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WAITE AGRICULTURAL RESEARCH INSTITUTE,
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Thesis

INVESTIGATIONS CONCERNING THE CATION EXCHANGE PROPERTIES, THE BEHAVIOUR UNDER ELECTRODIALYSIS AND THE NATURE OF SOIL ACIDITY OF SOME SELECTED AUSTRALIAN SOILS WITH SPECIAL REFERENCE TO THE TYPE OF CLAY MINERAL CHARACTERIZING THEM.

Submitted by

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in

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INTRODUCTION.

In 1850 Way set out to investigate the fate of the ammonium ion applied as a fertilizer to the soil and pointed out that ammonia was retained by soil due to its base or cation exchange properties[*]. Since then it has been shown that the cation exchange affects almost all the physical, chemical and biological properties of soils.

With the cation exchange properties of soils is very intimately associated the concept of "soil acidity". It has been generally accepted until very recently that the soil complex responsible for these exchange phenomena was a weak insoluble acid of colloidal dimensions (often called an "acidoid"). In 1949 Schofield put forward the view that an acid soil does not have the true properties of a weak acid. The portion responsible for cation exchange carries a permanent negative charge below pH 6 which is usually satisfied by Al ions but may be satisfied by cations other than hydrogen (Russell, 1950, p.107). At pH values higher than this new negative charges may develop due to proton transfer, and this is the range normally studied in exchange phenomena with neutral or alkaline soils.

Whichever view is adopted, the soil colloidal material is predominantly the seat of the cation exchange properties of the soil. The nature of soil acidity, its strength, the quality and quantity of the exchangeable cations influence the physical and chemical soil properties such as the mobility of various nutrients and their availability to crops, soil structure, soil permeability, swelling, heat of wetting, soil reaction, buffer capacity and other related properties. The effects on the physical and chemical properties in turn influence the various biological activities in the soil.

Because of the fundamental importance of the cation exchange and the soil acidity, considerable work and thought have been devoted to the understanding of these phenomena.

Present Studies.

There is sufficient evidence to justify the statement that with the possible exception of special instances the inorganic exchange complex resides largely in the clay material of the soil. In spite of all the interest in the clays, their true nature was not understood as late as 1927, when Ross first pointed out the crystalline nature of the soil clays. Previous to this scientific workers held the view that clays were amorphous in nature. The work of Ross (1927) was soon followed by the independent work of Hendricks and Fry (1930, 1930) and Kelley (1929), emphasizing the crystalline nature of clays. It is now a recognised fact that clays are crystalline minerals, chiefly montmorillonite, illite and kaolinite.

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[*] Since 1850 and until Arrhenius formulated the theory of electrolytic dissociation, the cation exchange phenomenon was called "base exchange". In this thesis the more correct term "cation exchange" has been adopted. Whenever it is necessary to distinguish between hydrogen ions and other cations, the term "metal ion" will be used for the latter. Unless otherwise stated "total exchangeable metal ions" mean Ca + Mg + Na + K.

The inorganic exchange complex of soils is usually one or another or a mixture of these clay minerals. At present a fair amount of information dealing mainly with the nature and properties of clay minerals, their origin and occurrence and to a certain extent their influence on soil properties is available (Grim 1942; Ross and Hendricks 1945; Kelley 1948; Marshall 1949). However, our knowledge in all these aspects is still far from complete.

The object of the present investigations was to study the behaviour of various soils characterized by different clay minerals under electrodialysis. (Electrodialysis of soils with and without lime (Wilson 1930; Alben 1930), or soluble salts (Oden & Wijkstrom 1931; Basu 1931; Loddesol 1932a) has been reported.) No information with regard to the behaviour of various clay minerals in soils during electrodialysis is available. It was therefore thought desirable to investigate the release of the exchangeable metal ions, the mobilization of silicon, iron and aluminium and the break-down of various clay minerals in the exchange complex during electrodialysis and also to compare the data obtained by electrodialysis with the chemical exchange methods of determining exchangeable metal ions. The second object of these studies was to investigate the nature of the acidity of the different clay minerals. Acid soils were prepared by three different methods and then they were brought to various degrees of saturation with different metal ions such as Na or K or Ca or Mg or mixtures of Na and Ca to study the changes in soil pH values.

The investigations are reported in two parts. The first part deals with the electrodialysis studies, while the second part deals with the soil acidity studies. During the electrodialysis of soils characterised by various clay minerals the technique of electrodialysis was also investigated.

PART I.

STUDIES ON THE ELECTRODIALYSIS OF SOILS CHARACTERISED BY DIFFERENT CLAY MINERALS.

A. Review of the Literature.

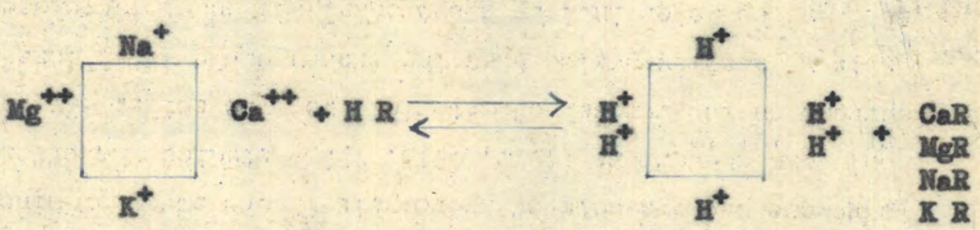
(a) Principles and practice of electrodialysis.

Because of the fundamental importance of cation exchange, numerous methods for determining the replaceable cations of soils by leaching the soils either with concentrated salt solutions (such as chlorides or ammonium, potassium, sodium or barium or barium acetate) or by dilute acids were evolved by various investigators.

Cameron and Bell (1905) were the first to use an electric current to remove the products of hydrolysis in the study of minerals. Later König and co-workers (1911, 1913, 1923) studied the effect of an electric current on the removal of material from the soils. It was in 1926 that Mattson first suggested that the exchangeable metal ions and anions of a soil may be determined by electrodialysis and he developed a three compartment cell for this purpose. His work was soon followed up by Bradfield (1927b, 1927c, 1928a, 1928b), Humfeld and co-workers (1927, 1928, 1928), Crowther and Basu (1927), Loddesol (1932a,b,c) and many others who made notable contributions to the theory and practice of electrodialysis.

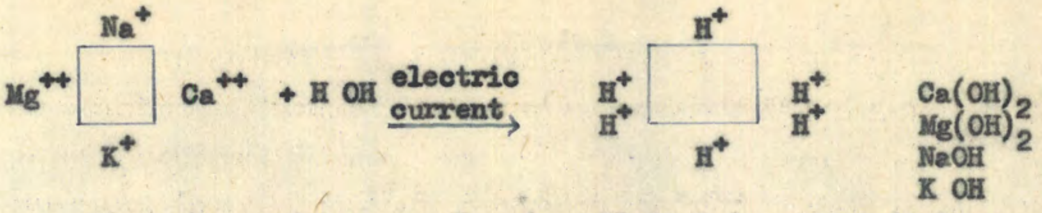
(b) Theory of electrodialysis.

It has long been accepted that it is possible to replace all the exchangeable metal ions from the exchange complex by hydrogen either by treating the soil with an acid or a salt of a trivalent metal. The reaction may be represented as follows:



In electrodialysis advantage is taken of this reaction. When an electric current is passed through a mixture of soil and water the hydrogen ions from the water replace the exchangeable metal ions and the metal ions go into solution as hydroxides. If the products of hydrolysis of the soil are continuously removed more and more hydrogen ions replace the exchangeable metal ions, the soil becomes completely unsaturated in relation to metal ions (Ca, Mg, K and Na). According to Schofield (1949), at this stage the acid soil will be saturated with Al^{+++}.

The older view is that the soil is then hydrogen saturated as graphically illustrated below.



$$\mathrm{Mg^{++}}\ \overset{\mathrm{Na^+}}{\underset{\mathrm{K^+}}{\boxed{}}}\ \mathrm{Ca^{++}} + \mathrm{H\,OH} \xrightarrow{\text{electric current}} \begin{matrix}\mathrm{H^+}\\ \mathrm{H^+}\end{matrix} \overset{\mathrm{H^+}}{\underset{\mathrm{H^+}}{\boxed{}}} \begin{matrix}\mathrm{H^+}\\ \mathrm{H^+}\end{matrix} \quad \begin{matrix}\mathrm{Ca(OH)_2}\\ \mathrm{Mg(OH)_2}\\ \mathrm{NaOH}\\ \mathrm{K\,OH}\end{matrix}$$

Since the exchange complex is colloidal in nature it is easy to separate the products of hydrolysis by the introduction of suitable membranes. The analysis of the dialysate will give the nature and amount of the exchangeable metal ions present in the soil, while an estimate of the total exchangeable metal ions may be at once obtained by the titration of the dialysate with standard acid.

The electrodialysis of soils does not suffer from such handicaps as the solubility effects, the slowness of filtration particularly with heavy soils, clays and colloids and the analytical difficulties due to the presence of large amounts of salt in the extract which accompany the methods of neutral salt extraction used for determining exchangeable metal ions. In addition to this the chief advantage of electrodialysis is that the acid soil obtained after electrodialysis is well suited for the determination of exchange capacity by titration, the preparation of single cation saturated soils and the preparation of soils for mechanical analysis (Bradfield 1927b, 1927c).

(c) <u>Apparatus and equipment.</u>

Mattson (1926) first made an electrodialysis cell for soils. It was a three compartment cell, the central chamber containing the soil suspension to be electrodialysed while the two side chambers contained platinum gauze electrodes. The membranes were of parchment and the cell walls were made of soft rubber. The chief advantage of this cell was that both the exchangeable metal ions and anions could be studied. The large area of the platinum electrodes and the small width of the central soil chamber reduced the resistance and were thus an added advantage to the quick electrodialysis of the soil.

Humfeld and co-workers (1927, 1928, 1928), Clark, Humfeld and Alben (1928), Rost (1927), McGeorge (1929), and Prince and Toth (1937) used the Mattson type of cell with slight modifications and improvements in the construction of cell, the cooling system, the electric current and the electrodes.

Bradfield (1927b, 1927c) developed a cell quite distinct from the one developed by Mattson (1926). He noted that in the case of soils from humid regions the amount of electrodialysable anions was very small in comparison with the metal ions. He proposed that if the study of exchangeable anions was not necessary, exchangeable metal ions could be studied by means of a two compartment cell by eliminating the anode chamber and placing the anode electrode in the same compartment as the soil suspension. The advantages of this cell are that the electrodes are placed closer to each other, the resistance due to one membrane is eliminated, and the dialysis is greatly accelerated. Unlike Mattson's arrangement where there was no continuous flow of water or of dialysate which had to be changed at specific intervals, Bradfield fed water continuously at a constant level in the anode chamber and the dialysate was continuously collected. He used a rheostat in series to control the current and the temperature of the cell.

Crowther and Basu (1927), Salagado and Chapman (1931), Puri (1930b), Loddesol (1932b & c) and Puri and Hoon (1937) suggested a number of modifications to the Bradfield cell, the electrodes and the temperature control. Loddesol (1932b & c) suggested that in a two compartment cell if the soil suspension in the anode chamber was stirred the replacement of exchangeable metal ions was facilitated. He used a mechanical stirrer to stir the soil suspension while Puri and Hoon (1937) suggested the use of a rotating anode.

(d) Experimental Technique.

In order to obtain an idea of the total exchangeable metal ions transported in the cathode chamber, Mattson (1926) suggested that the electrodialysis might be considered to be complete when the hourly cathode extract required less than one drop of N/10 acid for neutralisation when phenolphthalein was used as an indicator.

Bradfield (1927b) considered that electrodialysis was complete when the dialysate did not give any colour with a phenolphthalein indicator. He suggested that an excess of acid might be added to the dialysate, that the dialysate should then be boiled to drive off any CO_2 and the solution back-titrated with alkali. The difference in the titre value gives the exchangeable metal ions.

Humfeld and Alben (1927) were the first to note that at a certain stage, though the dialysate was neutral or acidic to phenolphthalein, it was alkaline to methyl red. They found that if Mattson's technique was followed a Carrington Loam registered 18.15 milligram equivalents per 100 gm. of soil*, while, if methyl red was used as an indicator, after the dialysate reacted acidic to phenolphthalein, the total metal ions extracted were 24.41 m.e. They considered that the end point with methyl red was more accurate than the one with phenolphthalein. Titration to the phenolphthalein end point would not include any replaceable iron and aluminium present since the solution becomes colorless before the hydroxides of these metal ions react with acid for titration. When methyl red is used as an indicator the end point is reached at a sufficiently low pH of the solution to ensure neutralisation of the iron and aluminium present.

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* Exchangeable cations are usually calculated as milligram equivalents per 100 gms. of soil. In this thesis the abbreviation m.e. has this meaning.

Humfeld (1928) used methyl red as the indicator and back-titrated the dialysate after adding excess of HCl. He did not boil the dialysate but ensured that the precipitate was dissolved. Humfeld did not analyse the dialysate.

In view of the above review it seems desirable that the dialysate should be back-titrated after sufficient boiling with an excess of acid to the methyl red end point.

Bradfield (1927c) noted that after some use the alundum thimble of his electrodialysis cell was partly clogged by a deposit of iron and aluminium hydroxides. He suggested that the thimble might be washed with acid and then again used for electrodialysis.

(e) Factors affecting the rate of electrodialysis.

Effect of temperature.

Holmes and Elder (1931) observed that when a solution of a salt, say NaCl, was electrodialysed the rate of removal of the ions increased as the temperature was increased. Oden and Wijkstrom (1931) noted that an increase in the temperature caused only a slight increase in the quantity of exchangeable metal ions during electrodialysis of the soil. The influence of temperature varied with different soils and for different metal ions; they reported that for each increase of 1°C in the temperature the replaceable metal ions increased from 0.02 to 2.5% and the quantities of metal ions which were released due to the weathering of the soil increased from 0,7 to 11.0%.

Puri, Hoon and Dhawan (1939) reported that the effect of temperature on the rate of electrodialysis was slight though the indications were that the maximum rate was reached at about 30°C.

Practically all the workers have tried to electrodialyse the soil within certain temperature limits though results obtained even at such high temperatures as 100°C have been reported (Loddesol 1932b). Increased temperature may or may not facilitate the rate of electrodialysis but it is certain that high temperatures decompose the exchange complex. It is therefore imperative that the electrodialysis should be carried out within reasonable temperature limits, for example, between 25 to 40°C.

Effect of the concentration of soil suspension.

Loddesol (1932a) found that the quantities of and the rate at which the total metal ions and anions came out per hour in various fractions depended on the ratio of soil to water in the cell; he noted that the smaller the soil-water ratio the greater was the amount of the metal ions and anions liberated per unit weight of soil in the early stages of the experiments. Ultimately all ratios gave the same value for the exchangeable metal ions.

Rost (1927) obtained similar information with regard to the mobilization of calcium and phosphate.

Effect of the distance between the electrodes.

As the distance between the electrodes is increased the resistance in the cell is increased with the result that the rate of electrodialysis will be reduced. Loddesol (1932a) observed that as the distance between the electrodes was increased from 6 to 9 and from 9 to 12 cms. metal ions and anions were liberated from the soil at a decreasing rate.

Thus due to the above considerations it is desirable that the soil sample should be small so that a small soil/water ratio may be obtained and at the same time the distance between the electrodes should be kept as small as possible.

Effect of the current.

Wilson (1928), Holmes and Elder (1931), Salagado and Chapman (1931) and Loddesol (1932) found that as the current was increased the rate of the release of the metal ions was increased.

Effect of the nature of the membranes.

Michaelis (1925) showed that the rate at which various ions are transported depends on the nature of the membranes. Consequently the choice of suitable cathode and anode membranes can be of great help in facilitating the rate of electrodialysis. It is known that the cations can easily pass through a negatively charged membrane and similarly anions can pass easily through a positively charged membrane. Bradfield (1928a, 1928b), Bradfield and Bradfield (1929), Oden and Wijkstrom (1931) and Loddesol (1932a) have examined this factor in detail and emphasised the need for use of suitable membranes.

The above short review on the apparatus and equipment used by various workers and the factors affecting the rate of electrodialysis stresses the need for having an efficient electrodialysis apparatus and also for conducting the experiments under exactly defined conditions. The chief requirements of a good electrodialysis apparatus and equipment are that the whole set up should give reproducible results for the exchangeable metal ions in a conveniently short time, with a reasonably small volume of dialysate. The work of various investigators indicates that the replacement of exchangeable metal ions can be facilitated by using a small soil sample with small soil/water ratio, by keeping the electrodes as near as possible, increasing the current without increasing the temperature of the soil suspension beyond a reasonable limit and by the correct selection of membranes. The volume of dialysate may be decreased by reducing the endosmotic area as suggested by Salagado and Chapman (1931) and by stirring the soil suspension either by a mechanical stirrer or a rotating anode.

(f) Rate at which ions are transported in electrodialysis.

Total metal ions.

The bulk of the exchangeable metal ions is transported to the cathode chamber in the first few hours of electrodialysis and then the amount of metal ions electrodialysed falls off gradually to a constant level. The time required to electrodialyse a soil, all things being equal, depends on the nature of the material. Alben (1930) noted that an acid soil which had a small amount of exchangeable metal ions required less time for electrodialysis than an alkaline soil having large amounts of exchangeable metal ions. Mattson (1926) noted that a soil having a higher SiO_2/R_2O_3 ratio and consequently more exchangeable metal ions required more time to be electrodialysed than one having a lower SiO_2/R_2O_3 ratio and less exchangeable metal ions.

Individual metal ions.

It has been established that the rate of electrodialysis is different for different metal ions. Mattson (1926), Alben (1930), Oden and Loddesol (1930) noted that the individual metal ions were transported into the cathode chamber in the following order:

Ca, K, Na; Mg; Al, Mn and Fe.

Mattson observed that the first clear portion of the dialysate before the turbidity appeared contained mostly Ca, K and Na while only a small quantity of Mg and traces of Al, Mn and Fe were present; subsequently Mg increased markedly and Al, Fe and Mn began to appear in determinable quantities. In the last stages of electrodialysis Mg, Al, Fe and Mn appeared in increasing quantities. He also stated that the order in which these metal ions appeared in the cathode chamber may not necessarily be the order in which they were released from the soil.

Bradfield (1927b) reported that the rate at which a metal ion was transported into the cathode chamber was dependent on the nature of the anion with which it was associated. He electrodialysed KCl; K_2SO_4, and KH_2PO_4 solutions and found that K was transported more quickly from the KCl solution, followed by K from the sulphate, and then phosphate. It is, therefore, reasonable to expect that the rate at which any particular metal ion will be electrodialysed will depend on the nature of the colloidal anion present.

Rost (1927), Alben (1930) and McGeorge (1929) observed that the amount of Ca, Na and K was high in the dialysate obtained during the first few hours and then it rapidly fell off.

Mattson (1933) concluded that Ca, Na and K are mobile at all pH values. Puri and Hoon (1937) and Best & Prescott (1929) noted that the exchangeable metal ions appeared in the cathode chamber in the following order:

$$Na > K > Ca > Mg.$$

Mg was transported with the greatest difficulty and they felt that it might not be possible to recover all the magnesium in a reasonable time.

