salts are dissolved by boiling with diluted HCl and removed by subsequent decantation. As a deflocculating agent Na_2CO_3 is used.

The suspension obtained is allowed to settle in cylindrical vessels; the amounts of particles $< 16\,\mu$ and $< 2\,\mu$ are determined by pipetting a small aliquot from the suspension at the appropriate time and depth. These samples are evaporated to dry, dried at 105 centigrades and weighed after cooling. A correction is made for the added Na_2CO_3.

ORGANIC MATTER is determined by elementary analysis, using the dry combustion method of TERMEULEN & HESLINGA, as described by SPITHOST (1933). The sample is heated in a CO_2-free air stream; the organic compounds are vaporized and further oxidized by a catalyst consisting of MnO_2 and PbO_2, which at the same time retains Cl, S, and P. The organic matter is quantitatively transformed into CO_2. Moreover, in calcareous samples CO_2 is liberated from $CaCO_3$.

After drying the gasses by $CaCl_2$, CO_2 is absorbed in U-shaped tubes with soda-lime covered by $CaCl_2$, which are weighed before and after the experiment. After correction for CO_2 liberated from $CaCO_3$ the organic matter content of the soil is calculated by assuming its carbon content to be 58%.

$CaCO_3$ CONTENT is estimated by volumetric analysis according to SCHEIBLER as described by BRUIN (1937). CO_2 is liberated by adding HCl (25%) to the sample; its volume is measured in a gas burette. It must be remarked, however, that in using this method also other carbonates – e.g. dolomite and siderite – will be destroyed; these compounds are therefore also calculated as $CaCO_3$ (BRUIN, 1938).

MOISTURE CONTENT (A) is determined by drying at 105 centigrades; it is expressed as g per 100 g dry matter.

SALT CONTENT (B) is determined by rotating the sample with a $CaSO_4$-solution for 4–8 hours. After settling an aliquot of the clear supernatant liquid is pipetted and titrated with decinormal $AgNO_3$, using K_2CrO_4 as an indicator (titration according to MOHR; TREADWELL, 1927). The Cl content found is expressed as g NaCl per 100 g dry matter.

SALT CONCENTRATION (C) is calculated from A and B according to $C = \frac{1000\ B}{A}$. For practical purposes an electrometic method is employed using an Ag-AgCl electrode and a calomel reference electrode with KCl salt bridge. Both electrodes are brought into contact with the field-moist sample; their potential difference appears to be closely related to the Cl concentration in the soil moisture (VERHOEVEN, 1953).

ADSORPTIVE CAPACITY is determined with Ca ions at pH 8.0. The sample is mixed with quartz sand in a ratio of 1 : 7 and filled into a percolation tube. The column thus obtained is percolated with excess 0.5 normal Ca acetate of pH 8.0 to obain complete saturation with Ca.

To remove excess solution the column is washed with 96% alcohol, after which the adsorbed Ca is driven off by percolating with excess normal NaCl. In the percolate Ca is determined according to SCHWARZENBACH by titration with decinormal versenate (Komplexon III), using eriochrome black as an indicator (KUANG & BRAY, 1951).

In calcareous soils, however, part of this Ca is originating from solid $CaCO_3$ dissolved into the percolating NaCl solution. This amount is assumed to be equivalent with the amounts of HCO_3 and CO_3 in the percolate; these amounts may be determined by titration (JARUSSOV, 1933). This titration may be carried out either directly with decinormal HCl, using methylorange as indicator or indirectly by adding a known excess of decinormal HCl, boiling to remove CO_2 and back-titration with decinormal NaOH[1]. The equivalent amount of Ca is subtracted from total Ca to obtain the adsorptive capacity for Ca at pH 8.0.