Puri and Hoon (1938) by electrodialysing soils saturated with single metal ions noted the following rate of transportation of various ions.

$$Na > K > Li > Ca > Ba > Sr > NH_4 > Mg.$$

They further concluded that these differences were due to the differences in the ionic activities.

Most of the workers (Wilson, 1928, 1929; Best and Prescott, 1929; Alben, 1930; Oden and Loddesol, 1930; Loddesol 1932b; Puri and Hoon, 1937 and 1938) have noted that Mg is incompletely electrodialysed. On the other hand Mattson (1926), Bradfield (1927b), Crowther & Basu (1929), and Salagado & Chapman (1931) observed that all Mg was electrodialysed. Wilson (1928) reported that the quantity of Mg released increased with the increasing current.

Loddesol (1932) and Mattson (1933) electrodialysed a Mg saturated soil and noted that the nature of the curve obtained for Mg was the same as that for Ca or K or Na, i.e. the bulk of the Mg came out in the beginning and it soon fell off. However the total quantity of Mg which was transported was less than that present in the soil. The appearance of Mg in the cathode chamber depends on the pH value of the soil suspension. As soon as magnesium hydroxide is formed it may be precipitated in the walls of the chamber and on the cathode due to the high pH prevailing there. By conducting exchange studies on Ba, Ca and Mg silicates, Mattson (1933) also concluded that the low replaceability of Mg was due to the stable nature of magnesium silicate. Loddesol (1932b) and Bradfield (1932) reported the appearance of magnesium in the anode chamber. This also may be one of the causes why all the magnesium was not transported to the cathode chamber.

Purvis and Hanna (1949) attributed this incomplete electrodialysis of Mg to the strongly alkaline reaction that develops in the cathode membrane and in the soil layer immediately adjacent to this membrane. They suggested that if the pH value of the soil suspension was lowered by using a boric acid solution instead of water for electrodialysis all the Mg was easily transported.

Mattson (1926 and 1933) noted that, as the amount of the metal ions started falling off in the cathode extracts, the cathode solution became turbid due to the formation of insoluble hydroxides of Mg and Al. Later on it acquired a brownish colour due to the appearance of iron hydroxide. He (1933) explained the appearance of aluminium and iron in the cathode chamber of a three compartment cell as follows. He considered that as the electrodialysis proceeds and the pH value of the soil suspension reaches a certain level (pH 5.0 to 5.4 ~~pH~~) Fe and Al are mobilized and are transported to the cathode chamber. He visualized that a pH gradient is established in the soil from the anode membrane to the cathode membrane, the soil near the anode membrane having the lowest pH value. As soon as Fe and Al are mobilized they start moving towards the cathode and they are precipitated in the soil as soon as they reach a zone of high pH. They will again dissolve as the soil pH value in that zone is lowered. By this process of repeated precipitation and solution they gradually move towards the cathode and ultimately appear in the cathode chamber. However, the quantities of iron and aluminium which will appear in the cathode chamber will be very small since iron and aluminium hydroxides will be precipitated on the cathode membrane due to an alkaline environment prevailing there. He likened this zone of precipitation to the B horizon of a podzol. Rost (1927) found that "the maximum amounts of alumina, as shown by qualitative tests, appeared to come out in the second and third eight-hour periods, while the maximum amount of iron was in the fifth and sixth". He further noted that the alkaline reaction of the cathode dialysate depended on the quantity of the exchangeable metal ions electrodialysed. In the initial stage when a large quantity of the exchangeable metal ions was transported the pH of the cathode dialysate was 12.4 and it gradually fell to 9.2 at the end of 112 hours. Humfeld & Alben (1927) observed that as the reaction in the cathode chamber approached a neutral or acidic reaction to phenolphthalein, a whitish flocculent precipitate apparently of aluminium hydroxide appeared in increasing amounts. Later on the precipitate was brownish indicating increasing amounts of iron and possibly decreasing amounts of aluminium.

Mattson (1933) also noted that soil colloids which had highest SiO_2/R_2O_3 ratio gave the greatest quantity of Al and Fe, while a so-called laterite, which was very rich in Al and Fe, gave only traces of them.

In a three compartment cell it has been noted that, in addition to Mg, iron and aluminium also migrate to the anode chamber. This behaviour is discussed in the following paragraph.

(g) Appearance of Fe, Al and Mg in the anode chamber.

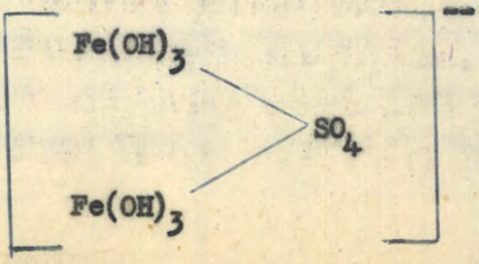
Loddesol (1932b) found that iron, aluminium and magnesium were transported to both the cathode and anode chambers. It is very improbable that these positive ions will be transported to the anode compartment as such unless during the process of electrodialysis these ions join with some anions and acquire a negative charge. He postulated that at a certain stage during the process of electrodialysis molecules of $Fe(OH)_3$ are formed in the middle compartment which absorb other anions such as SO_4^{--} and Cl^- and become negative in charge and migrate to the anode compartment. Bradfield (unpublished data, 1932) suggested the following equation to explain the appearance of Fe^{+++}, Al^{+++} and Mg^{++} in the anode chamber.

$$Fe_2(SO_4)_3 \rightleftarrows 2\,Fe^{+++} + 3\,SO_4^{--}$$

$$6\,HOH \rightleftarrows 6\,OH^- \quad + \quad 6\,H^+$$

$$\downarrow\uparrow \qquad\qquad \downarrow\uparrow$$

$$2\,Fe(OH)_3 \quad + \quad 6\,H^+ \; + \; 3\,SO_4^{--} \; (4\,H^+ + 2\,SO_4^{--} \text{ removed}).$$



$$\left[\begin{matrix} Fe(OH)_3 & \\ & SO_4 \\ Fe(OH)_3 & \end{matrix}\right]^{--} + 2H^+$$

Thus it can be seen that as the electrodialysis proceeds some hydrogen and sulphate ions would be liberated and at a certain degree of acidity in the solution the $Fe(OH)_3$ molecules might absorb sulphate ions remaining in solution thus acquiring a negative charge and then migrate to the anode.

(h) Comparison between results obtained by electrodialysis and extraction methods.

Mattson (1926), Bradfield (1927b) and Crowther and Basu (1929) observed that the exchangeable metal ions as determined by electrodialysis were almost identical with those obtained by extraction with normal ammonium chloride or $\frac{N}{20}$ HCl, while the values for Fe, Al, Si and Mg were variable. Wilson (1928) noted that electrodialysis released smaller amounts of metal ions, particularly Ca and K, than the extraction with N - NH_4Cl, especially when they were present in soils in greater amounts. Best and Prescott (1929) on the other hand found that more Ca, K and Na were electrodialysed than were determined by extraction with NH_4Cl.

Salagado and Chapman (1931) compared electrodialysis with extraction with ammonium acetate and obtained identical results except for Mg.

(i) Ultimate pH of the soil.

The pH value of the soil after all the exchangeable metal ions have been removed by electrodialysis or an acid is referred to as the ultimate pH value of the soil. The ultimate pH value of a soil is determined by two factors, namely the chemical nature of the soil and the experimental technique. In the latter will be included the voltage used, quantity of the soil used, frequency of changing the dialysate, length of run, etc. Variations in the pH value of the same soil would be mainly due to variations in the above factors.

It has been observed that the pH value falls very rapidly during the earlier period of electrodialysis while in the later stages the change in the pH value is very small and practically negligible. Alben (1930) noted that a soil which had an initial pH value of 5.7 had a pH value of 2.12 after 3 hours of electrodialysis. 42 hours more of electrodialysis reduced the pH by only 0.08 units.

Keeping all the above experimental factors constant, the initial pH value, the content of the exchangeable metal ions and the SiO_2/R_2O_3 ratio of the soil play an important role in determining the ultimate pH value. Anderson and Byers (1936) concluded that the ultimate pH value varied with the SiO_2/R_2O_3 ratio of the soil colloids. The soil colloids with high ratios tended to have lower ultimate pH values (2.5 to 3.0), while the pH values of colloids of low ratios were usually from 3.5 to 4.5.

Sen and Deb (1941) noted that as the SiO_2/R_2O_3 ratio increased the exchange capacity increased and the ultimate pH value decreased. They could not find an exact correlation between the SiO_2/R_2O_3 ratio and the ultimate pH value since it was not possible to know the true SiO_2/R_2O_3

ratio because of the presence of free silica and sesquioxides in the clays examined. However, they noted that there was a close relationship between the ultimate pH and exchange capacity which are governed by the same set of factors in the clay. Prescott (1931) reported ultimate pH values (obtained by Prescott & Best) as ranging from 3.7 to 4.3 for eight Australian soils. Unpublished data of Best and Prescott show even wider range from pH 3.5 to 4.5. Prescott and Arthur (1943) found that the ultimate pH value was governed by the following regression equation.

$$\text{Ultimate pH} = 5.06 - 0.488 \frac{SiO_2}{R_2O_3}$$

Prince and Toth (1937) pointed out that in addition to the SiO_2/R_2O_3 ratio the nature of the colloidal anion (i.e. whether the anion was humate, phosphate or silicate) determined the ultimate pH value of the soil.

Mattson (1936) and Prince and Toth (1937) encountered certain soils where the ultimate pH value was higher than the original pH. They explained that these soils contained diffusible acids which were removed during the electrodialysis and a soil with a higher pH value was left behind.

B. Experimental.

(a) Soils.

Five soils were used in these investigations.

	Percentage Mineral Composition.		
	**M	I	K
Tomki Clay (T.C.)*	80 ± 5	-	20 ± 5
Caniaba Clay Loam (C.C.L.)	80 ± 5	-	20 ± 5
Urrbrae Loam (U.L.)	-	65 ± 5	35 ± 5
Laffer Sand (L.S.)	-	>90	-
Kent Sand (K.S.)	-	-	98 - 100

Urrbrae Loam.

The soil sample used for these investigations represented the B_1 horizon of the Waite Institute Soil Profile (A_1 = 0-4"; A_2 = 4"-14"; B_1 = 14"-46").

According to Piper (1938) the soil has developed on alluvial parent material derived from Pre-Cambrian shales and slates. The surface soil consists of a loam or fine sandy loam and overlies a clay loam to clay with heavy clay at greater depth. The surface soils have a characteristic brown colour due to the presence of organic matter in this horizon but as its amount decreases in the profile the colour of the mineral portion of the soil predominates gradually changing to reddish brown at 12-18" and to red in the deep clay.

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* The abbreviations in brackets have been used very frequently in the text to designate the soil and clay mineral type.

** M = Montmorillonite, I = Illite, K = Kaolinite.

A mild leaching of this soil has occurred and the soil is characterised by very weak podzolisation and accompanying eluviation of clay and the development of distinct profile characteristics. Calcium carbonate has been completely removed from the upper part of the profile. There has been a very little decomposition of the clay in the surface layers and a small amount of leaching of sesquioxides from the surface layers into the lower horizons.

The soil is somewhat unsaturated in respect to metal ions in the surface horizons, the percentage saturation increasing progressively with depth. The pH value of the soil varies from 6.0 at the surface to 8.6 in the lower horizons. Ca is the dominant exchangeable metal ion~~s~~ in the surface soil followed by Mg, Na and K. Exchangeable Na is low throughout the profile. Exchangeable Mg increases with the depth.

These soils have been classed as red brown earths. The soil sample used in the present work was taken at a depth of 24-36", roughly in the middle of the B_1 horizon. The soil was a heavy clay in texture. X-ray analysis had shown that the exchange complex was 65 ±5% illite and the remainder was kaolinite. (Radoslovich, 1951).

Caniaba Clay Loam.

The soil profile from which the sample was obtained is described below:- (From the records of the Division of Soils, C.S.I.R.O. Soil Survey of the Northern Rivers Area, N.S.W.) -

Depth.	Horizon.	Description.
0 - 1"	A_1	Dark grey clay loam; friable because of organic matter.
1" - 3"	A_2	Very dark grey light clay; nutty to cloddy structure.
3" - 10"	B_1	Very dark grey heavy clay; light nodules of basalt; massive columnar structure.
10" - 19"	B_2	Mottled dark grey and dark yellow grey; odd pockets of basalt nodules.
19" - 24"	B_2C_1	Mottled dark, yellowish grey and light yellowish grey transitional layer with powdery decomposed basalt.
24" - 30"	B_2C_2	Mottled grey and yellow grey, and light yellowish grey, mealy clay with decomposed basalt.
30" - 42"	C	Light yellow grey rotten rock.

This soil has been classified as a chernozem-like soil or black earth. A typical black earth is characterised by the complete absence of soluble salts throughout the profile, and incomplete leaching of $CaCO_3$ and $CaSO_4$. In fact the $CaCO_3$ zone is an unfailing mark of black earths. It will however be noted that the $CaCO_3$ zone is absent in the Caniaba clay loam profile described above. These black earths of Australia have evidently formed in an environment which has contributed to complete leaching of $CaCO_3$; hence these soils are classed as chernozem-like soils. (Stephens, C. G., private communication).

The soil sample for these investigations was obtained at a depth of 10-19" (C.S.I.R.O. Lab. No. 13418) more or less in the middle of the B horizon. The soil was a heavy clay in texture and x-ray studies had shown that montmorillonite was the predominant clay mineral. (80 ± 5% montmorillonite and 20 ± 5% kaolinite) (Norrish; Tucker (1948)).

Tomki Clay.

The soil profile from which the sample was obtained is described below:- (From the records of the Division of Soils, C.S.I.R.O. Soil Survey of the Northern Rivers Area, N.S.W.).

Depth.	Horizon.	Description.
0 - 6"	A	Dark grey brown with rusty flecks, heavy clay, cloddy in structure.
6" - 15"	B_1	Dark brownish grey with rusty brown flecks, heavy, plastic clay.
15"- 29"	B_2	Dark brownish grey with rusty brown flecks, heavy, plastic clay.
31"- 47"	B_2C_1	Dark grey rusty brown mottled heavy clay.
47"- 64"	C	Light grey, yellow brown mottled heavy clay.
64"- 81"		Light brownish grey, yellow brown mottled heavy clay.
81"- 90"		Light brownish grey, heavy clay.
90"-109"		Yellow brown, light grey mottled heavy clay.
109"-129"		Bright orange brown, light grey mottled heavy clay with black streaks.

This soil has also been classed as a chernozem-like or black earth soil. (Stephens, C. G. - private communication).

Like the Caniaba clay loam profile, a $CaCO_3$ zone is absent in the Tomki clay profile; the 31-47" soil layer was used for the present studies. (C.S.I.R.O. Lab. No.14939). X-ray studies had shown that the clay mineral was 80 ± 5% montmorillonite and 20 ± 5% kaolinite (Tucker, 1948). (Norrish).

Laffer Sand.

The soil profile from which the sample was obtained is described below:- (From the records of the Division of Soils, C.S.I.R.O., Soil Survey of the Hundreds of Laffer and Willalooka, S.A., Taylor, 1933).

Depth.	Horizon.	Description.
0 - 2"	A_1	Grey sand.
2" - 6"	A_2	White sand.
6" - 8"	B	Yellowish grey light clay.
$CaCO_3$ bed	C	

This soil has been classed as a solonetz. (Taylor, 1951). The clay mineral is more than 90% illite. (Norrish, K.). The soil sample was obtained at a depth of 6-8" (C.S.I.R.O. Lab. No.15849.).

Kent Sand.

The soil profile from which the soil sample was obtained is described below:- (From the records of the Division of Soils, C.S.I.R.O., Soil Survey of the Rocky Gully Area, W.A.).

Depth.	Horizon.	Description.
0 - 3"	A_1	Dark grey sand with organic matter.
3" - 10"	A_2	Grey to light grey sand.
10"- 24"	B_1	Light brown organic stained sand.
24"- 32"	B_2	Yellowish brown gravel layer of pisolitic laterite, hard and compact.
32"- 54"	B_3C	Strongly mottled light grey brown red heavy clay.
54"- 60"	C	Very light grey clay.

This soil has been classed as a relict lateritic podzol. (Stephens, C.G., Private communication).

The sample was obtained at a depth of 33-54" (C.S.I.R.O. Lab. No. 10668). X-ray data, thermal studies, hygroscopicity studies and density studies by Norrish and Hutton (1950) showed that the clay mineral was almost pure kaolinite.

New soil samples were obtained specially for these investigations from the respective type areas.

(b) Methods.

1. Moisture.

10-15 gms. of air dry soil were transferred to a weighed silica dish fitted with an aluminium cover. The dish was uncovered and placed in an oven at 105°C. After 12-16 hours the dish was removed, covered, and cooled in a desiccator and weighed. The loss in weight represented loss in moisture. Moisture was calculated both on an air dry and oven dry basis.

$$\text{moisture on air dry soil} = \frac{\text{loss} \times 100}{\text{weight of air dry soil.}}$$

$$\text{moisture on oven dry soil} = \frac{\text{loss} \times 100}{\text{weight of oven dry soil.}}$$

2. Exchangeable metal ions.

Since $CaCO_3$ was absent from all the soils used, ammonium chloride was used for leaching them to determine the exchangeable metal ions.

50-100 gm. of the soil were taken in a 400 ml. beaker, 125 ml. of water added and the suspension allowed to stand for some time to disperse. After stirring, 125 ml. of 2 N ammonium chloride solution were added. The beaker was then placed for one hour in a water bath maintained at 70°C, the suspension being stirred at frequent intervals. The beaker was then removed from the water bath and allowed to stand over night. The extract was filtered through 18.5 cm. Whatman No.44 filter paper. The soil was leached with 1 N ammonium chloride solution until 1 litre of filtrate was collected. Si, Al, Ca, Mg, Na and K were determined in the filtrate.

A suitable aliquot of the ammonium chloride extract was taken in a silica basin and evaporated to dryness on a water bath. When completely dry, the basin was removed from the water bath and allowed to cool for 5-10 minutes. Then 3½ ml. of water and 5 ml. of concentrated nitric acid for each 50 ml. of extract originally taken were added to the basin. The basin was covered with a watch glass and decomposition allowed to proceed on a water bath. When the decomposition was complete the watch glass was rinsed and removed and the contents evaporated to dryness.

Calcium was precipitated as calcium oxalate and determined volumetrically by titration with standard potassium permanganate. Magnesium was precipitated with 8-hydroxyquinoline reagent and determined gravimetrically. Sodium was precipitated as sodium-uranyl-magnesium acetate and determined gravimetrically. Potassium was precipitated as potassium-sodium-cobaltinitrite and determined volumetrically by titration with standard potassium permanganate. The analytical methods as suggested by Piper (1947) were strictly adhered to.

3. Exchangeable Hydrogen.

Exchangeable hydrogen was determined by the meta-nitrophenol method. 100 ml. of 0.025 N, 0.03 N and 0.035 N in $Ca(OH)_2$ and 0.06 N in m-nitrophenol buffer solutions were pipetted into dry pyrex test tubes (200 mm. x 32 mm) and 10 gm. of soil added to them. The tubes were closed tightly with rubber stoppers and shaken over night. The contents were filtered without dilution through a dry 11 cm. Whatman No.30 filter paper, collecting the filtrate in a dry 125 ml. Erlenmeyer flask. The first few ml. of the filtrate were rejected. 25 ml. portions of the filtrate were titrated with 0.05 N hydrochloric acid, using 5 drops of mixed indicator (Bromocresol green 75 mg. and methyl red 50 mg. dissolved in 100 ml. alcohol - Kolthoff & Stenger, 1942). 25 ml. of the original buffer solution were titrated to serve as a blank determination.

For 25 ml. aliquots used the amount of Ca absorbed was calculated as follows:

Ca absorbed (in m.e.%)

$$= \frac{B - T}{20} \times \frac{100}{25} \times \frac{100}{W}$$

$$= \frac{B - T}{W} \times 20$$

where B = Blank titration, in ml. of 0.05 N HCl.
T = Actual titration, in ml. of 0.05 N HCl.
and W = Weight of soil.

From three separate determinations for each soil three values were obtained giving the amount of Ca absorbed by the soil corresponding to the final basicities of the buffers at equilibrium. A graph was constructed for each soil by plotting the three basicity values (T values) along the abscissa and the corresponding values of Ca absorbed along the ordinate. The amount of exchangeable hydrogen originally present was interpolated at a basicity value of 11.5 ml. which corresponds to a pH value of 8.4.

In the above calculations, the small amount of water present in the soil introduces a small error due to dilution of the buffer solution giving apparently greater Ca absorption. A correction was therefore made in calculating the amount of calcium absorbed by deducting an amount, $y \times \frac{T}{500}$ from each of the values previously calculated. In the above expression y represents the % of moisture in air dry soil. The corrected values were then used for the interpolation of exchangeable hydrogen. The analytical details as suggested by Piper (1947) were strictly adhered to.

Note:- Exchangeable hydrogen values depend upon the pH value at which they are determined. The higher the pH value the greater will be the amount of exchangeable hydrogen. Thus any pH value at which the exchangeable hydrogen is determined will be arbitrary. Parker (1929), Scholenberger and Driebelbis (1930) and Schofield (1933) adopted pH 7 as the end point. Bradfield and Allison (1933) suggested an end point at pH 8.4 since most normal soils under natural conditions in equilibrium with $CaCO_3$ have pH values of about 8.4 or less. Piper (1936) modified the techniques of Schofield (1933) by using m-nitrophenol and adopted the end point suggested by Bradfield and Allison (1933). Thus even pH 8.4 is an arbitrary end point but it can be logically adopted as a reference point for soils under natural conditions containing free calcium carbonate.

4. Total exchange capacity and degree of saturation.

The total exchange capacity of the soil was obtained by summation of the values of total exchangeable metal ions (Ca + Mg + Na + K) determined by extraction with NH_4Cl and exchangeable hydrogen, determined at pH 8.4.

The degree of saturation was then calculated as follows:

$$\text{Percentage saturation} = \frac{S}{T} \times 100$$

where T = total exchange capacity.
and S = total exchangeable metal ions (Ca + Mg + K + Na)
both expressed in m.e. per 100 gm. soil.

5. Mechanical analysis of soils.

The mechanical analysis of soils was carried out by the International Pipette Method as described by Piper (1947). The texture of the soils was checked by reference to the triangular diagram proposed by Prescott, Taylor and Marshall (1934). (The revised diagram proposed by Marshall (1947) does not use the term "heavy" clay).

6. Organic carbon.

Organic carbon was determined by the dry combustion method described by Piper (1947).

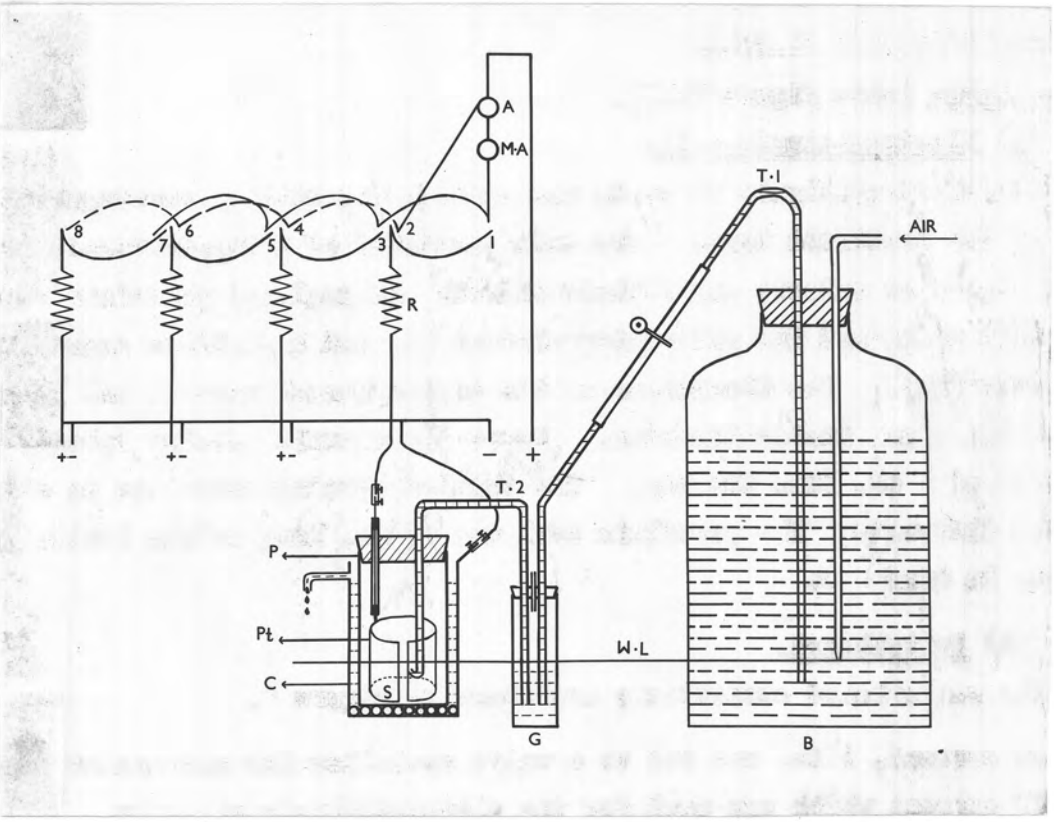

Figure 1.
Electrodialysis Apparatus.

7. Soil pH values.

Soil pH values were determined with the glass electrode. A quinhydrone half cell was used as a reference cell with the glass electrode. A 1:5 soil-water suspension was prepared and shaken mechanically in an end-over-end shaker for 2 hours. All the pH determinations were done in duplicate and were carried out in a constant temperature (20 ± 0.2°C) room. All the necessary procedural precautions in the preparation of the soil-water suspensions, the set-up of the apparatus, the use of buffers and the pH determination as described by Piper (1947) were taken.

8. Electrodialysis of soils.

Apparatus (vide Figure No.1).

(i) Electrodialysis cell.

The electrodialysis of soils was carried out with a two-compartment cell of the Bradfield type. The cell consisted of a copper vessel (C) which served as cathode and cathode chamber, an unglazed porcelain vessel (P) which contained the soil-water mixture (S) and a platinum gauze anode electrode (Pt). The dimensions of the copper vessel were 11 cm. inside length and 6 cm. inside diameter. There was a small tubular opening at a distance of 1 cm. from the top. The tubular opening served as an outlet for the dialysate. The porcelain cell was 11 cm. long on the inside and 4.6 cm. in diameter.

(ii) Switchboard.

The switchboard connections are shown in Figure 1.

AC current, 210v. was fed to a valve rectifier for conversion into a 60v. DC current which was used for the electrodialysis of soils. The current was first carried to an ammeter (A) and then to a milliammeter (MA). The switchboard consisted of eight switches, 1, 2, 3, 4, 5, 6, 7 and 8. Switches, 2, 4, 6 and 8 were connected to 4 rheostats which in turn could be connected with 4 cathodes (C) of the electrodialysis cells. Thus 4 samples of soil could be electrodialysed at one time. When switch 1 was on the current passed through the ammeter (A) and milliammeter (MA), to switch 1; from 1 it went to switch 2, then through resistance R to the cathode (C).

When switch 3 was also put on, the current flowed from 3 to switch 4, to resistance R_2 and cathode C_2. Similarly when switches 5 and 7 were put on current passed to cathodes C_3 and C_4 respectively. However when switches 2, 4, 6 and 8 were put on the milliammeter (MA) was cut out and did not record the current. During the course of electrodialysis switches 2, 4, 6 and 8 were put on while switches 1, 3, 5 and 7 were used when the current in milliamps was to be measured.

(iii) Constant level water feeding arrangement.

As the electrodialysis proceeds it is essential to replace the water, which is removed from the anode chamber. The water was therefore fed into the anode chamber by means of a constant level water feeding arrangement as shown in Figure 1.

Water was carried from the water reservoir (B) by a syphon tube (T.1) into the guard chamber (G). The guard chamber (G) was a cylindrical tube closed tightly on the upper end with a three-holed rubber stopper. Through one of the holes passed the syphon tube (T.1); the second hole was fitted with a glass rod which was used for stopping the flow of water as and when required; through the third hole passed the syphon tube (T.2) which carried water into the anode chamber (S). (W.L.) is the water level which is adjusted throughout the whole system by the tube carrying air into the water reservoir (B). By lowering or raising its tip the water level could be lowered or raised respectively. This electrodialysis set-up was devised by Best in 1929.

(iv) Procedure.

About 75 ml. of water were put into the porcelain vessel and air-dry soil equivalent to 50 gm. of oven dry soil put into it. The soil-water mixture was stirred with a motor stirrer for half an hour to disperse the soil. The stirrer was completely washed free of soil and care was taken to see that the total volume of soil-water mixture in the cell did not exceed 110 ml. and that it did not rise in the porcelain vessel above the adjusted water level. The porcelain vessel was put into the copper vessel which contained some glass rods at the bottom so as to facilitate a free flow of water round the cell. Distilled water was then put into the jacket to bring it flush with the outlet tube. The platinum gauze electrode, thermometer and water lead were then inserted into the porcelain vessel (Note: before the water lead is inserted it must be ascertained that the constant level water feeding system is working efficiently). The cathode (copper vessel) and the anode (platinum electrode) were then joined to the negative and positive leads respectively and the current was allowed to pass through the system. The current was read on a milliammeter, with and without resistance. The temperature of the anode chamber was taken before electrodialysis was started and then it was recorded at regular intervals. The temperature and current were not allowed to exceed 50°C and 150 m. amps. respectively. Almost immediately the dialysate was delivered into the receiving beaker. If the level of soil-water mixture in the anode chamber was below the adjusted water level in the whole system the water was allowed to go into the chamber by first opening the clip and then removing the glass rod. However if the level of soil water-mixture was above the adjusted water level, electrodialysis was allowed to proceed for some time so that the level in the chamber fell and then the water feeding system was worked. (Note: if this precaution is not taken the soil may be sucked back in the guard chamber "G").

For fractional electrodialysis of soils the dialysate was collected at predetermined intervals. In order to wash the porcelain cell and the copper vessel free from the precipitate sticking to their walls, first the water system was closed by plugging the small tube in the guard chamber with a glass rod and then clipping the siphon tube (T.1) in the order mentioned; the current was then cut off. After the dialysate was removed and the vessels washed free from the adhering precipitate the electrodialysis was started again.

(v) Analysis of dialysate.

The volume of dialysate obtained at each interval was measured and the rate per hour at which the dialysate came out was recorded. An excess of standard hydrochloric acid and a few drops of methyl red were then added to the dialysate. The dialysate was then boiled to dissolve any precipitate. An aliquot of the dialysate was then titrated back with standard sodium hydroxide to obtain the total exchangeable metal ions which were dialysed.

If 50 gm. of oven dry soil were taken for electrodialysis, the dialysate was reduced to 500 ml. volume, a 75 ml. aliquot was taken for back titration with 0.1 N HCl and NaOH, the total exchangeable metal ions per 100 gm. of oven dry soil

$$= \frac{x}{5} - 0.75\,y$$

where x = ml. 0.1 N HCl added

and y = ml. 0.1 N NaOH used for back titration.

The dialysate was analysed for Si, Fe and Al; Ca, Mg, K and Na. The analytical methods used were the same as adopted for analysis of ammonium chloride extract (p.16) except that the step dealing with destruction of NH_4Cl was not necessary.

TABLE 1.

THE MECHANICAL ANALYSIS OF SOILS.

(All results expressed on 100 gm oven dry soil).
(Average of duplicate determinations)

Soils.	Loss on solution.	Silt.	Clay.	Fine sand.	Coarse sand.	Total.	Organic carbon.	Soil Texture.
T.C.	3.78	13.13	81.20	2.31	1.44	101.86	0.69	Heavy clay.
C.C.L.	4.00	16.08	57.70	12.66	10.37	100.81	1.14	"
U.L.	2.69	20.17	59.45	17.40	0.60	100.31	0.63	"
L.S.	3.62	2.42	56.27	37.41	2.45	102.17	0.76	"
K.S.	1.00	5.84	53.75	10.32	29.00	99.91	0.18	"

Note: T.C. - Tomki Clay; C.C.L. - Caniaba Clay Loam; U.L. - Urrbrae Loam; L.S. - Laffer Sand;
K.S. - Kent Sand.

These abbreviations will be used throughout the thesis.

TABLE 2.

EXCHANGEABLE METAL IONS, EXCHANGEABLE HYDROGEN, EXCHANGE CAPACITY AND PERCENTAGE SATURATION.

(All results are average of duplicate determinations and are reported on oven dry basis).

M.E. per 100 gm. oven dry soil.

Soil.	(NH$_4$Cl Extraction)						Total*	Exchangeable H. at pH 8.4.	Exchange Capacity	Percentage Saturation	pH
	Si.	Al.	Ca.	Mg.	Na.	K.					
Tomki Clay.	1.02	0.16	27.18	24.18	3.04	0.33	54.73	7.45	62.18	88.02	7.10
Caniaba Clay Loam.	3.27	0.67	22.82	14.80	1.41	0.11	39.14	9.75	48.89	80.06	6.95
Urrbrae Loam.	1.95	0.90	15.87	7.15	1.45	1.26	25.73	7.05	32.78	78.50	6.86
Laffer Sand.	1.51	0.35	14.43	9.18	2.49	3.53	29.63	5.00	34.63	85.62	7.47
Kent Sand.	0.13	0.71	-	2.11	0.34	0.05	2.50	4.30	6.8	36.76	5.34

* Unless otherwise stated "Total" signifies sum of exchangeable Ca + Mg + Na + K throughout the whole thesis.

TABLE 3.

FLOW OF CURRENT DURING THE COURSE OF ELECTRODIALYSIS.

Current expressed in milliamps.

Time in hours.	Tomki Clay (1)	Caniaba Clay Loam.	Urrbrae Loam.	Laffer Sand.	Kent Sand.	Tomki Clay (2).
0	700	400	400	340	255	80
0.5	-	-	295	-	105	-
1	650	345	290	325	75	215
1.5	-	-	-	-	-	275
2	590	250	270	270	65	-
2.5	-	-	-	-	-	340
3	510	220	220	240	65	320
4	475	210	180	-	60	270
5	400	205	170	180	-	230
6	395	185	135	150	-	210
7	360	165	110	135	45	200
8	310	150	105	125	43	185
9	270	140	-	-	39	180
10	250	-	-	-	-	165
11	-	-	-	115	-	-
12	215	105	75	105	34	130
23	-	-	46	70	-	-
24	130	58	45	70	34	60
25	-	60	-	60	28	-
26	140	65	60	60	28	50
27	135	65	55	60	26	-
28	145	65	55	55	26	55
29	145	65	55	55	26	55
30	135	65	50	55	26	50
31	130	65	49	55	27	48
32	115	65	-	-	26	45
33	115	65	-	-	-	44
34	115	-	-	55	-	42
36	110	60	-	55	-	40
47	65	-	38	55	-	-
48	60	55	38	55	22	-
49	-	-	45	60	24	-
50	60	-	65	65	24	27
51	60	-	-	60	24	25
52	60	-	44	55	-	26
53	60	-	44	50	-	26
54	60	-	43	60	-	26
55	-	55	-	60	26	26
56	60	50	-	-	25	26
57	60	50	-	-	-	26
58	-	50	-	-	-	-
60	60	50	-	-	-	26
69	-	-	-	-	24	-
70	-	-	-	-	23	-
71	-	-	-	45	-	-
72	-	50	-	45	22	-
73	-	-	-	-	22	-
74	43	-	37	45	24	19
75	44	-	-	-	-	-
76	43	-	-	-	24	20
77	42	-	36	-	23	20
79	41	-	-	-	23	20
80	41	-	-	40	-	21
81	45	-	-	-	-	21
84	42	-	-	-	-	21
95	-	-	27	-	-	-
96	-	-	27	35	21	-
98	38	-	-	-	-	19
99	38	-	-	-	-	19
100	40	-	-	-	-	19
101	43	-	-	-	-	20
102	39	-	-	-	-	20
103	39	-	-	-	-	21
105	42	-	-	-	-	21
108	37	-	-	-	-	23

C. Results and discussion.

(Table 1) (Page 21).

(a) The Mechanical analysis of soils.

It will be seen from Table 1 that all the soils used in these investigations were heavy clays. The organic carbon figures were very low since all these soils were obtained from the subsoil horizons. It was expected that by choosing the soils which were rich in clay and low in organic carbon a fair picture of the behaviour of various clay minerals would be obtained.

(b) Exchangeable metal ions, exchangeable hydrogen, exchange capacity and percentage saturation.

(Table 2) (Page 22).

Reference to Table 2 will show that Tomki Clay, Caniaba Clay Loam, Urrbrae Loam and Laffer Sand (montmorillonitic and illitic soils) were saturated with metal ions to the extent of 80 to 90%. Their pH was about 7. In all four soils Ca was the predominant exchangeable metal ion followed by Mg, Na and K. In Laffer Sand and Urrbrae Loam potassium was present to a greater extent than in any other soil. This is to be expected if illite constitutes the greater part of the clay minerals.

The kaolinitic soil was characterized by the absence of exchangeable calcium. It was very poor in exchangeable metal ions; the exchange complex was saturated with metal ions to the extent of 36.8% only and was acidic in nature, the soil pH being 5.34.

Fractional electrodialysis of soils.

All five soils were fractionally electrodialysed, i.e. the dialysate was collected at predetermined time intervals, e.g. 1, 4, 8, 12, 24, 36, 60, 72, 84, 96 and 108 hours, to study the quantity and the nature of metal ions removed, the rate at which they were dialysed and the rate at which iron and aluminium were mobilised during electrodialysis.

During the course of electrodialysis hourly observations on the flow of the current and temperature of the soil-water suspension in the anode chamber were recorded.

(c) Flow of the current during the course of electrodialysis.

The current recorded in milliamps at hourly intervals is given in Table 3 and graphically represented in Figure 2.

(Table 3) (Page 23).

It will be noted that as soon as the electrodialysis was started, the maximum current passed through the cell in all soils. The amount of the current passing through the cell fell off very sharply and after a period of about 24 hours' electrodialysis it tended to be constant in value.

TABLE 4.

TEMPERATURE OF THE ANODE CHAMBER DURING ELECTRODIALYSIS.