EXCHANGEABLE CATIONS IN NON-SALINE SOILS may be determined by extracting the sample with neutral salt solutions. Usually part of the sample is extracted with excess normal NH_4NO_3, another part with excess normal NaCl. In the first extract the cations Na and K are determined, in the second the cations Mg and Ca, the sum of HCO_3 and CO_3, and SO_4. It may be assumed that the ions Na, K, and Mg are entirely originating from exchange positions, but part of the Ca may originate from $CaCO_3$, dissolving into the NaCl solution. By assuming this dissolved Ca to be equivalent with the amount of HCO_3/CO_3 in the NaCl extract, the amount of exchangeable Ca can be found by difference (JARUSSOV, 1933). If $CaSO_4$ is present another part of the Ca in the NaCl extract will originate from this compound. Correction is possible by assuming this Ca to be equivalent with SO_4 in the extract. If gypsum is absent no appreciable amounts of SO_4 are found in the extract.

EXCHANGEABLE CATIONS IN SALINE SOILS can only be determined if a separation is made between the exchangeable cations and the cations in the soil solution. In practice such a separation may be obtained in two ways. The first involves determination of total cations present in the soil and subsequent correction for dissolved cations obtained via analysis of the soil moisture.

The second method involves complete removal of the soil moisture without altering the exchangeable cations. The first principle is followed in the "expressed fluid method", the second in the "alcohol method" of determining exchangeable ions.

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[1] The indirect method has the advantage of a better defined end-point.

In both methods the exchangeable ions are removed by extraction with neutral salt solutions (normal NH_4NO_3 for Na and K, normal NaCl for Mg and Ca). A complication is that solid $CaCO_3$ and $CaSO_4$ may be present; these compounds will dissolve into the NaCl solution, thus giving too high values for Ca unless appropriate corrections are made.

Expressed fluid method (ZUUR, 1938; RAPPORT, 1945).

The analysis of saline soils according to the expressed fluid method is carried out in three steps, viz.:

a) Determination of total cations and anions in neutral salt extracts and of the sum of exchangeable metal cations S,

b) Correction for ions in the soil solution by analysis of expressed fluid,

c) Correction for $CaCO_3$ and $CaSO_4$ dissolved into the NaCl extraction fluid.

a) Total ions and sum S. Part of the field-moist sample is percolated with excess normal NH_4NO_3; in the extract Na, K, and Cl are determined. A second part of the sample is percolated with excess normal NaCl; in the extract Mg, Ca, HCO_3/CO_3, ans SO_4 are determined. The ions NH_4 and NO_3, both occurring only in minor quantities in the soil, are usually neglected; if desired their estimation is made in the NaCl extract.

The amounts of Na, K, and Mg found in this way represent the totals of exchangeable ions and ions in solution; the amount of Ca found is the total of exchangeable Ca, Ca in solution, and Ca dissolved from $CaCO_3$ and $CaSO_4$. Of the anions, Cl is entirely originating from the soil solution, HCO_3/CO_3 largely from dissolved $CaCO_3$[1] and SO_4 partly from the soil solution, partly from dissolved $CaSO_4$. These anions are accompanied by equivalent amounts of cations.

By diminishing the total milli-equivalents of metal cations (Na, K, Mg, Ca) by the total milli-equivalents of anions (Cl, HCO_3/CO_3, SO_4) the sum of exchangeable metal cations, S, may be found.

b) Correction for soil solution. Another part of the field-moist sample is sqeezed out in a hydraulic press under a pressure of approximately 400 atmospheres. The expressed fluid obtained is analyzed for cations (Na, K, Mg, Ca) and anions (Cl, HCO_3/CO_3, SO_4). Ionic balance serves as a control on the accuracy of the results.

The expressed fluid comprises only part of the soil moisture. Due to the negative adsorption of anions by the clay- and humus- particles the anionic concentrations in the expressed fluid are higher than those in the entire soil moisture; as the cations in solution are by definition equivalent with these anions, the same will hold for them. This negative adsorption is clearly demonstrated by the observation that the Cl concentration in the expressed fluid is always higher than the average Cl concentration in the soil moisture, calculated from total Cl content of the soil and moisture content.

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[1] In Dutch saline soils no appreciable amounts of alkali carbonates and bicarbonates occur.

From such observations the negative adsorption of Cl appeared to be equivalent with an amount of salt-free moisture of 12 grams per 100 g of active matter.