°C.

Time in Hours.	Tomki Clay (1)	Caniaba Clay Loam.	Urrbrae Loam.	Laffer Sand.	Kent Sand.	Tomki Clay (2).
0.0	21.8	16.8	16.8	12.8	17.2	23
0.5	38.2	26.6	29.5	34.3	27.9	-
1	40.8	33.6	33.1	33.1	29.0	44.8
1.5	-	-	-	-	-	45.2
2	40.8	36.0	36.8	31.3	27.0	-
2.5	-	-	-	-	-	50.6
3	46.0	39.6	38.2	33.0	27.5	50.9
4	48.0	41.3	39.1	-	27.9	51.0
5	46.8	47.4	45.5	35.0	-	49.1
6	49.9	46.6	45.3	36.4	-	52.6
7	51.0	47.0	41.8	36.6	29.9	54.0
8	50.5	46.8	43.1	34.6	30.5	54.0
9	45.9	47.8	-	-	29.9	54.0
10	47.8	-	-	-	-	53.6
11	-	-	-	32.5	-	-
12	46.8	46.6	40.6	32.1	28.6	53.6
23	-	-	-	26.8	-	-
24	42.8	33.2	32.8	-	28.9	40.5
25	-	30.4	-	26.8	27.0	-
26	45.7	33.6	35.2	26.0	28.2	36.3
27	46.1	34.2	36.0	26.6	28.0	-
28	47.1	35.1	36.6	26.5	28.3	39.3
29	47.6	36.1	35.8	26.7	28.5	39.3
30	46.6	35.6	36.2	27.3	28.3	39.5
31	46.6	36.0	36.0	27.7	28.5	39.5
32	43.6	36.5	-	-	28.5	39.6
33	44.3	36.6	-	-	-	39.6
34	45.3	-	-	27.6	-	39.6
36	44.6	35.7	-	27.4	-	39.4
47	35.5	-	29.2	-	-	-
48	35.1	33.9	29.6	25.6	23.6	-
49	-	-	28.4	-	23.3	-
50	35.0	-	32.2	30.0	24.1	31.1
51	34.9	-	-	32.0	24.2	31.1
52	35.4	-	31.6	32.0	-	31.4
53	35.9	-	32.0	31.6	-	31.7
54	36.1	-	31.7	31.8	-	32.0
55	-	33.6	-	32.3	26.2	32.0
56	37.4	33.2	-	-	26.2	32.0
57	38.1	33.4	-	-	-	31.9
58	-	33.2	-	-	-	-
60	38.4	33.4	-	-	-	31.9
69	-	-	-	-	-	-
70	-	-	-	-	-	-
71	-	-	-	-	-	-
72	-	22.6	-	-	23.6	-
73	-	-	-	-	24.0	-
74	32.9	-	-	-	24.8	26.8
75	33.2	-	-	-	-	-
76	33.5	-	-	-	25.4	27.6
77	34.2	-	-	-	25.6	27.9
78	34.7	-	-	-	26.8	28.9
80	35.3	-	-	-	-	29.4
81	37.1	-	-	-	-	29.9
84	36.7	-	-	-	-	30.0
95	-	-	25.1	-	-	-
96	-	-	25.0	-	22.5	-
98	35.1	-	-	-	-	27.2
99	35.2	-	-	-	-	27.4
100	35.9	-	-	-	-	27.7
101	37.1	-	-	-	-	28.1
102	37.5	-	-	-	-	28.5
103	37.7	-	-	-	-	28.9
105	39.2	-	-	-	-	29.9
108	38.2	-	-	-	-	31.7

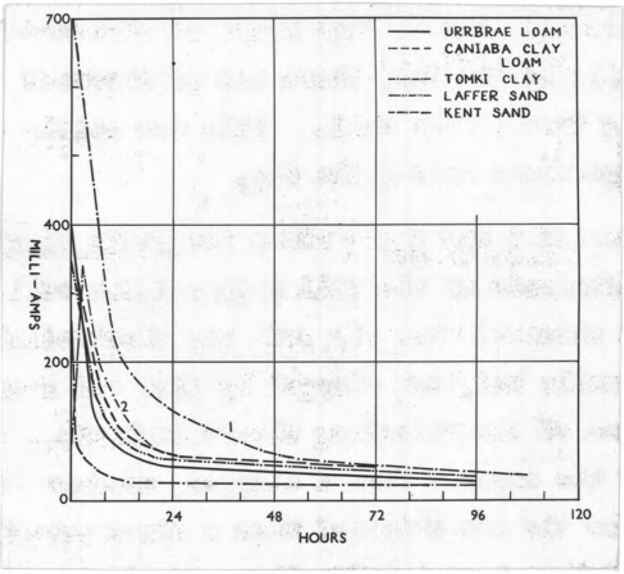

Figure 2.
Flow of Current during Electrodialysis.

The quantity of current required to electrodialyse the soil was closely associated with the nature of the clay mineral and the quantity of exchangeable metal ions. The flow of current through the various clay minerals followed the order:

montmorillonite > illite > kaolinite.

Since the quantity of exchangeable metal ions present is closely associated with the nature of the clay mineral, it can also be said that the greater the quantity of exchangeable metal ions the greater will be the quantity of current required to electrodialyse the soil.

It may be mentioned that in the graph the curves have been made smooth. However, if a reference is made to Table 3 it will be noted that from the 24th to 28th hours and 48th to 52nd hours of electrodialysis, which fell during the middle of the day, there was an increase in the quantity of current flowing through the cell. This was mainly due to an increase in the room temperature during the day.

In Figure 2, two curves marked 1 and 2 are shown for Tomki Clay. Curve 1 represents the electrodialysis of the soil with a clean cell, while curve 2 depicts the data obtained when the soil was electrodialysed in a porcelain cell whose walls had been clogged by iron and aluminium hydroxides during the course of the preceding electrodialysis. The curve obtained for the flow of the current when a clogged, unclean cell was used was quite distinct from the one obtained when a clean porcelain cell was used. In the case of the clogged cell, the current rose slowly till it reached a maximum after about 3 hours and then fell off quickly just like the other curves. The amount of current drawn was much less in the case of the clogged cell than that drawn in the case of the clean cell. This difference is due to an incomplete electrodialysis in the case of the unclean cell, the data for which are reported in Tables 22 and 23 and Figure 6. Since the amount of current drawn affects the rate of electrodialysis of soils (Wilson, 1928; Holmes and Elder, 1931; Salagado and Chapman, 1931; and Loddesol, 1932a), the flow of current was controlled in the present studies by means of resistances and an effort was made not to allow the current to exceed 150 milliamps.

(d) Temperature of the anode chamber during electrodialysis.

The temperature of the anode chamber was recorded in °C at hourly intervals during the course of electrodialysis. The data obtained are given in Table 4 and are graphically represented in Figure 3.

(Table 4) (Page 25)

All other things being equal the temperature of the anode chamber will be determined by the room temperature and the nature of the soil material.

Reference to Figure 3 will show that the temperature of the anode chamber was related to the type of the clay mineral and the quantity of the exchangeable metal ions present.

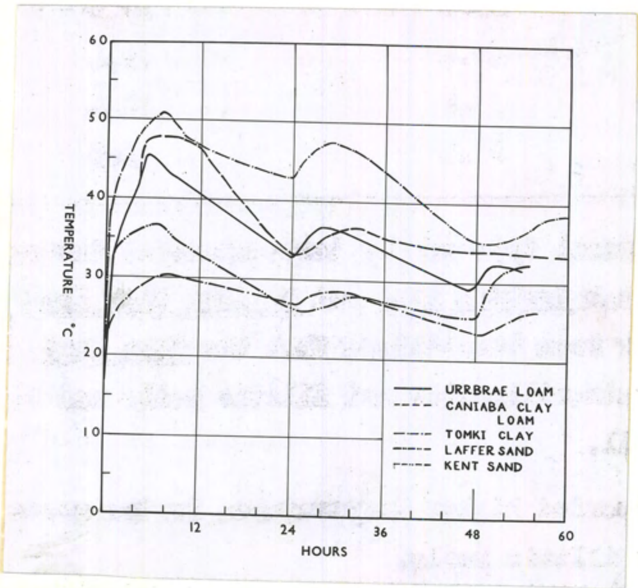

Figure 3.

Temperature of the anode chamber during Electrodialysis.

The montmorillonitic soils recorded higher temperature of the anode chamber than the illitic soils which were followed by Kent Sand (Kaolinite). In Table 5 are recorded the average room temperature and the temperature of the anode chamber for the first 12 hours of electrodialysis.

TABLE 5.

Average room temperature and temperature of the anode chamber for the first 12 hours of electrodialysis.

Soil.	Average room Temperature. °C.	Average temperature of the anode chamber. °C.	Difference °C.
T.C.	23.1	46.8	23.7
C.C.L.	17.7	43.3	25.6
U.L.	21.0	40.4	19.4
L.S.	15.5	33.9	18.4
K.S.	22.9	28.8	5.9

The effect of the clay mineral type on the temperature of the anode chamber was quite marked. Though Urrbrae Loam and Caniaba Clay Loam were electrodialysed at a lower room temperature than the Kent Sand, yet the cell temperature of the montmorillonitic and illitic soils was higher than that of the kaolinitic soil.

Montmorillonitic soils recorded higher temperatures in the anode chamber than those recorded by illitic soils.

In Figure 3 it will be noted that the curves are not smooth but they have bumps at about 24-32 hours and 48 to 60 hours of electrodialysis. These bumps are due to variations in the temperature of the anode chamber caused by rise in the room temperature during the day.

The general tendency of a temperature curve is that it rises gradually to the maximum often between 8 to 12 hours of electrodialysis and then falls off gradually as the electrodialysis proceeds.

The cell temperature will naturally be affected by the amount of the current passing through the cell. However, as pointed out earlier, the flow of the current was controlled by introduction of resistances and an effort was made not to allow more than 150 milliamps to pass.

Holmes and Elder (1931); Oden and Wijkstrom (1931); Puri, Hoon and Dhawan (1939) have shown that the rate of electrodialysis and breakdown of the exchange complex increased as the temperature at which soils were electrodialysed increased. However, all workers have tried to electrodialyse the soil within certain limits, though results obtained even at such a high temperature as 100°C have been reported (Loddesol, 1932b). It is almost certain that high temperatures favour decomposition of the exchange complex, hence in these investigations the temperature of the anode chamber was never allowed to exceed 50°C, though in most cases the temperature was well below 45°C.

Fractional Electrodialysis of Soils.

TABLE 6.

TOMKI CLAY.

Time in hours at which dialysate collected.	Al.		Ca.			Mg.			Na.			K.			Total			Remarks.
	m.e. per 100 gms. soil.	Rate/hour m.e. %.	m.e. per 100 gms. soil.	%-age of Ca dialysed *	Rate/hour %-age of Ca.	m.e. per 100 gms. soil.	%-age of Mg dialysed.	Rate/hour %-age of Mg.	m.e. per 100 gms. soil.	%-age of Na dialysed.	Rate/hour %-age of Na.	m.e. per 100 gms. soil.	%-age of K dialysed.	Rate/hour %-age of K.	m.e. per 100 gms. soil.	%-age of metalions dialysed.	Rate/hour %-age total metalions.	
1	0.16	0.16	1.96	7.21	7.21	0.02	0.08	0.08	1.86	61.19	61.19	0.01	3.03	3.03	3.85	7.03	7.03	-
4	0.39	0.13	7.57	27.85	9.28	T**	T	T	1.13	37.17	12.39	0.11	33.33	11.11	8.81	16.10	5.37	White ppt.***
8	0.55	0.14	7.64	28.11	7.03	0.050	0.21	0.05	0.27	8.88	2.22	0.11	33.33	8.33	8.07	14.74	3.69	More white ppt.
12	0.71	0.18	4.73	17.40	4.35	0.03	0.12	0.03	0.17	5.59	1.40	0.14	42.43	10.61	5.07	9.26	2.32	do.
24	2.59	0.22	4.12	15.16	1.26	7.00	28.95	2.41	0.29	9.54	0.80	0.15	45.46	3.79	11.56	21.12	1.76	do.
36	1.88	0.16	1.08	3.97	0.33	3.47	14.35	1.20	0.19	6.25	0.52	0.08	24.24	2.02	4.82	8.81	0.73	Brownish ppt.
60	2.27	0.10	0.71	2.61	0.11	1.66	6.87	0.29	0.20	6.58	0.28	0.04	12.12	0.51	2.61	4.77	0.20	do.
84	1.96	0.08	0.44	1.62	0.07	0.57	2.36	0.10	0.14	4.61	0.19	0.03	9.09	0.38	1.18	2.16	0.09	do.
108	1.57	0.07	0.44	1.62	0.07	1.20	4.96	0.21	0.11	3.62	0.15	0.01	3.03	0.13	1.76	3.22	0.12	do.
Total	12.08		28.69	105.55		14.00	57.90		4.36	143.43		0.68	206.06		47.73	87.21		
Cell Extract	31.61					2.91									2.91			
Exch. metalions by NH$_4$Cl	0.16		27.18			24.18			3.04			0.33			54.73			

* Percentage of Ca, Mg, etc. obtained by NH$_4$Cl.

** T = Trace.

*** ppt. = precipitate adhering to the porcelain cell.

Fractional Electrodialysis of Soils.

TABLE 7.

CANIABA CLAY LOAM.

Time in hours at which dialysate collected.	Al.		Ca.			Mg.			Na.			K.			Total			Remarks.
	m.e. per 100 gms. soil.	Rate/ hour m.e. %	m.e. per 100 gms. soil.	%-age of Ca dialysed.	Rate/ hour %-age of Ca *	m.e. per 100 gms. soil.	%-age of Mg. dialysed.	Rate/ hour %-age of Mg	m.e. per 100 gms. soil.	%-age of Na dialysed.	Rate/ hour %-age of Na	m.e. per 100 gms. soil.	%-age of K dialysed.	Rate/ hour %-age of K	m.e. per 100 gms. soil.	%-age of metal ions dialysed.	Rate/ hour %-age Total metal ions.	
1	0.16	0.16	1.91	8.37	8.37	0.13	0.88	0.88	0.68	48.23	48.23	0.01	9.09	9.09	2.73	6.98	6.98	-
4	0.47	0.16	5.86	25.68	8.56	0.19	1.28	0.43	0.64	45.39	15.13	0.03	27.27	9.09	6.72	17.17	5.72	Whitish ppt.**
8	0.71	0.18	6.66	29.18	7.29	0.12	0.81	0.20	0.28	19.86	4.97	0.11	100.00	25.00	7.17	18.32	4.53	Brownish ppt.
12	0.90	0.22	3.95	17.31	4.28	2.55	17.23	4.31	0.17	12.06	3.02	0.07	63.63	15.91	6.74	17.22	4.31	Brown ppt.
24	3.29	0.27	2.47	10.82	0.90	0.24	1.62	0.14	0.18	12.77	1.06	0.08	72.72	6.06	2.97	7.59	0.66	More brown ppt.
36	2.55	0.21	0.65	2.85	0.24	0.77	5.20	0.43	0.13	9.22	0.77	0.02	18.18	1.51	1.57	4.01	0.33	do.
48	1.88	0.16	0.46	2.02	0.17	1.46	9.86	0.82	0.11	7.80	0.65	0.01	9.09	0.76	2.04	5.21	0.43	do.
60	2.04	0.17	0.06	0.26	0.02	0.42	2.84	0.24	0.13	9.22	0.77	0.05	45.45	3.79	0.66	1.69	0.14	do.
72	3.06	0.26	0.06	0.26	0.02	0.38	2.56	0.21	0.05	3.55	0.30	0.06	54.54	4.55	0.55	1.41	0.12	do.
Total	15.06	-	22.08	96.75	-	6.26	42.28	-	2.37	168.10	-	0.44	400.00	-	31.15	79.60		
Cell Extract	29.46	-	-	-	-	1.84	-	-	-	-	-	-	-	-	1.84	-		
Exch. metal ions by NH_4Cl	0.67	-	22.82	-	-	14.80	-	-	1.41	-	-	0.11	-	-	39.14	-		

* Percentage of Ca, Mg, etc. obtained by NH_4Cl method.

** ppt = precipitate adhering to the porcelain cell.

Fractional Electrodialysis of Soils.

TABLE 8.

URRBRAE LOAM.

Time in hours at which dialysate collected.	Al.		Ca.			Mg.			Na.			K.			Total.			Remarks.
	m.e. per 100 gms. soil.	Rate/hour m.e. %.	m.e. per 100 gms. soil.	%-age of Ca dialysed.[*]	Rate/hour %-age of Ca.	m.e. per 100 gms. soil.	%-age of Mg dialysed.	Rate/hour %-age of Mg.	m.e. per 100 gms. soil.	%-age of Na dialysed.	Rate/hour %-age of Na.	m.e. per 100 gms. soil.	%-age of K dialysed.	Rate/hour %-age of K.	m.e. per 100 gms. soil.	%-age of metalions dialysed.	Rate/hour %-age total metalions.	
1	0.71	0.71	2.50	15.75	15.75	T[**]	T	T	0.82	56.55	56.55	0.26	20.63	20.63	3.58	13.91	13.91	-
4	0.63	0.21	6.27	39.50	13.17	0.21	2.80	0.90	0.35	24.14	8.04	0.63	50.00	16.67	7.46	28.99	9.66	White ppt.[***] sticking to cell.
8	1.41	0.35	3.46	21.80	5.45	2.59	36.23	9.06	0.19	13.10	3.28	0.25	19.84	4.96	6.49	25.22	6.31	Whitish brown ppt.
12	0.71	0.18	0.26	1.64	0.41	0.75	10.49	2.62	0.09	6.21	1.55	0.04	3.17	0.79	1.14	4.43	1.11	Brown ppt.
24	3.92	0.33	0.77	4.85	0.40	1.29	18.04	1.50	0.13	8.97	0.75	0.09	7.14	0.60	2.28	8.86	0.74	do.
48	3.53	0.15	0.61	3.84	0.16	0.29	4.06	0.17	0.20	13.79	0.57	0.09	7.14	0.30	1.19	4.63	0.20	More brown ppt.
96	2.75	0.06	0.61	3.84	0.08	0.04	0.56	0.01	0.10	6.90	0.18	0.11	8.25	0.17	0.86	3.34	0.07	do.
Total	13.66	-	14.48	91.24	-	5.17	72.18	-	1.88	129.66	-	1.47	116.70	-	23.00	89.38	-	
Cell Extract	21.73	-	-	-	-	0.32	-	-	-	-	-	-	-	-	0.32	-	-	
Exch. metalions by NH_4Cl	0.91	-	15.87	-	-	7.15	-	-	1.45	-	-	1.26	-	-	25.73	-	-	

[*] Percentage of Ca, Mg, etc. obtained by NH_4Cl extract.

[**] T = Traces.

[***] ppt = precipitate adhering to the porcelain cell.

Fractional Electrodialysis of Soils.

TABLE 9.

LAFFER SAND.

Time in hours at which dialysate collected.	Al.		Ca.			Mg.			Na.			K.			Total			Remarks.
	m.e. per 100 gms. soil.	Rate/ hour m.e. %	m.e. per 100 gms. soil.	%-age of Ca dial-ysed. *	Rate/ hour %-age of Ca.	m.e. per 100 gms. soil.	%-age of Mg dial-ysed.	Rate/ hour %-age of Mg.	m.e. per 100 gms. soil.	%-age of Na dial-ysed.	Rate/ hour %-age of Na.	m.e. per 100 gms. soil.	%-age of K dial-ysed.	Rate/ hour %-age of K.	m.e. per 100 gms. soil.	%-age of metal ions dialy-sed.	Rate/ hour %-age total metal ions.	
1	0.47	0.47	2.17	15.04	15.04	0.08	0.87	0.87	1.59	63.60	63.60	0.71	20.11	20.11	4.55	15.35	15.35	-
4	0.55	0.18	4.69	32.50	10.83	0.08	0.87	0.29	0.34	13.60	4.53	1.50	42.50	14.17	6.61	22.30	7.43	White ppt.**
8	0.47	0.12	2.99	20.72	5.18	1.13	12.31	3.08	0.17	6.80	1.70	0.48	13.60	3.40	4.77	16.10	4.03	Whitish brown ppt.
12	0.47	0.12	1.02	7.07	1.77	0.05	0.54	0.14	0.12	4.80	1.20	0.26	7.37	1.84	1.45	4.89	1.22	Brown ppt.
24	0.31	0.03	0.95	6.58	0.55	1.61	17.54	1.46	0.17	6.80	0.57	0.13	3.68	0.31	2.86	9.65	0.60	do.
36	1.18	0.10	0.07	0.49	0.04	0.07	0.76	0.06	0.12	4.80	0.40	0.11	3.12	0.26	0.37	1.25	0.10	More brown ppt.
48	0.86	0.07	0.07	0.49	0.04	0.13	1.42	0.12	0.05	2.00	0.17	0.12	3.40	0.28	0.37	1.25	0.10	do.
72	3.29	0.14	0.61	4.23	0.18	0.13	1.42	0.06	0.06	2.40	0.10	0.25	7.08	0.29	1.05	3.54	0.15	do.
96	2.75	0.11	0.20	1.39	0.06	0.12	1.31	0.06	0.10	4.00	0.17	0.15	4.25	0.18	0.57	1.92	0.08	do.
Total	10.35	-	12.77	88.51	-	3.40	37.04	-	2.72	108.80	-	3.71	105.11	-	22.59	76.25	-	
Cell extract.	33.18	-	-	-	-	0.30	-	-	-	-	-	-	-	-	0.30	-	-	
Exchang. metal ions by NH_4Cl.	0.35	-	14.43	-	-	9.18	-	-	2.50	-	-	3.53	-	-	29.64	-	-	

* Percentage of Ca, Mg, etc. obtained by NH_4Cl method.

** ppt. = precipitate adhering to the porcelain cell.

Fractional Electrodialysis of Soils.

TABLE 10.

KENT SAND.

Time in hours at which dialysate collected.	Al.		Ca.			Mg.			Na			K			Total			Remarks.
	m.e. per 100 gms. soil.	Rate/ hour m.e. %	m.e. per 100 gms. soil.	%-age of Ca dialysed. [*]	Rate/ hour %-age of Ca.	m.e. per 100 gms. soil.	%-age of Mg dialysed.	Rate/ hour %-age of Mg.	m.e. per 100 gms. soil.	%-age of Na dialysed.	Rate/ hour %-age of Na.	m.e. per 100 gms. soil.	%-age of K dialysed.	Rate/ hour %-age of K.	m.e. per 100 gms. soil.	%-age of metal ions dialysed.	Rate/ hour %-age Total metal ions.	
1	T	T[**]	-			0.35	16.59	16.59	0.33	97.06	97.06	0.01	20.00	20.00	0.69	27.60	27.60	No precipitate adhering to the cell at any stage.
4	T	T	-			0.51	24.17	8.06	0.27	79.40	26.50	0.03	60.00	20.00	8.81	32.40	10.80	
8	0.78	0.10	-			0.05	2.37	0.59	0.02	5.88	1.47	0.02	40.00	10.00	0.09	3.60	0.90	
12	2.12	0.53	-			0.03	1.42	0.36	nil			nil			0.03	1.20	0.30	
24	T	T	-			0.02	0.95	0.08	nil			nil			0.02	0.80	0.07	
48	T	T	-			0.18	8.53	0.36	nil			nil			0.18	7.20	0.30	
96	0.08	0.001	-			0.06	2.84	0.06	nil			nil			0.06	2.40	0.05	
Total	2.98		-			1.20	56.87		0.62			0.06	120.00		1.88	75.20	-	
Cell extract	8.00					0.07			-			-			0.07			
Exch. metal ions by NH_4Cl	0.71					2.11			0.34			0.05			2.50			

[*] Percentage of Ca, Mg, etc. obtained by NH_4Cl method.

[**] T = Trace.

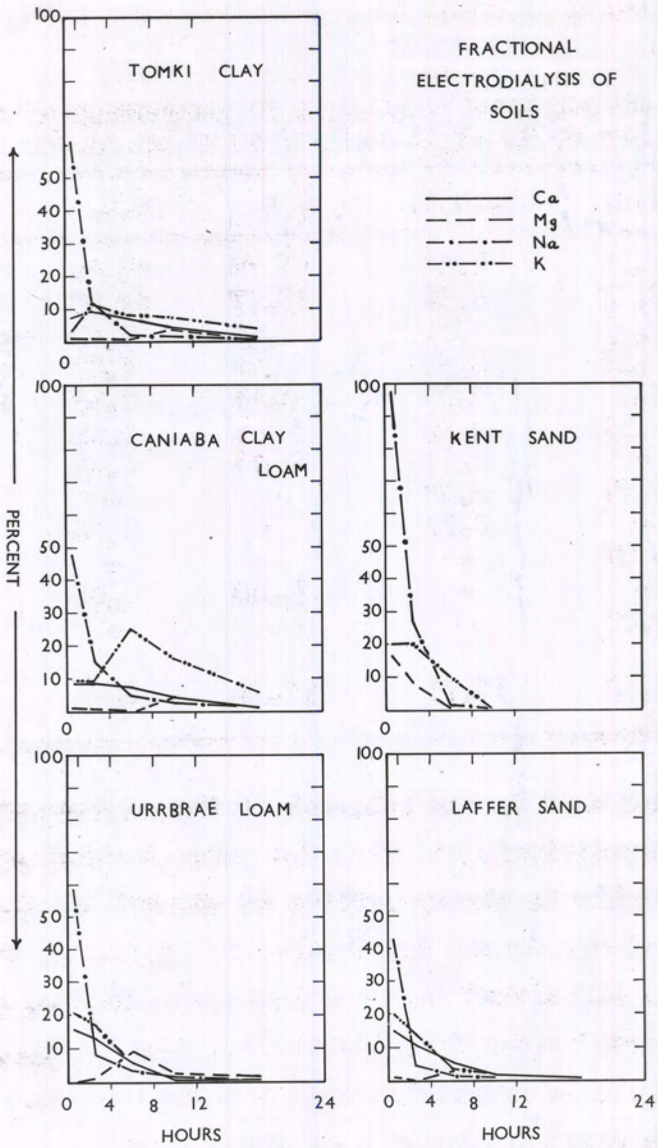

Figure 4a.

Rate of electrodialysis of various metal ions.

"Percent." = Exchangeable Ca, Mg. etc. electrodialysed expressed as a percentage of that obtained by NH_4Cl extraction.

The rate of electrodialysis has been plotted at the mid point of the interval, e.g. rate of electrodialysis during 12 to 24 hours interval is plotted at 18 hours.

(e) Fractional electrodialysis of various metal ions.

The complete data obtained for the fractional electrodialysis of soils are recorded in Tables 6, 7, 8, 9 and 10 and Figures 4a and 4b.

(Tables 6, 7, 8, 9 and 10) (Pages 28, 29, 30, 31, 32).

Fractional electrodialysis of Ca.

TABLE 11.

Rate per hour (in percentage of exchangeable Ca determined by NH_4Cl extract method) at which Ca was dialysed in various soils.

Time in hours at which fractional dislysate collected.	Rate per hour (expressed in percentage of exchangeable Ca by NH_4Cl method) at which Ca was dialysed.				
	T.C.	C.C.L.	U.L.	L.S.	K.S.
1	7.21	8.37	15.75	15.04	
4	9.28	8.56	13.17	10.83	No exchangeable Ca in the soil.
8	7.03	7.29	5.45	5.18	
12	4.35	4.28	0.41	1.77	
24	1.26	0.90	0.40	0.55	
36	0.33	0.24	-	0.04	
48	-	0.17	0.16	0.04	
60	0.11	0.02	-	-	
72	-	0.02	-	0.18	
84	0.07	-	-	-	
96	-	-	0.08	0.06	
108	0.07	-	-	-	
Total Ca electrodialysed.	105.55	96.75	91.24	88.50	

The above data show that Ca was released at the maximum rate during the first hour of electrodialysis and that the rate at which calcium was dialysed fell off gradually to almost nothing at the end of electrodialysis. The shape of the curves for calcium in Figure 4a. indicated that there was no great difference in the behaviour of various clay minerals, although it does appear from the limited data available that there is a more rapid release of calcium from illitic than from montmorillonitic soils, in the early stages of electrodialysis.

In all the soils 88.5 to 105.5% of calcium, as compared with exchangeable calcium obtained by the ammonium chloride extract method, was electrodialysed. The cumulative percentage curves for exchangeable calcium showed that the major portion of calcium was released during the first 24 hours of electrodialysis and thereafter the curves were almost flat (vide Figure 4b).

Kent Sand did not contain any demonstrable calcium, hence the release of Ca could not be discussed.

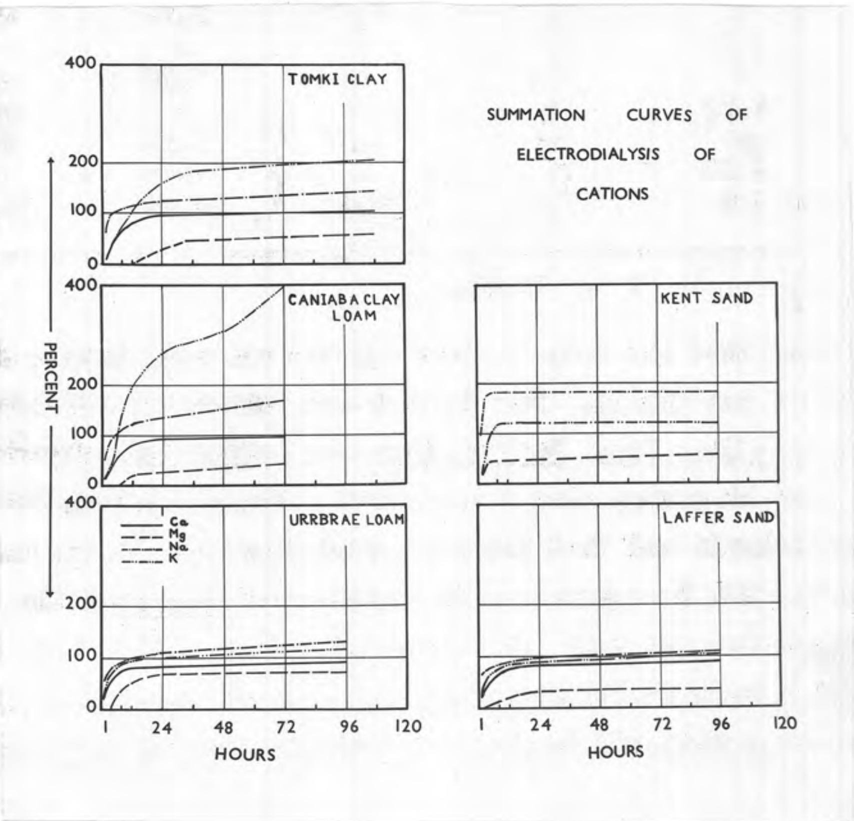

Figure 4b.

Summation Curves of the release of metal ions during electrodialysis.

"Percent." = Exchangeable Ca, Mg, etc. electrodialysed expressed as a percentage of that obtained by NH_4Cl extraction.

Fractional electrodialysis of Mg.

TABLE 12.

Rate per hour (expressed in percentage of exchangeable Mg determined by NH_4Cl method) at which Mg was dialysed.

Time in hours at which fractional dialysate collected.	Rate per hour (expressed in percentage of exchangeable Mg by NH_4Cl method) at which Mg was dialysed.				
	T.C.	C.C.L.	U.L.	L.S.	K.S.
1	0.08	0.88	T	0.87	16.59
4	T	0.43	0.90	0.29	8.06
8	0.05	0.20	9.06	3.08	0.59
12	0.03	4.31	2.62	0.14	0.36
24	2.41	0.14	1.50	1.46	0.08
36	1.20	0.43	-	0.06	-
48	-	0.82	0.17	0.12	0.36
60	0.29	0.24	-	-	-
72	-	0.21	-	0.06	-
84	0.10	-	-	-	-
96	-	-	0.01	0.06	0.06
108	0.21	-	-	-	-
Total Mg dialysed	57.9	42.28	72.18	37.04	56.87

T = Trace.

It can be seen that the rate at which Mg was released during electrodialysis exhibited two trends. The first trend, which was exhibited by Tomki Clay, Caniaba Clay Loam, Urrbrae Loam and Laffer Sand showed that magnesium appeared at a very slow rate in the catholyte during the first hour of electrodialysis and that the rate gradually rose to its maximum during the 8th to 12th hour period. In the case of Kent Sand the behaviour of magnesium was just like calcium in other soils, i.e. the maximum rate of release in the dialysate was observed during the first hour which gradually fell off to almost nothing by the end of the 24th hour.

This difference is very striking and throws a great deal of light on the behaviour of calcium and magnesium during electrodialysis. In Tomki Clay, Caniaba Clay Loam, etc. calcium and magnesium are both present in the exchangeable form. As electrodialysis is started both Ca and magnesium are released and they start moving towards the cathode. Since the hydroxide of magnesium is precipitated in an alkaline medium its passage through the porcelain cell is checked as long as $Ca(OH)_2$ is also passing through. However, when the bulk of $Ca(OH)_2$ is removed after about 8-12 hours magnesium hydroxide also starts coming out.

On the other hand, in the case of Kent Sand, there was no exchangeable calcium present in the exchange complex. Hence, due to the absence of alkaline conditions in the porcelain cell walls, magnesium was able to pass out early in the catholyte. Due to this reason, the magnesium curve for Kent Sand is similar to the calcium curves (vide Figure 4a). Loddesol (1932b) and Mattson (1933) also reported that the magnesium curve was similar to the calcium curve when a magnesium saturated single cation soil was electrodialysed.

It may further be noted that during the fractional electrodialysis of the soils, magnesium was incompletely electrodialysed. On the other hand, when a large number of soil samples was subjected to continuous electrodialysis to prepare acid soils, (Tables 31 to 35), it was noted that the quantities of magnesium released were very variable.

TABLE 13.

Mg released when a number of soil samples were subjected to continuous electrodialysis.(96 hours).
(m.e. per 100 gm. oven dry soil).

Soil Sample No.	C.C.L.	U.L.
1	11.73	7.53
2	12.82	5.90
3	12.83	9.10
4	15.89	6.39
5	13.90	6.85
6	16.88	6.52
7	19.60	-
8	19.78	-
9	16.06	-
10	16.95	-
11	17.43	-
Exchang. Mg by NH_4Cl.	14.80	7.15

Note:- The above data include Mg retained by the porcelain cell.

In the first place it will be noted that the continuous electrodialysis tended to release more Mg than that released by the fractional electrodialysis. In the second place there were wide differences between different samples of the same soil. The reasons for these differences are not understood. During the review of the literature it was shown that, though most workers have obtained incomplete electrodialysis of Mg, there are a few who have obtained Mg in quantities equivalent to those determined by the usual salt extraction methods. Wilson's paper (1928) is particularly notable since with the same apparatus he obtained increasing quantities of Mg as the current was increased.

Fractional electrodialysis of Na.

TABLE 14.

Time in hours at which fractional dialysate collected.	Rate per hour (expressed in percentage of exchangeable Na determined by NH_4Cl method) at which Na was dialysed.				
	T.C.	C.C.L.	U.L.	L.S.	K.S.
1	61.19	48.23	56.55	63.60	97.06
4	12.39	15.13	8.05	4.53	26.50
8	2.22	4.97	3.28	1.70	1.47
12	1.40	3.02	1.55	1.20	Nil
24	0.80	1.06	0.75	0.57	Nil
36	0.52	0.77	-	0.40	Nil
48	-	0.65	0.57	0.17	Nil
60	0.28	0.77	-	-	-
72	-	0.30	-	0.10	-
84	0.19	-	-	-	-
96	-	-	0.18	0.17	Nil
108	0.15	-	-	-	-
Total Na dialysed.	143.43	168.1	129.66	108.8	182.34

It will be seen from Table 14 and Figure 4a that sodium was released at a very high rate in the beginning of electrodialysis and its rate of appearance in the catholyte soon fell off within four hours of electrodialysis. The general trend was similar to that of calcium. In the case of Kent Sand, which was very low in exchangeable sodium (0.34 m.e. per 100 gm. soil) all the sodium was dialysed in the first hour and no more sodium came out after eight hours of electrodialysis. Reference to Figure 4b will show that except in the case of Laffer Sand all the exchangeable sodium as determined by the ammonium-chloride extract method was electrodialysed out in 8-12 hours.

In all five soils more sodium than that found by the ammonium chloride method was released. The increase varied from 29.7% in the case of Urrbrae Loam to 82.3% in the case of Kent Sand. This increase in the quantities of Na released is discussed in detail subsequently (p.39).

Fractional electrodialysis of K.

TABLE 15.

Time in hours at which fractional dialysate collected.	Rate per hour (expressed in percentage of exchangeable K determined by NH_4Cl method) at which K was dialysed.				
	T.C.	C.C.L.	U.L.	L.S.	K.S.
1	3.03	9.09	20.63	20.11	20.00
4	11.11	9.09	16.67	14.17	20.00
8	8.33	25.00	4.96	3.40	10.00
12	10.61	15.91	0.79	1.84	Nil
24	3.79	6.06	0.60	0.31	Nil
36	2.02	1.51	-	0.26	-
48	-	0.76	0.30	0.28	Nil
60	0.51	3.79	-	-	-
72	-	4.55	-	0.29	-
84	0.38	-	-	-	-
96	-	=	0.17	0.18	Nil
108	0.13	=	-	-	-
Total K dialysed.	206.06	400.00	116.70	105.11	120.00

The general trend of the appearance of the potassium in the catholyte was similar to that of Ca and Na, i.e. the maximum quantity of exchangeable K came out in the first hours and then the amount of K dialysed fell off quickly. However, if the data in Table 15 and Figure 4a are critically examined, it will be seen that at least in the case of Tomki Clay and Caniaba Clay Loam the rate of release of potassium during the 8 and 12 hour period exceeded that of the first hour. This was probably due to the ability of electrodialysis to release exchangeable metal ions which are not ordinarily replaced by the NH_4Cl method. This factor, however, does not alter the fact that the general trend of appearance of K in the catholyte was similar to that of Ca and Na. This was confirmed by the electrodialysis of Caniaba Clay Loam and Urrbrae Loam when these were saturated with potassium. The data are reported in Table 16.