By assuming the ratios of cations in solution to Cl to be the same throughout the entire soil moisture, the amounts of cations in solution may be calculated by multiplying their concentrations in the expressed fluid with the factor:

$$\frac{\text{Cl in soil}}{\text{Cl concentration in expressed fluid}}$$

In soils low in Cl, this factor cannot be established with sufficient accuracy; in that case it is supposed that the cations in solution – like Cl – are present with „expressed fluid concentration" in an amount of moisture equal to the soil moisture content minus 12 g of moisture per 100 g of active matter. Comparison of both methods – in cases where it was possible – revealed that the differences were negligible (RAPPORT, 1945).

If the amounts of dissolved cations calculated in one of these ways are subtracted from the total amounts mentioned sub *a*), the amounts of exchangeable Na, K, and Mg are found. For Ca, further corrections are necessary due to dissolution of $CaCO_3$ and eventually $CaSO_4$ into the percolation fluid.

c) Correction for dissolved Ca compounds. If $CaSO_4$ is absent, a correction for dissolved $CaCO_3$ may be obtained by assuming the amount of dissolved Ca to be equivalent with the amount of HCO_3/CO_3 in the NaCl extract. If also $CaSO_4$ is present, exchangeable Ca is usually obtained by difference, viz. by subtracting the totals of exchangeable Na, K, and Mg from the sum of exchangeable metal cations, S.[1]

The following analytical methods were used:

Na was determined according to KAHANE (WRIGHT, 1938); it was precipitated as Na-Mg-uranyl-acetate and weighed.

K was precipitated as K-Na-cobalto-nitrite; the precipitate is oxidized by a known excess of $KMnO_4$, the remainder of which is titrated with oxalic acid.

Ca was precipitated as the oxalate, which was titrated with $KMnO_4$. In the filtrate *Mg* was precipitated as $MgNH_4PO_4$ and weighed as pyrophosphate.

Cl was titrated according to MOHR with $AgNO_3$, using K_2CrO_4 as an indicator.

HCO_3/CO_3 was determined by titrating with HCl, using methylorange as an indicator.

SO_4 was precipitated as $BaSO_4$ and weighed.

The expressed fluid method is based upon a few plausible assumptions, the principal of which is the similarity in ionic ratios between expressed fluid and soil moisture. Its principal drawback is the large number of analyses involved; on the other hand, it renders information not only on the exchangeable cations, but also on the composition of the equilibrium solution.

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[1] The same method may be followed if alkali carbonates and bicarbonates occur in appreciable amounts.

Alcohol method

The analysis of saline soils according to the alcohol method is carried out in three steps, viz.:

a) Removal of soluble salts by washing with ethyl alcohol,

b) Determination of exchangeable cations by percolation with NH_4NO_3 and NaCl respectively,

c) Correction for $CaCO_3$ and $CaSO_4$ dissolved into the NaCl extraction fluid.

a) Removal of soluble salts. The field-moist sample is washed with excess alcohol 80% to remove the soluble salts and dried. As $CaCO_3$ and $CaSO_4$ are insoluble in alcohol, these compounds will remain in the sample.

b) Determination of exchangeable cations. Part of the alcohol-treated sample is percolated with excess normal NH_4NO_3, another part with excess normal NaCl. In the first extract Na and K are estimated, in the second extract Ca, Mg, HCO_3/CO_3, and SO_4. The amounts of Na, K, and Mg represent exchangeable cations; for Ca a correction for dissolved $CaCO_3$ and $CaSO_4$ is necessary.

c) Correction for dissolved Ca compounds.
As the soluble salts have already been removed by the alcohol treatment, the amounts of dissolved Ca must be equivalent with the amounts of HCO_3/CO_3 and SO_4 in the NaCl extract. Consequently a correction for dissolved Ca is easily made.

The following analytical methods were used:

Na and *K* were determined by using a flame photometer.

Ca was precipitated as the oxalate, which was titrated with $KMnO_4$. In the filtrate *Mg* was precipitated as $MgNH_4PO_4$ and weighed as pyrophosphate. More recently Mg was determined in the Ca filtrate by titration with versenate, using eriochrome black as an indicator.

Cl was titrated according to MOHR with $AgNO_3$, using K_2CrO_4 as an indicator.

HCO_3/CO_3 was determined directly by titration with HCl on methylorange or indirectly by adding excess HCl, boiling to remove CO_2 and back-titration with NaOH.

SO_4 was precipitated as $BaSO_4$ and weighed.

The alcohol method is based upon the following assumptions:

a) Addition of alcohol to field-moist samples does not give rise to precipitation of Na, K, or Mg compounds.

b) The equilibrium between exchangeable ions and ions in solution is not changed during the removal of the soluble salts.

The first assumption was checked by experiments (DOMINGO, 1956); the second one may only be verified by comparing the results obtained with those found by the expressed fluid method.

Comparison of the results

A large number of samples has been analyzed according to both methods. As a rule the results were in good accordance, at least within the limits of experimental errors. Some typical results of these comparisons have been listed in table 72, whereas in figs 59–62 all available evidence has been collected. As appears from these data no systematic differences were observed for Na, Mg and Ca. For K, which is only present in small amounts, the expressed fluid method seems to yield somewhat higher results than the alcohol method; this systematic difference, however, is not larger than about 1–2 mval per 100 g of active matter. The scattering of the dots must be ascribed to analytical errors; especially for Mg these errors were fairly large due to the inaccuracy of the gravimetric method used in the analyses.

TABLE 72. Comparison of the expressed fluid method with the alcohol method of determining exchangeable cations in saline soils.

Kind of soil	Salinity C g/l	Method	Exchangeable cations mval/100 g of active matter				
			Na	K	Mg	Ca	S
Calcareous, saline	27.3	e.f.	24.9	6.6	25.1	15.6	72.2
		alc.	22.2	5.5	24.1	15.2	67.0
Calcareous, brackish	8.5	e.f.	15.3	2.8	10.7	44.1	72.9
		alc.	15.4	3.0	12.7	44.6	75.7
Calcareous, non-saline	0.0	e.f.	0.3	2.2	1.3	59.0	62.8
		alc.	0.2	2.0	1.6	64.2	68.0
Non-calcareous, saline	13.9	e.f.	13.2	2.1	12.7	12.2	40.2
		alc.	12.9	2.6	14.8	14.4	44.7
With solid gypsum, non-saline	0.0	e.f.	0.0	2.4	9.2	56.0	67.6
		alc.	0.1	2.4	9.9	56.8	69.2

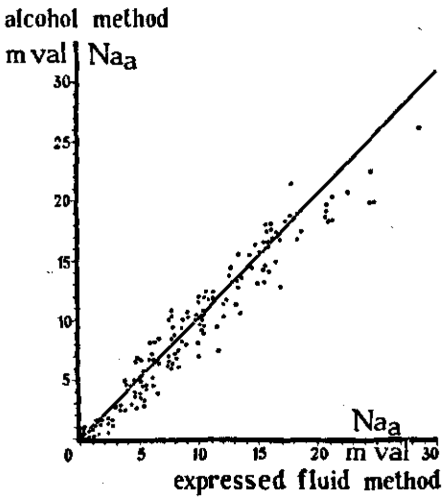

FIG. 59. Comparison of expressed fluid method and alcohol method; exchangeable Na