TABLE 16.

Fractional electrodialysis of K - saturated soils.

Time in hours at which fractional dialysate collected.	Rate per hour at which K was dialysed (expressed in m.e.%). (Data obtained by titration of dialysate). C.C.L.	U.L.
1	12.67	11.33
4	2.01	2.47
8	0.44	0.40
24	0.25	0.08
48	0.07	0.04

It will also be noted from Figure 4b that all the K as determined by NH_4Cl extraction was dialysed in about 8 to 12 hours and after that K which appeared in the catholyte was obtained because of the intense action of electrodialysis and consequent availability of K which is not replaced by NH_4Cl.

TABLE 17.

Comparison between the exchangeable K obtained by NH_4Cl extraction and electrodialysis.

Soil.	T.C.	C.C.L.	U.L.	L.S.	K.S.
Exchangeable K in m.e.% by NH_4Cl extraction.	0.33	0.11	1.26	3.53	0.05
Exchangeable K by E.D.* in m.e.%.	0.68	0.44	1.47	3.71	0.06
Increase in exchangeable K due to E.D. in m.e.%.	0.35	0.33	0.21	0.28	0.01
Exchangeable K by E.D. expressed as percentage of K obtained by NH_4Cl.	206.06	400.00	116.70	105.11	120.00

The above data indicate that in all soils more K was obtained by electrodialysis than was obtained by NH_4Cl extraction; this was particularly marked in the case of Tomki Clay and Caniaba Clay Loam. These soils were originally low in exchangeable potassium and any slight increase in the exchangeable potassium pushed up the percentage figures to a very high level. However it can be seen that the increase of exchangeable potassium if expressed in terms of m.e. per cent. was more uniform and comparable in Tomki Clay, Caniaba Clay Loam, Urrbrae Loam and Laffer Sand.

If a reference is made to Table 15 it will be noted that in the case of Kent Sand no more potassium was transported into the cathode chamber after 12 hours of electrodialysis indicating that no more potassium was available in the exchange complex. This behaviour was similar to that of sodium. Best and Prescott (1929), working with a Waite Institute soil

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* E.D. = Electrodialysis.

TABLE 18.

Fractional electrodialysis of Fe & Al (expressed as Al m.e. per 100 gm. soil).

Soil	T.C.		C.C.L.		U.L.		L.S.		K.S.	
Time in hours at which dialysate collected.	Al m.e. per 100 gm.	Rate per hour.	Al m.e. per 100 gm.	Rate per hour.	Al m.e. per 100 gm.	Rate per hour.	Al m.e. per 100 gm.	Rate per hour.	Al m.e. per 100 gm.	Rate per hour.
1	0.16	0.16	0.16	0.16	0.71	0.71	0.47	0.47	T*	T
4	0.39	0.13	0.47	0.16	0.63	0.21	0.55	0.18	T	T
8	0.55	0.14	0.71	0.18	1.41	0.35	0.47	0.12	0.78	0.10
12	0.71	0.18	0.90	0.22	0.71	0.18	0.47	0.12	2.12	0.53
24	2.59	0.22	3.29	0.27	3.92	0.33	0.31	0.03	T	T
36	1.88	0.16	2.55	0.21	-	-	1.18	0.10	-	-
48	-	-	1.88	0.16	3.53	0.15	0.86	0.07	T	T
60	2.27	0.10	2.04	0.17	-	-	-	-	-	-
72	-	-	3.06	0.26	-	-	3.29	0.14	-	-
84	1.96	0.08	-	-	-	-	-	-	-	-
96	-	-	-	-	2.75	0.06	2.75	0.11	0.08	0.001
108	1.57	0.07	-	-	-	-	-	-	-	-
Total	12.08	-	15.06	-	13.66	-	10.35	-	2.98	-
Al in cell extract.	31.61	-	29.46	-	21.73	-	17.82	-	8.00	-
Total	43.69	-	44.52	-	35.39	-	28.17	-	10.98	-
Al by NH_4Cl method.	0.16	-	0.67	-	0.91	-	0.35	-	0.71	-
Al expressed as % of that obtained by NH_4Cl.	27,306.0	-	6644.8	-	3922.0	-	8048.5	-	1546.5	-

* T = Trace

sample, are the only other workers who noted release of more Na and K than that determined by NH_4Cl extraction.

These data clearly emphasise the nature and behaviour of various clay minerals. It is known that in the kaolinite structure (Grunner, 1932, and Kelley, 1948) the charges of the lattice are electrically balanced and that the external cations are not attracted to it except by the negative charges due to the broken bonds of the terminal oxygens or the hydrogens of the hydroxyls on the lattice edges. The broken bonds at the edges are not large in number since the kaolinite does not break down into very thin sheets (particle size 10^{-4} to 10^{-5} cm. as compared with 10^{-5} to 10^{-6} cm. for montmorillonite. Hendricks, 1942) and consequently few broken bonds are exposed for replacement by a cation. When Kent Sand, a kaolinite soil, was subjected to electrodialysis, Na and K which were carried on the surface were electrodialysed during the first 12 hours and after that no more Na or K appeared in the catholyte. On the other hand, the release by electrodialysis of sodium and potassium in excess of that released by NH_4Cl extraction was quite marked in the case of the montmorillonitic and the illitic soils, suggesting that some exchangeable sodium and potassium are locked up in the mineral complex, which are not accessible to NH_4Cl. This is in line with the finding of Kelley, Dore and Brown (1931) in which they showed that when soil colloids, in which montmorillonite was the predominant clay mineral, were subjected to grinding more magnesium and potassium were made exchangeable.

Appearance of silicon, aluminium and iron in the catholyte.

The catholyte was anlaysed for silicon, iron and aluminium. The various quantities of iron and aluminium expressed as m.e. per cent. Al are given in Table 18.

(Table 18) (Page 38).

The rate at which Fe and Al appeared in the catholyte was very irregular. Iron and aluminium hydroxides are precipitated in and on the porcelain cell walls and very little of the Fe and Al released from the soil appears in the catholyte. From the data obtained it is difficult to say definitely at what rate iron and aluminium appeared in the catholyte. Two forms of iron and aluminium could be distinguished, namely, an exchangeable form and that which is obtained due to the breakdown of the complex. It may be assumed that the exchangeable form of iron and aluminium is electrodialysed from the complex in a similar way to the other ions. However, the appearance of the exchangeable iron and aluminium in the catholyte will be irregular since the iron and aluminium hydroxides will get precipitated as they strike an alkaline environment near and in the cell walls. During the course of electrodialysis it was noted that after about 12 hours a white fluffy precipitate appeared in the catholyte. However, that was no indication that iron and aluminium were mobilized after 8 to 12 hours of electrodialysis. When the fractional dialysate was collected qualitative observations were made on the nature and colour of the precipitate adhering to the cell walls at various intervals. The observations may be summarised below.

TABLE 19.

Time in hours at which fractional dialysate collected.	Colour of the precipitate adhering to the cell.	
	T.C., C.C.L., U.L., L.S.	K.S.
1	no precipitate.	no precipitate adhering to the cell wall at any time.
4	whitish ppt.	
8	whitish brown ppt.	
12	brown ppt.	
24	more brown ppt.	
36	do.	
48	do.	
60	do.	
72	do.	
84	do.	
96	do.	
108	do.	

It will be seen that in the case of montmorillonitic and illitic soils, a whitish precipitate was adhering to the cell after 4 hours of electrodialysis and that the colour of the precipitate had become distinctly brown after 12 hours of electrodialysis. Thus the first indication of the mobilization of iron and aluminium in the case of Tomki Clay, Caniaba Clay Loam, Urrbrae Loam and Laffer Sand was available in about 4 hours. On the other hand, in the case of the kaolinite soil (Kent Sand) there was no precipitate adhering to the cell and thus there was no apparent indication of the mobilization of large quantities of iron and aluminium. The whitish colour of the precipitate in the earlier stages indicated that aluminium was mobilized first and iron was mobilized later on.

In order to obtain an estimate of the extent to which the iron and aluminium were mobilized in various clay minerals the porcelain cells were boiled in 3-5% HCl for some time till all the precipitate was dissolved and the cell extract was analysed for iron and aluminium. The data obtained are given in Table 18. The montmorillonitic and illitic soils on electrodialysis released as much as 3822 to 27,306 % more iron and aluminium than that obtained by the ammonium chloride method. The release of iron and aluminium in the kaolinitic soil was much less than that in the montmorillonitic and illitic soils.

Mattson (1933) noted that greater quantities of iron and aluminium were transported to the cathode chamber in the case of soil colloids which had a high SiO_2/R_2O_3 ratio, while in the case of so-called laterites which were very rich in iron and aluminium only traces of them appeared in the dialysate. He explained the difference by stating that in the case of lateritic soil colloids the cell was clogged due to the release of large quantities of iron and aluminium and consequently very little of them appeared in the dialysate in spite of the fact that these colloids were very rich in them. The data obtained in the present investigations confirm his finding, namely that the quantity of iron and aluminium which appeared in the catholyte was more in the case of soil exchange complex having wider SiO_2/R_2O_3 ratio (montmorillonites and illite), than in the case of kaolinite. However, the qualitative observations on the precipitate adhering to the cell wall and anlaysis of the cell extract in the present investigations did not confirm his explanation that the clogging of the cell was the cause of this difference. It can be seen from Table 18 that in the case of <u>Kent Sand</u>, which was a pure kaolinite, and a <u>lateritic soil</u>, the iron and aluminium which clogged the cell was much less than that obtained in the case of montmorillonitic and illitic soils. In an earlier paper (1928) Mattson reported that on acid treatment more iron and aluminium were released for a soil colloid having a SiO_2/R_2O_3 ratio of 3.18 than those released from a soil colloid having a SiO_2/R_2O_3 ratio of 1.63; he was of the opinion that Fe and Al in the former colloid existed in a more "reactive condition" than in the latter. This seems to be the real cause of the differences between the quantities of iron and aluminium released by electrodialysis from the montmorillonitic and the illitic soils on the one hand and the kaolinitic soil on the other.

Recently Mukherjee, Chatterjee and Banerjee (1947) have shown that the amounts of Fe and Al released by acid treatment were greater from montmorillonite than from kaolinite.

It therefore seems that the different quantities of Fe and Al carried to the cathode chamber were mainly due to the differences in the nature of clay minerals and their differential resistance to breakdown. Kaolinite seems to be a more stable mineral and breaks down much more slowly than the other two minerals. Hofman and Bilke (1936) reported that on leaching the montmorillonite with an acid solution aluminium was lost until there was only 1.7 Al to 4 Si before the lattice structure was destroyed. In a normal montmorillonite lattice structure suggested by Hofmann, Endell and Wilm (1933) or by Edelman and Favejee (1940) there are 2 Al to every 4 Si.

Electrodialysis of silicon.

In all cases the dialysate was analysed for silicon and fairly large quantities were obtained. There was no doubt about the fact that silicon was transported to the cathode compartment but, as there was reason to believe that some silicon was mechanically transported from the porcelain cell, it was difficult to arrive at definite conclusions. For this reason the data are not reported.

Fractional electrodialysis of all the metal ions.

Reference to Tables 6, 7, 8, 9 and 10 and Figure 4a will show that the general trend of the rate at which exchangeable calcium, magnesium, sodium and potassium appeared in the dialysate was the same, i.e. each metal ion appeared at maximum rate in the first hour of electrodialysis and the rate subsequently fell off very quickly. Comparing among themselves the rate at which various ions were dialysed, we get the following series -

Na > K > Ca > Mg > Fe and Al.

It may be mentioned that it is known that the exchangeable cations are attracted to the clay minerals to satisfy the negative charges carried by them. The negative charges arise due to isomorphous replacements in the mineral structure and secondly due to the broken oxygen or hydroxyl bonds near the flake edges of the clay minerals. In the case of montmorillonites and illites both these factors play an important part in the development of negative charges. Hendricks, Nelson and Alexander (1940) have shown that 80% of the exchange positions of montmorillonite are on the basal plane surfaces and that the remainder are on the edges of the flakes. In the case of kaolinites the exchangeable cations are mainly attracted because of the latter cause. Isomorphous replacement plays a very limited role in attraction of cations by the kaolinite. Besides these fundamental differences, electrodialysis released various metal ions in a similar way from all the clay minerals under investigation.

TABLE 20.

The rate at which all the metal ions combined together appeared in the dialysate and the percentage progressive total of their dialysis.

Time in hours at which fractional dialysate collec.	Rate per hour (expressed as percentage of total metal ions determined by NH_4Cl) at which total metal ions appeared in dialysate.					Progressive total of the electrodialysis of total metal ions (expressed as percentage of total metal ions determined by NH_4Cl).				
	T.C.	C.C.L.	U.L.	L.S.	K.S.	T.C.	C.C.L.	U.L.	L.S.	K.S.
1	7.03	6.98	13.91	15.35	27.6	7.03	6.98	13.91	15.35	27.60
4	5.37	5.72	9.66	7.43	10.8	23.13	24.15	42.90	37.65	60.00
8	3.69	4.58	6.31	4.03	0.90	37.87	42.47	68.12	53.75	63.60
12	2.32	4.31	1.11	1.22	0.30	47.13	59.69	72.55	58.64	64.80
24	1.76	0.66	0.74	0.60	0.07	68.25	67.28	81.41	68.29	65.60
36	0.73	0.33	-	0.10	-	77.06	71.29	-	69.54	-
48	-	0.43	0.20	0.10	0.30	-	76.50	86.04	70.79	72.80
60	0.20	0.14	-	-	-	81.83	78.19	-	-	-
72	-	0.12	-	0.15	-	-	79.60	-	74.37	-
84	0.09	-	-	-	-	83.99	-	-	-	-
96	-	-	0.07	0.08	0.05	-	-	89.38	76.25	75.20
108	0.12	-	-	-	-	87.21	-	-	-	-

It can be seen from the above Table that the rate at which all the metal ions, combined together, appeared in the catholyte followed the same trend as that of individual metal ions, i.e. the metal ions appeared in the catholyte in maximum quantities in the first hour and the rate fell off during subsequent intervals. After about 24 hours of electrodialysis the rate of dialysis was very slow. The progressive total of the exchangeable metal ions also indicated that the bulk of the metal ions was dialysed in the first 24 hours.

TABLE 21.

Exchangeable metal ions transported during prolonged (continuous) electrodialysis of soils. (216 hours).
M.E. per 100 gm. soil.

	Al.	Ca.	Mg.	Na.	K.	Total.
T.C.						
(1) E.D. for 216 hours.	65.96	29.31	28.70	3.67	1.21	62.86
(2) Continuous E.D. for 108 hours.	61.53	27.00	25.70	3.90	0.93	57.53
(3) Excess of 1 over 2.	4.43	2.31	3.00	-	0.28	
** (4) Rate per hour.	0.041	0.021	0.028	-	0.0026	
(5) By NH_4Cl method.	0.16	27.18	24.18	3.04	0.33	54.73
C.C.L.						
(1) E.D. for 216 hours.	40.16	24.19	20.06	2.58	0.67	47.50
*(2) Continuous E.D. for 96 hours.	38.82	21.61	15.81	1.96	0.41	39.79
(3) Excess of 1 over 2.	1.34	2.58	4.25	0.62	0.26	
(4) Rate per hour.	0.011	0.021	0.035	0.005	0.002	
(5) By NH_4Cl method.	0.67	22.82	14.80	1.41	0.11	39.14
U.L.						
(1) E.D. for 216 hours.	31.29	15.71	7.53	1.41	1.82	26.46
*(2) Continuous E.D. for 96 hours.	33.65	16.13	7.05	1.73	1.76	26.64
(3) Excess of 1 over 2.	-	-	0.48	-	0.06	-
(4) Rate per hour.	-	-	0.004	-	0.0005	-
(5) By NH_4Cl method.	0.91	15.87	7.15	1.40	1.26	25.73
L.S.						
(1) E.D. for 216 hours.	41.33	15.11	9.82	2.67	4.11	31.70
(2) Continuous E.D. for 96 hours.	51.00	14.13	9.00	2.72	3.71	29.56
(3) Excess of 1 over 2.	-	0.98	0.82	-	0.40	-
(4) Rate per hour.	-	0.006	0.007	-	0.003	-
(5) By NH_4Cl method.	0.35	14.43	9.18	2.50	3.53	29.65
K.S.						
(1) E.D. for 216 hours.	9.96	-	2.39	1.08	0.09	3.56
(2) Continuous E.D. for 96 hours.	10.98	-	2.20	0.62	0.06	2.88
(3) Excess of 1 over 2.	-	-	0.19.	0.46	0.03	-
(4) Rate per hour.	-	-	0.002	0.004	0.0003	-
(5) By NH_4Cl method.	0.71	-	2.11	0.34	0.05	2.50

* Average values of a number of samples analysed for preparing acid soils - data for which reported in Tables 32 and 33.

** Rate per hour = Rate per hour of the release of metal ions during the interval 96 hours (or 108 hours as the case may be) to 216 hours.

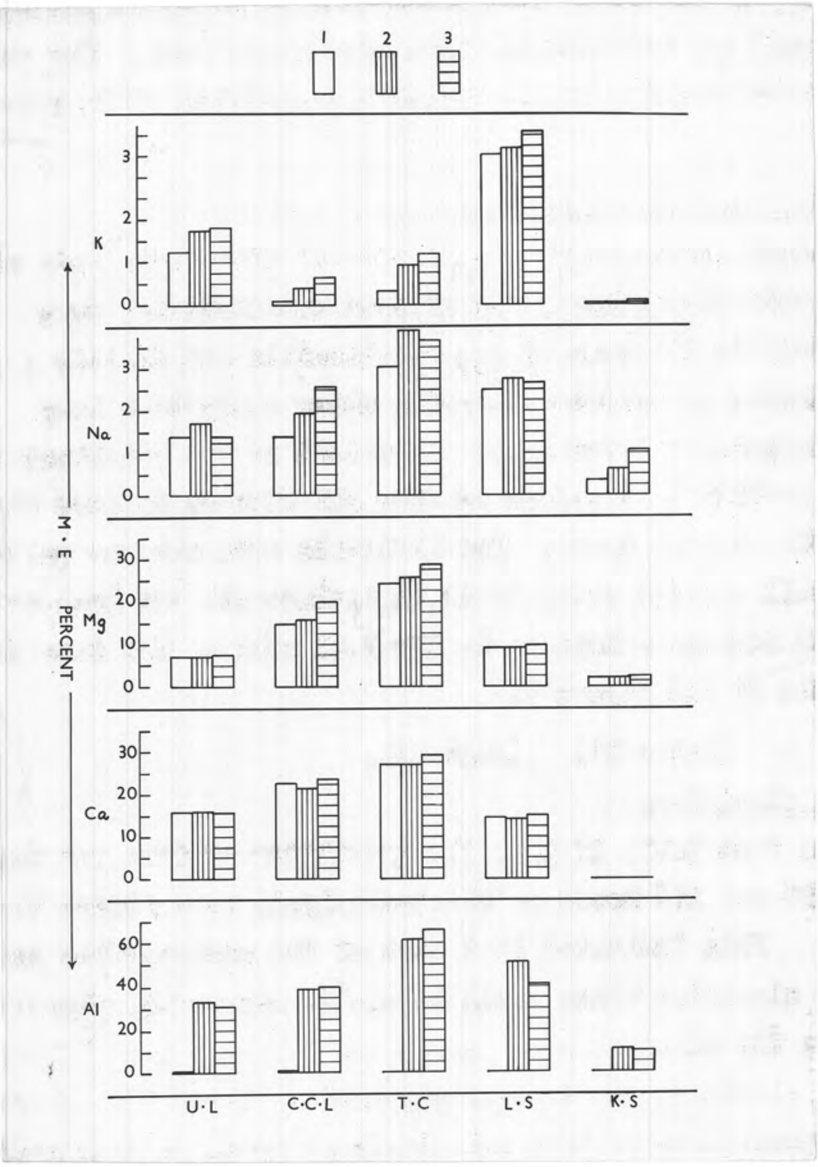

Figure 5.