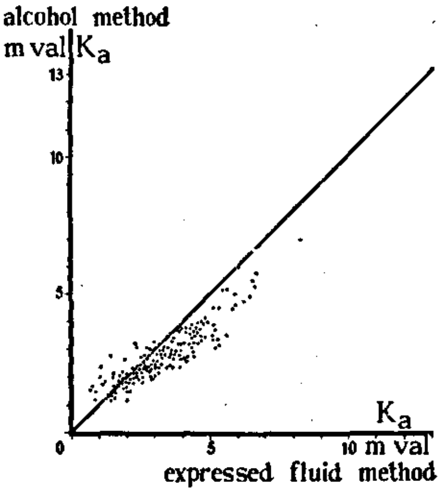

FIG. 60. Comparison of expressed fluid method and alcohol method; exchangeable K

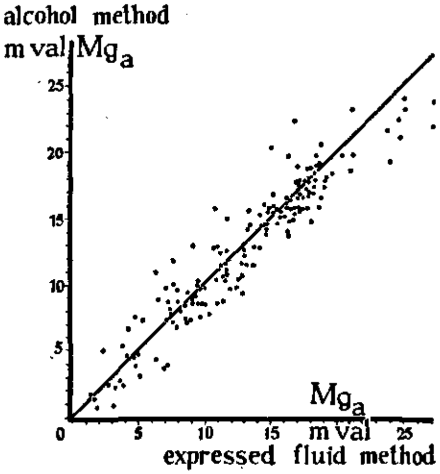

FIG. 61. Comparison of expressed fluid method and alcohol method; exchangeable Mg

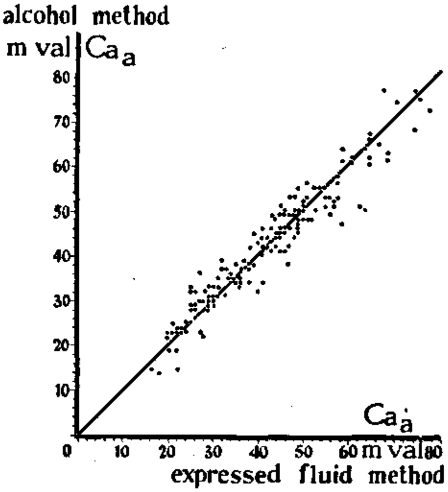

FIG. 62. Comparison of expressed fluid method and alcohol method; exchangeable Ca

LIST OF SYMBOLS

A.U.	Ångström unit (10^{-8} cm)
cm	centimetre
g	gram
ha	hectare (10^4 m^2)
hrs	hours
kg	kilogram
l	litre
m	metre
min	minute
ml	milli-litre
mm	millimetre
mval	milligram-equivalent
t	ton (10^3 kg)
$\mathrm{erfc}\, p = 1 - \frac{2}{\sqrt{\pi}} \int_0^p e^{-p^2}\, dp$	
$\exp p = e^p$	
ln	natural logarithm
log	decimal logarithm
Σ	sum
A	moisture content of soil (ml per 100 g of dry matter)
a_i	activity of substance i
a	NERNST distribution coefficient (eq. *2.50*)
a	constant in linear adsorption isotherm (pore space included)
a^*	constant in linear adsorption isotherm (pore space excluded)
$_a$	index referring to active matter
$a_1 \ldots\ldots a_4$	amounts of exchangeable cations taking part in equilibrium (mval) (section 3.63)
B	salt content of soil (g of Cl, calculated as NaCl, per 100 g of dry matter)
b	constant in quadratic adsorption isotherm (eq. *2.73*)

$b_1 \dots b_4$	amounts of ions in solution taking part in equilibrium (mval) (section 3.63)
C	salt concentration (g of Cl, calculated as NaCl per 1 of water or soil moisture)
c	concentration
c_i	concentration of ion i in solution (mval/l, sometimes mval/ml) concentration of ion i in the adsorbed state (mval per 100 g of exchanger)
c_0	initial value of c_i
d	depth (cm)
$\overline{d}$	depth at which the concentration of a substance in an exchange column becomes equal to half its initial value (at large values of N)
e	base of natural logarithms
F	the Faraday
f_i	activity coefficient of substance i
$f_\pm$	mean activity coefficient of electrolyte
$f(c_i)$	amount of ions i present in an exchange column in equilibrium with a solution of concentration c_i, including ions in pore space (mval per g of exchanger)
$f^*(c_i)$	ibidem, but excluding ions in pore space (mval per g of exchanger)
$f'(c)$	first derivative of f (c)
$f''(c)$	second derivative of f (c)
f_0	initial value of f (c)
G	gypsum equivalent of difference in exchangeable Na between treated and untreated plots of trial fields (t/ha of $CaSO_4 . 2H_2O$)
I	ionic strenght: $I = \frac{1}{2} \Sigma z_i^2 m_i$
i	index referring to ions
K	constant in ionic distribution equations
k	BOLZMANN's constant (section 2.11)
k	constant in column performance equations, denoting half the thickness of the theoretical plates (g/cm² of exchanger)
k'	ibidem, (cm)
$k_1 \dots k_4$	constants in equation for equilibria with dilute sea water and brackish water (section 3.62)
m	index referring to mixed solution (section 2.11)
m_i	molality of substance i (mols/1000 g of solvent)