Exchangeable metal ions by NH_4Cl extraction (1) Continuous electrodialysis for 96 hours (2) and Continuous electrodialysis for 216 hours (3).

There were no pronounced differences in the behaviour of various clay minerals. In all cases the total metal ions obtained by fractional electrodialysis were short of the quantity determined by the ammonium chloride method; about 75 to 90% of the total metal ions present were electrodialysed. During the continuous electrodialysis of a large number of soil samples to prepare acid soils, 91 to 116% (Table 32) and 99 to 113% (Table 33) of the metal ions determined by NH_4Cl in Caniaba Clay Loam and Urrbrae Loam respectively were electrodialysed. The chief cause of this variation was due to the variable quantities of Mg electrodialysed (p.35).

(f) Prolonged continuous electrodialysis of soils.

In the experiments dealing with the fractional electrodialysis of soils it was noted that large quantities of iron and aluminium were mobilized, particularly in the case of montmorillonitic and illitic soils. It was thought desirable to subject the soils under study to a long period of electrodialysis to investigate the extent of the mobilization of iron and aluminium. With that object in view all five soils were electrodialysed continuously for 216 hours. The dialysate obtained was reduced in volume and the cell extract added to it to include all the iron and aluminium and slight magnesium held up in the cell walls. The data obtained are given in Table 21 and Figure 5.

(Table 21) (Page 43).

Release of iron and aluminium.

It will be seen from Table 21 that the quantities of iron and aluminium released after 96 and 216 hours of electrodialysis were almost the same for each soil. This indicated that most of the exchangeable and structural iron and aluminium which could be easily removed by electrodialysis came out in the first 96 hours and after 96 hours the rate of release of iron and aluminium was exceedingly small. There were distinct differences in the quantities of iron and aluminium released from montmorillonitic and illitic soils on the one hand and kaolinitic soil on the other. The reasons for these differences have been discussed earlier (p.39).

Release of Ca, Mg, Na and K.

Almost in all cases slightly greater quantities of Ca, Mg, Na and K were released when the soils were electrodialysed for 216 hours than the quantities of metal ions removed when the soils were electrodialysed continuously for 96 hours. The rate per hour of the release of the metal ions after 96 hours of continuous electrodialysis was exceedingly small. This was an indication that these minute quantities of various metal ions would continue to come out, probably almost indefinitely, as the exchange complex slowly but progressively breaks down.

(g) Effect of clogging of the cell on the rate of electrodialysis.

A reference has earlier been made to the deposition of iron and aluminium hydroxide precipitates in the porcelain cell wall. During the course of electrodialysis of a large number of soil samples for preparation of acid soils, it was noted that if the same cell was used a number of times the rate and the quantity of metal ions dialysed progressively decreased.

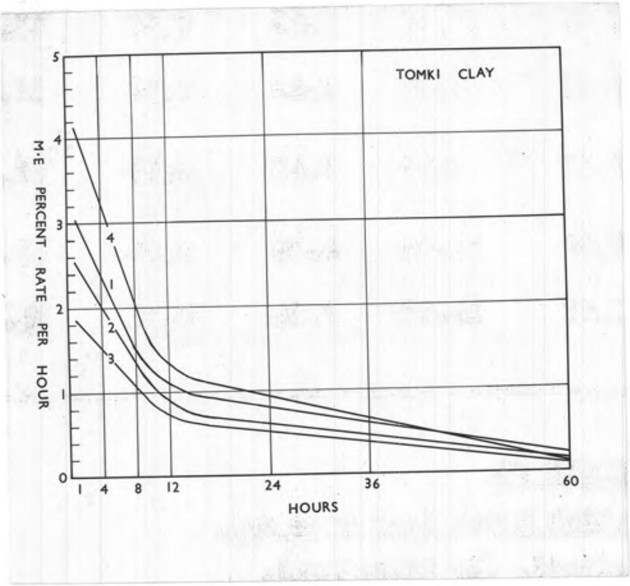

Figure 6.

Effect of Clogging of the Cell on the Rate of Electrodialysis.

It was suspected that this slow rate of, and incomplete electrodialysis were due to the clogging of the cell. The effect of the clogging of the cell on the flow of current has already been discussed (p.26). It was essential to investigate this point and overcome this difficulty for smooth working. The data obtained are given in Tables 22 and 23 and are graphically represented in Figure 6.

<u>Effect of clogging of the cell on the amount of metal ions dialysed.</u>

TABLE 22.

Electrodialysis of Tomki Clay (108 hrs.).

% m.e. metal ions.

	Al.	Ca.	Mg.	Na.	K.	Total.
1. Clean cell.	9.33	27.85	11.09	3.46	0.60	43.00
2. Cell used from 1. above.	3.06	25.07	6.34	3.49	0.52	35.42
3. Cell used from 2. above.	2.35	22.57	0.10	3.43	0.45	26.55
4. Same cell after acid washing.	12.08	28.69	14.00	4.36	0.68	47.73
NH_4Cl Extract.	0.16	27.18	24.18	3.04	0.33	54.73

TABLE 23.

Rate per hour at which metal ions came out.

M.E. % electrodialysed. (By titration).

Time in Hours.	1	4	8	12	24	36	60	84	108
(1) Clean cell.	3.04	2.38	1.51	1.03	0.79	0.53	0.22	0.25	0.07
(2) Cell used from (1) above.	2.56	2.06	1.35	1.10	0.62	0.33	0.16	0.07	0.07
(3) Cell used from (2) above.	1.87	1.42	1.12	1.17	0.52	0.24	0.10	0.05	0.06
(4) Same cell after acid washing.	4.13	2.96	2.02	1.41	0.94	0.40	0.12	0.09	0.06

The rate at which various metal ions appeared in the catholyte was significantly reduced when a porcelain cell which had been previously used once, was employed to electrodialyse a second sample of the same soil. When a third sample was electrodialysed, the rate of dialysis was further reduced when compared with that of the previous sample. The effect of clogging of the cell on the rate of transport of metal ions and incomplete electrodialysis was quite distinct throughout the whole period of electrodialysis. After electrodialysing the third sample of <u>Tomki Clay</u>, the cell was heated in 3-5% hydrochloric acid solution to dissolve the hydroxides present in the cell wall. When all the precipitates had been dissolved the cell was thoroughly washed in running water to remove all the traces of hydrochloric acid. The clean cell was then used to electrodialyse a fourth sample of <u>Tomki Clay.</u> It can be seen from Tables 22 and 23 and

Figure 6 that the rate of electrodialysis was significantly improved when the clogging material was removed.

The clogging of the cell not only affected the rate of electrodialysis but it also resulted in an incomplete electrodialysis of the soil. The quantities of calcium and magnesium were particularly low. With a clean cell 43.00 m.e. per 100 gms. soil were electrodialysed; with the second and the third samples the amount of metal ions electrodialysed fell to 35.4 and 26.55 m.e. per 100 gms. soil respectively. After acid washing the cell there was distinct improvement in the efficiency of electrodialysis and 47.7 m.e. per 100 gms. soil were electrodialysed.

Due to these considerations it is suggested that when a porcelain cell of this type is used it must always be acid washed before a second sample is electrodialysed.

After fractional electrodialysis all the cells were boiled in 3 to 5 % ~~HCl~~ hydrochloric acid and cell extracts from all the soils were analysed to determine the chief cause of clogging of the cell. The data obtained are reported in Table 24.

TABLE 24.

Analysis of the cell extract.*

Soil.	M.E. Percent.				
	Al.	Ca.	Mg.	Na.	K.
T.C.	31.61	nil	2.91	nil	nil
C.C.L.	29.46	nil	1.84	nil	nil
U.L.	21.73	nil	0.32	nil	nil
L.S.	33.18	nil	0.30	nil	nil
K.S.	8.00	nil	0.07	nil	nil

---

* Data taken from Tables No. 6, 7, 8, 9 and 10 dealing with Fractional electrodialysis of soils.

It is evident from the above Table that the clogging of the cell was associated with deposition of iron and aluminium hydroxide. Only traces of calcium, sodium and potassium were retained by the cell while magnesium was precipitated to a small extent.

(h) Relation between the exchangeable metal ions obtained by titration and those obtained by analysis of dialysate.

It was mentioned in the review of the literature that a rough measure of the exchangeable metal ions could be obtained by titration of the dialysate. Some workers have in many cases taken titration values as the final values for exchangeable metal ions and have consequently not analysed the dialysate. In the present studies a large number of soil samples were electrodialysed and exchangeable metal ions obtained by titration as well as analysis of dialysate. It was noted that the analytical values, though very close to the titration values, were still significantly lower than the latter.

Humfeld and Alben (1927) were the first to suggest the use of methyl red indicator for back titration of the dialysate in order to take into consideration the presence of iron and aluminium. They did not report any data to establish a quantitative relationship between the analytical values and the titration values. It was noted in the present investigations that if all the aluminium were included in the exchangeable metal ions the value for total exchangeable metal ions as obtained by analysis was much more than that obtained by titration. If the values of aluminium were not included in the exchangeable metal ions, the total exchangeable metal ions were significantly less than those obtained by titration. This behaviour was noted in all the 41 values obtained in the case of fractional electrodialysis of soils (reported in Tables 6, 7, 8, 9 and 10) and the other 21 values obtained in connection with the preparation of acid soils by electrodialysis and progressive pH values of electrodialysed soils. It was quite evident that the titration figures did not give a correct picture of the total exchangeable metal ions present in the dialysate. It was further noted that this discrepancy was more marked particularly in the later portions of the fractional dialysate when most of the exchangeable metal ions had been removed and the amount of iron and aluminium was proportionately more.

A regression equation was therefore calculated from the date on hand reported in Table 25.

TABLE 25.

Relation between titration and analytical values.

Sample.	% m.e. by analysis. x.	% m.e. by titration. y.	Difference. (x-y).	% m.e. Al.	% m.e. by analysis as calculated "y_1".
<u>Tomki Clay.</u>					
Electrodialysed					
for ... 1 hr.	3.92	3.52	+ 0.40	0.39	4.37
4 hrs.	11.82	11.60	+ 0.22	0.86	12.74
8 hrs.	18.89	19.06	- 0.17	0.31	18.55
24 hrs.	24.67	24.54	+ 0.13	2.27	23.55
108 hrs.	47.73	49.36	- 1.63	12.08	46.19
<u>Caniaba Clay Loam.</u>					
Electrodialysed					
for ... 1 hr.	4.19	4.20	- 0.01	Trace	5.11
4 hrs.	9.99	11.07	- 1.08	0.55	11.26
8 hrs.	13.36	14.20	- 0.84	0.55	14.13
12 hrs.	13.17	14.27	- 1.10	0.31	14.18
24 hrs.	24.42	25.80	- 1.38	3.45	24.70
36 hrs.	30.94	33.13	- 2.19	6.51	31.38
48 hrs.	38.28	44.40	- 6.12	6.35	41.66
96 hrs. (a)	35.76	37.33	- 1.57	5.41	35.21
(b)	33.12	38.07	- 4.95	4.95	35.89
(c)	33.21	35.20	- 1.99	8.17	33.27
<u>Urrbrae Loam.</u>					
Electrodialysed					
for ... 24 hrs.	23.41	22.80	+ 0.61	5.25	21.96
96 hrs. (a)	25.37	25.46	- 0.09	10.98	24.38
(b)	29.04	29.47	- 0.43	15.92	28.05
(c)	26.72	25.06	+ 1.66	-	24.02
(d)	25.93	25.60	+ 0.33	13.57	24.51

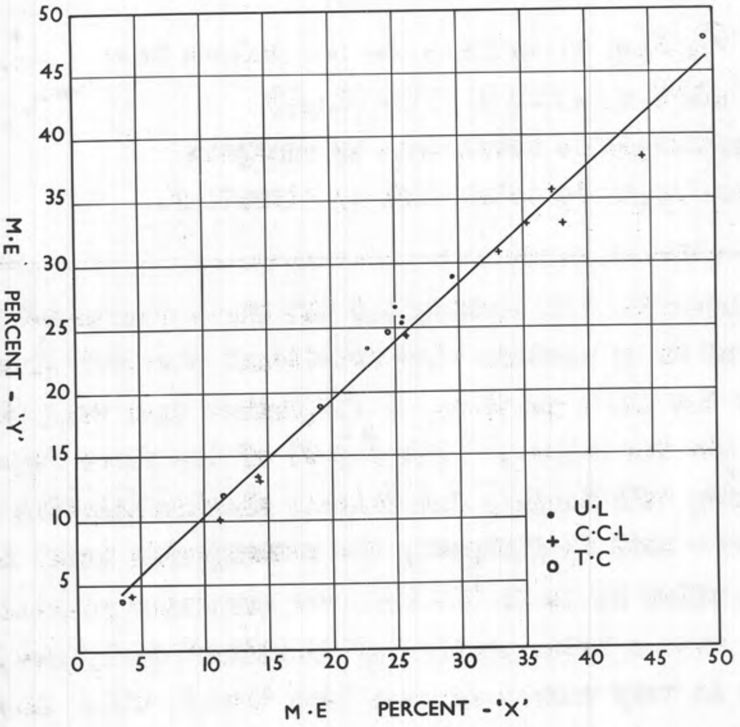

Figure 7.

Regression equation for exchangeable metal ions obtained by titration (X) and analysis (Y) of dialysate.

The analysis of variance for the regression of exchangeable metal ions obtained by analysis on those obtained by titration (expressed as m.e. per 100 gm. soil) is given in Table 26.

TABLE 26.

Analysis of Variance.

Variation due to	d.f.	s.s.	m.s.	v.r.
Variation due to regression	1	2515.0654	2515.0654	1108.20^{xxx}
Deviation from regression	18	40.8502	2.2695	-
Total	19	2555.9156	-	-

The regression equation connecting the two values is -

$$y_1 = 1.1568 + 0.9123\, x \text{ (Vide Fig.7)}$$

where y_1 = exchangeable metal ions by analysis

and x = exchangeable metal ions by titration.

It may be mentioned that in working out the above regression equation the data obtained in connection with fractional electrodialysis were not included because the later portions of dialysates gave very wide differences between the two values. The object of the above regression was to obtain a working relationship for quickly electrodialysing the soils. Normally when a soil is dialysed, the exchangeable metal ions in the dialysate bear a wider ratio to the iron and aluminium present in the dialysate. However, when a later portion of fractional dialysate is considered the ratio is very narrow or even less than 1, which is not the usual case. For this reason the fractional dialysate values were not included in the regression equation.

This regression equation should give a more reliable picture of the exchangeable metal ions present in the dialysate than that obtained from the usual titre value.

(i) pH values of fractionally electrodialysed soils.

Each of the five soils under investigation was electrodialysed for 1, 4, 8, 12, 24, 36, 48, 72, 96 hour periods. At each period the electrodialysed soil was washed with water till free from chlorides. The soil was then dried, powdered and its pH value determined.

The object of this experiment was to obtain a series of soil samples from which metal ions had been partially removed in increasing quantities and then to see how the soil pH varied. The dialysate in each case was analysed to determine the metal ions removed. The data obtained are given in Table 27 and are graphically presented in Figure 8. Each thick dot, in Figure 8 means a time period at which the soil sample was prepared and pH value determined. The first thick dot at the highest pH value in the curve represented 0 hour.

TABLE 27.

pH Values of fractionally electrodialysed soils.

Time. in hrs.	pH value of soils at each interval.					m.e. per cent. metal ions removed at each interval.					m.e. per cent. metal ions present in the complex at each interval.					Percentage saturation at each interval.				
	T.C.	C.C.L.	U.L.	L.S.	K.S.	T.C.	C.C.L.	U.L.	L.S.	K.S.	T.C.	C.C.L.	U.L.	L.S.	K.S.	T.C.	C.C.L.	U.L.	L.S.	K.S.
0	7.1	6.95	6.86	7.47	5.34	Nil	Nil	Nil	Nil	Nil	54.73	39.14	25.73	29.65	2.50	88.02	80.06	78.50	85.62	36.76
1	5.46	5.42	5.30	4.92	5.02	3.92	4.19	3.51	4.27	1.20	50.81	34.95	22.22	25.38	1.30	81.70	71.49	67.78	73.30	19.12
4	4.63	4.32	4.45	4.16	4.86	11.82	9.99	11.09	11.50	2.20	42.91	29.15	14.64	18.15	0.30	69.00	59.62	44.66	52.41	4.41
8	4.69	4.39	4.34	3.95	4.64	11.89	13.36	13.09	18.47	2.30	42.84	25.78	12.64	11.18	0.20	68.90	52.73	38.56	32.28	2.94
12	-	4.35	4.20	3.88	4.55	-	13.17	20.18	19.98	2.57	-	25.97	5.55	9.67	0.00	-	53.12	16.93	27.92	0.00
24	3.86	4.15	4.19	3.88	4.57	24.67	24.42	23.41	21.95	2.55	30.06	14.72	2.32	7.70	0.00	48.34	30.11	7.08	22.23	0.00
36	-	4.17	-	-	-	-	30.94	-	-	-	-	8.20	-	-	-	-	16.77	-	-	-
48	3.62	4.15	-	-	4.41	37.07	31.78	-	-	2.45	17.66	7.36	-	-	0.05	28.40	15.05	-	-	0.73
72	3.67	4.01	-	-	-	44.66	38.28	-	-	-	10.07	0.86	-	-	-	16.20	1.76	-	-	-
96	-	-	3.99	3.80	4.59	-	-	26.67	29.27	2.51	-	-	0.00	0.38	0.00	-	-	0.00	1.10	0.00
108	3.49	-	-	-	-	57.53	-	-	-	-	0.00	-	-	-	-	-	-	-	-	-

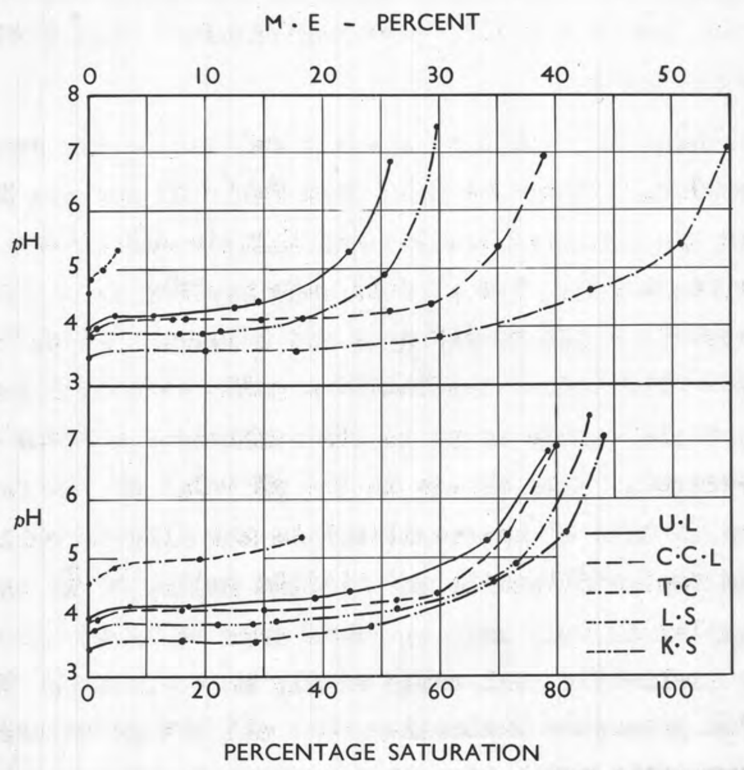

Figure 8.

pH values of partially electrodialysed soils.