N	number of theoretical plates above depth x
Na_a	amount of exchangeable Na (mval/100 g of active matter)
Na_s	ibidem (mval/100 g of dry matter)
Na_{sol}	amount of Na present in soil solution (mval/100 g of dry matter)
$_0$	index referring to initial stage
P	amount of soil taking part in equilibrium (g) (section 3.63)
p	unknown auxillary quantity
Q	amount of sea water taking part in equilibrium (l) (section 3.63)
q	active matter percentage of soil (clay + 3 humus)
R	gas constant
R	gypsum requirement (t/ha of $CaSO_4 . 2H_2O$)
S_a	sum of adsorbed metal cations (mval/100 g of active matter)
S_s	ibidem (mval/100 g of dry matter)
$_{\mathit{s}}$	index referring to single salt solution
$_{\mathrm{s}}$	index referring to soil dry matter
$_{sol}$	index referring to solution
T	absolute temperature (section 2.1)
$t_1 \ldots . t_4$	total amounts of ions taking part in equilibrium (mval) (section 3.63)
U_a	exchange capacity for Ca ions at pH 8.0 (mval/100 g of active matter)
U_s	ibidem (mval/100 g of dry matter)
$\bar{v}_i$	partial molal volume of substance i (section 2.1)
v	volume of influent passed through exchange column (ml/cm^2)
$\bar{v}$	volume of influent at which – at given depth and at large N – the concentration of the ions in solution is equal to half its initial value
$\bar{\bar{v}}$	ibidem for adsorbed ions
x	depth (g/cm^2 of exchanger)
$\bar{x}$	depth at which – at large N – the concentration of the ions in solution has become equal to half its initial value
$x_1 \ldots . x_4$	amounts of exchangeable cations after equilibrium (section 3.63)
z_i	valency of ion i
$\triangle$ Na	loss of adsorbed Na during natural regeneration (mval/100 g of soil) (section 5.4)
$\triangle$ Na_a	difference in exchangeable Na between gypsum treated and untreated plots of trial fields (mval per 100 g of active matter) (section 6.44)

$\Delta \pi$	osmotic pressure difference
$\Delta \psi$	electric potential difference
Σc	total ionic concentration of soil solution (mval/l)
$\Sigma \mathrm{Na}$	total amount of Na present in the soil (mval/100 g of dry matter)
$\Sigma \mathrm{Cl}$	total amount of Cl present in the soil (mval/100 g of dry matter)
α	pore space filled with liquid (ml/g of exchanger)
$\delta = \frac{\Sigma \mathrm{Na}}{\Sigma \mathrm{Cl}}$	ratio of total Na to total Cl in flooded soils
$\frac{1}{\varkappa}$	parameter denoting "thickness" of double layer
λ	DONNAN distribution coefficient
$\mu = \frac{\mathrm{Na}_s}{\mathrm{S}_s}$	fraction Na among the adsorbed ions
$\nu = \frac{c_{\mathrm{Na}}}{\Sigma c}$	fraction Na among the ions in solution
π	osmotic pressure
ϱ	density of soil in its natural position (g/cm^3); $\varrho \cong 1.4$
φ	STERN adsorption potential (section 2.13)
$\varphi_{\mathrm{Na}} = \frac{\mathrm{Na}_s}{\Sigma \mathrm{Na}}$	fraction of total Na present in the adsorbed state
ψ	electric potential

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