It will be seen from the above Table that the soil pH fell very rapidly in the first few hours of electrodialysis and then the rate of fall was very slow. In the case of Urrbrae Loam the soil pH fell from 6.86 to 4.2 in the first 12 hours of electrodialysis; 84 hours later the pH value had decreased only by another 0.21 units. In the case of Kent Sand the soil pH fell by 0.79 units in the first 12 hours; 84 hours later the pH was still the same. All the clay minerals behaved alike, i.e. the pH value fell very rapidly during the first 12 hours but after that the fall in pH was very slow. Alben (1930) also noted that a soil which had an initial reaction of 5.7 had a pH value of 2.12 after 3 hours, and 42 hours more of electrodialysis reduced the pH value only by 0.08 units. Best and Prescott (1929) have made similar observations with the Waite Institute soil.

However, the pH value of a soil is closely related to the degree of saturation of its complex. It can be seen from Table 27 and the lower part of Figure 8 that the montmorillonitic and illitic soils were 80 to 90% saturated in the beginning. The pH fell very rapidly as the degree of saturation decreased from 90% to 60% in about 4 hours. After that the curves were almost flat indicating that the soils were well buffered and underwent a very small change in pH as the exchangeable metal ions were progressively removed. The change in the pH value of the kaolinitic soil was not so sharp as that of montmorillonitic and illitic soils. If, on the anology of the montmorillonitic and illitic soils, it is accepted that the exchange complex is very well buffered from 60 to 0% saturation, the behaviour of the kaolinitic soil could easily be explained. Initially, Kent Sand was only 36% saturated indicating that all the pH values obtained as the exchangeable metal ions were progressively removed would lie in the buffered zone; consequently the change in pH would not be great. Subsequent studies on the nature of soil acidity (reported in part 2) have shown that the kaolinitic soil was buffered in this zone, hence this small change in the pH value of the kaolinitic soil on progressive removal of exchangeable metal ions. In the upper part of Figure 8, the progressive pH curves are drawn when the abscissa represents m.e. per cent. in the exchange complex, while in the lower part the curves are drawn when the abscissa represents percentage saturation of the complex. It can easily be seen that though curves in both the upper and lower parts clearly indicate the general trend of soil pH, each gives a different picture when various clay minerals are compared among themselves. The upper part suggests that each clay mineral is different from the other while the lower part shows that the nature of changes in the pH values on progressive removal of exchangeable metal ions was similar in all clay minerals. In the lower graph the curves are almost all alike and have the same shape. This is not so in the upper part of the figure. This aspect of the presentation of data will be dealt with in greater detail in part 2.

(j) Ultimate pH value of the soils.

The pH value of the soil after all exchangeable metal ions are removed is referred to as "the ultimate pH value". Table 28 gives the ultimate pH values of the acid soils prepared by various methods.

TABLE 28.

Ultimate pH values.

Soils / Method	T.C.	C.C.L.	U.L.	L.S.	K.S.
0.01NHCl	4.00*	4.10**	4.16***	4.16****	4.59*****
Electrodialysis	3.48	3.97	3.99	3.95	4.59
E.D. of NH_4-soil.	3.90	4.10	4.18	3.93	4.53

* Average of 26 samples.
** Average of 20 samples.
*** Average of 20 samples.
**** Average of 16 samples.
***** Average of 3 samples.

It will be seen from the above Table that the ultimate pH value of the soils varied with the nature of the exchange complex as well as the experimental technique adopted for preparing the acid soil.

The ultimate pH value of the soils followed the order -

acid washing > electrodialysis of NH_4-soil > electrodialysis.

These differences were attributed to the differences in the ability of various methods to mobilize iron and aluminium. Table 29 gives the amount of iron and aluminium released by different methods.

TABLE 29.

Amount of iron and aluminium (expressed as Al) obtained by various methods.

	m.e. per cent. Al.				
Soil / Method	T.C.	C.C.L.	U.L.	L.S.	K.S.
0.01 NHCl	5.68	9.14	7.23	11.27	1.53
E.D.	49.95	38.82	33.65	51.00	11.98
E.D. of NH_4 - soil.	31.22	13.49	23.45	16.39	9.10

It will be noted that the quantities of iron and aluminium released by various methods were in the following order.

E.D. > E.D. of NH_4-Soil > 0.01 NHCl.

Thus it is evident that the method which released greater quantities or iron and aluminium from the exchange complex gave lower ultimate pH values. (This will be discussed in greater detail in part 2 of the thesis).

With regard to the behaviour of various clay minerals the ultimate pH values were in the following order -

Kaolinite > Montmorillonite = Illite.

It is known that montmorillonite and illite are both Si-Al-Si type or double lattice layer type clay minerals and their SiO_2/R_2O_3 ratios are of the same order; on the other hand, kaolinite is a single layer (Si-Al) type clay mineral with much lower SiO_2/R_2O_3 ratio than those of montmorillonite and illite. Anderson and Byers (1936), Prescott and Arthur (1943) and Sen and Deb (1941) showed that the ultimate pH varied with the SiO_2/R_2O_3 ratio of the soil colloids. The soil colloids with high SiO_2/R_2O_3 ratio tended to have low pH values and vice versa. The differential behaviour of various clay minerals viewed in this way can thus be explained to be due to differences in the SiO_2/R_2O_3 ratio.

It will also be noted that the ultimate pH value of the kaolinite did not vary with different methods. This was because of the fact (already discussed in detail, p.40) that the kaolinite is a stable clay mineral and resists decomposition by electrodialysis.

PART II.

NATURE OF SOIL ACIDITY AND RELATED PROPERTIES.

A. Introduction.

The soils from which the metal ions have been removed by various methods offer ideal materials for studying the nature of soil acidity and its effects on the various related properties. Such acid soils have been used to study the exchange capacity of soils, buffer capacity of soils, the nature of soil acidity and the nature and extent of weathering processes in the soils.

An understanding of the nature of soil acidity is of fundamental and practical importance in Agriculture. It is the colloidal clay anion which largely determines the retention, availability and fixation of plant food nutrients naturally present and applied as fertilizers. When the nature of soil acidity, its buffer properties and changes in soil pH resulting from application of various cations are known, it is possible to formulate sound fertilizer amendments and liming practices for efficient crop production and soil management.

Mukherjee, Mitra and Co-workers (1942, 1943, 1946), Marshall and Co-workers (1942a, b, c, d, 1946, 1948, 1949) and Schofield (1949) have tried to arrive at an understanding of the nature of acidity of various clay minerals or soils characterized by them though our understanding of the problem is far from complete. The object of these studies was to investigate the nature of soil acidity and various related properties of some Australian soils which were characterized by different clay minerals.

B. Present Studies.

Five Australian heavy clay subsoils (described in Part I, p.12), each one of them characterized predominantly by one clay mineral type, were selected. The acid soils were prepared by various methods such as washing with 0.01 N acid or electrodialysis of natural soil or electrodialysis of a single ion saturated soil. So far no worker has reported comparative studies on the acid soils prepared by different methods. It was therefore thought desirable to investigate the effect of different monovalent and divalent metal ions on the behaviour of all the soils by these three methods.

The chief way of investigating these soil properties has been to study the neutralization or titration curves of the acid soils.

C. Review of Literature.

(a) Titration curves.

Titration curves of soils have been very widely used to investigate the nature of soil acidity, the buffer capacity, the lime requirements of the soils and the nature and extent of weathering processes in the soils.

Sharp and Hoagland (1916) were the first to use an electrometric titration curve to study the lime requirements of soils. However, it was Bradfield (1923b) who pointed out that the titration curve of an acid clay was analogous to that of a weak acid. Since then a titration curve has been one of the important tools of soil investigations.

(b) Technique of obtaining a titration curve.

(i) Preparation of the soil material.

Bradfield (1923b, 1925) in his studies on the soil neutralization curves used the natural soil for titrations. This naturally meant that all the exchangeable metal ions had not been removed from the exchange complex and consequently the curve obtained represented only a part of the full neutralization curve.

Thereafter, with the exception of a few workers (Myers and Gilligan, 1927; Smith and Coull, 1932; Wilson and Flice, 1933), all the investigators have tried to use soils from which the exchangeable metal ions have been completely removed.

An acid soil can be prepared by any of the following methods:-

(1) Leaching the soil with an acid, usually hydrochloric, until all the exchangeable metal ions are removed and then washing the soil free from chlorides.

(2) Electrodialysis of the natural soil.

(3) Electrodialysis of a soil previously saturated with a single metal ion.

In the preparation of the acid soil, two important factors to be considered are:-

(a) To remove all the exchangeable metal ions.

(b) To prevent the decomposition of the exchange complex or any other alterations taking place in the exchange complex.

Puri and Asghar (1938) suggested that the soil should be leached with 0.05 N HCl until the leachate was free from calcium, the soil then to be washed with water until free from chlorides. Matsusaka and Sherman (1950) followed Puri's method. Mehlich (1941, 1942a and 1942b) treated air dry soils with 0.1 N HCl containing one symmetry concentration of hydrogen ions. The soil was allowed to stand overnight, filtered and leached with 0.05 N HCl (no mention was made as to when the leaching was stopped or of how much acid was used) and then washed with water.

Mukherjee, Mitra and Co-workers (1942, 1943, 1946) prepared the acid soils by acid washing but, in order to remove the last traces of chlorides, the acid washed soils were then electrodialysed.

Bradfield (1927a and 1931), Anderson and Byers (1936), Baver (1929, 1930, 1931), Baver and Scarseth (1931a and b), Myers and Gilligan (1927) and Wilson and Plice (1933) used electrodialysed soils. Some of them used a two-compartment cell and others used a 3-compartment cell.

In view of the fact that variable quantities of magnesium are released from the soil during electrodialysis, it is desirable to replace all the exchangeable metal ions by one ion first and then to electrodialyse the soil in the same way that Prescott and Arthur (1943) electrodialysed Na-soils to prepare acid soils for studying ultimate pH values.

Jones and Hoover (1950) obtained a curve by preparing a Ba-saturated soil and then titrating it with sulphuric acid, a practice which is very uncommon. This type of titration would give free $BaSO_4$ precipitate in the soil-water suspension resulting in lowering of pH values as reported by Aarnio (1926), Crowther (1925), Puri and Asghar (1938) and Mitra (1942).

It is evident from the above short review that the acid soils obtained by different methods must have been desaturated and decomposed to different degrees and it may reasonably be expected that the titration curves obtained would differ among themselves.

(ii) Titration.

A titration curve is obtained by adding increasing quantities of a hydroxide to separately weighed equal quantities of the acid soil and determining the pH value of the suspension after equilibrium has been reached. If a titration curve is carried out with one sample of acid soil and incremental quantities of the hydroxide are added to it, the pH values obtained would be high since it is known that equilibrium between a hydroxide and the acid soil takes place more slowly than in an ordinary reaction between substances entirely in solution (Baver and Scarseth, 1931a). The time required for equilibrium to be achieved between the hydroxide and acid soil suspension varies from 6 to 72 hours. Anderson and Byers (1936), Puri and Asghar (1938) and Matsusaka and Sherman (1950) used a 48 hour period while Baver (1931), Baver and Scarseth (1931a) adopted 24 hour period. Mehlich (1941) adopted a 48 hour equilibrium period for montmorillonite soils and a 24 hour period for kaolinite soils. An even longer period for the attainment of equilibrium was reported by Baver (1929) who allowed the soil suspension to stand with NaOH for 3 months. In general 24 to 48 hours are the time periods frequently used. (Spruway 1921, Stephenson 1921, Saint 1926, and Scarseth 1932). Wilson and Plice (1933) observed that if in the case of peat soils the mixtures containing NaOH were allowed to stand for more than 8 hours it was difficult to obtain reproducible results due to decomposition of the organic matter.

On the other hand, Veitch (1902, 1904) and Prescott and Stephens

(1934) have followed a different procedure to achieve the equilibrium between $Ca(OH)_2$ and soils in their lime requirement studies. Their technique consisted in adding increasing quantities of $Ca(OH)_2$ to different samples and evaporating them to dryness on a water bath. This technique was partly based on the known fact that a chemical reaction is accelerated by application of heat. Carolan (1942) suggested that the soil and hydroxide may be heated for five minutes on a water bath to attain the equilibrium. He found that when a soil suspension in $Ca(OH)_2$ was heated the pH value was less than that obtained by long shaking.

In the preparation of soil suspensions for pH determination, soil/water ratio playz an important part. There is no uniformity of soil/water ratio used by various workers. Mukherjee and Mitra (1946) showed that the cation exchange capacity of a hydrogen bentonite calculated at the inflexion point of the titration curve with NaOH increased from 81 to 103 m.e. per 100 gm. of bentonite when the concentration of the suspension increased from 0.25 to 8.8%; the pH values decreased as the concentration increased. Marshall (1949) reported similar results for a bentonite. On the other hand Marshall and Krinbill (1942) noted that the exchange capacities at the inflexion points of Na curves for beidellite, kaolinite and illite were respectively the same for various concentrations of the clay suspensions used. Marshall & Krinbill (1942) and Marshall & Ayers (1946) further noted that the effect of the concentration of clay suspension on the pH values depended on the cation used for the titrations; for example in the case of Putnam clay (Beidellite) they noted that a tenfold increase in the concentration of the clay suspension changed the pH value by one unit when Na was used for the titrations while the calcium curves changed by only 0.2 pH unit for a tenfold change in the clay concentration. Ratios ranging from 1/1 (Mehlich, 1941) to 1/100 (Baver and Scarseth, 1931a) have been used, though a 1/10 soil/water ratio seems to be more frequently used (Anderson and Byers, 1936; Puri and Asghar, 1938; and Matsusaka and Sherman, 1950).

In the present investigations after the soil and hydroxide suspensions were dried and soils repowdered, the pH was determined with a 1/5 soil/water ratio. This ratio has been adopted for much Australian work. (Piper, 1947).

(c) Effect of different metal ions on the shape of the titration curves.

The shape of the titration curves and the pH values at the same percentage saturation points in the curve vary markedly when the titration is carried out with different metal ions.

Bradfield (1927a) titrated an electrodialysed soil with NaOH and $Ba(OH)_2$ and noted that the inflexion points were at pH 8.5 and 7.0 for NaOH and $Ba(OH)_2$ respectively. He considered that the higher pH values obtained were due to the greater hydrolysis of Na-clay.

Baver (1929, 1930) noted that the pH value at a particular point on the curve was a function of the nature of the exchangeable metal ion present. The pH values with different metal ions came in the order LiOH > NaOH   KOH > $Mg(OH)_2$ > $Ca(OH)_2$. He attributed these differences to the differences in the hydration values of the ions. Anderson (1929) reported a similar series except that in his case Ca gave higher pH values than Mg.

Mukherjee, Mitra and Co-workers (1942, 1943, 1946) used three metal ions for titrating a number of soils characterized by different clay minerals and found that the soil pH values were in the order Na > Ba > Ca. The data obtained by them may be summarized as follows:-

	Clay Mineral Type.			
	Montmorillonite.		**Kaolinite.**	
Metal ion.	Na	Ca & Ba	Na	Ca & Ba
Type of curve				
Weak monobasic	Yes	Yes	Yes	x
Strong monobasic	x	Yes	x	Yes
Initially weak dibasic	x	x	Yes	x
Initially strong dibasic	Yes	Yes	Yes	x

The curves were variable in their indications of the basicity of the acid soils. However, most of the curves with Ba and Ca had the tendency to be similar to that of a strong monobasic acid and the Na curves to be similar to that of a weak monobasic acid.. Bradfield's Ba curve (1927a) was also similar to that of a strong monobasic acid in so far as the curve showed a comparatively flat initial run followed by a more or less sharp inflexion point.

These differences in the influence of various cations on the pH values and the shape of the curves may be explained by the energy of absorption of cations and their hydration values. Wiegner (1931) reported the following data.

Cations:-	H	Li	Na	K	Rb	Cs
Diameter of ions Å	1.06	3.00	3.55	4.15	4.50	4.75
Maximum hydration in mols. of H_2O	0	120	66	17	14	13

He concluded that the smaller the radius of the ion the greater is its hydration, and the greater is its volume including the sheath of the water molecules. Also the greater becomes the distance between the inner and outer layer and the less does the ion adhere to the particle. (According to Coulomb's law, the force of attraction between two ions in a given dielectric varies inversely as the square of distance between them). Thus, for example, lithium ion, with its high hydration (and consequently bigger diameter) would be loosely bound to the clay anion and would be more easily hydrolysed and dissociated than any of the other ions in the series, thus causing an increase in the pH value. The divalent cations have a greater energy of absorption than monovalent cations and among themselves are absorbed in the following order $Ba > Sr > Ca > Mg$.

The energy of absorption of the principal exchangeable ions according to Wiegner is $H > Ca > Mg > K > Na$; consequently it has been concluded that the pH value of similar systems with different cations would be in the order $Na > K > Mg > Ca > H$. Hissink (1919, 1920) on the other hand reported that the binding power of Mg was greater than that of Ca, though the differences were small.

(d) <u>Degree of Saturation of the Soils</u>.

Exchange capacity has been defined in Part I (p.17) as the sum of exchangeable metal ions determined by extraction with NH_4Cl plus exchangeable hydrogen at pH 8.4. When all these exchange positions are occupied by metal ions, the soil is said to be saturated. Throughout this thesis the degree of saturation is expressed as a percentage of the exchange capacity as defined above.

The concept of saturation (or "base saturation" as it is still incorrectly called) is often linked with the neutralization of the acidity of the clay (e.g. Hissink, 1924). Bradfield (1923a, 1923b) was the first to suggest that the soil exchange complex was a weak acid. The idea gradually developed that soil acidity was due to exchangeable hydrogen and that a soil was fully saturated when the exchangeable hydrogen was replaced by metal ions. Various workers developed methods to determine the "saturation" or "exchange capacity" based on this idea (Parker, 1929; Schollenberger & Dreibelbis, 1930; Schofield, 1933; Hosking, 1948). However, since the exchangeable hydrogen varies with the pH at which it is determined, it is clear that there is no such thing as a fully neutralized or fully saturated soil unless we choose some arbitrary pH value at which exchangeable hydrogen is determined.

Bradfield and Allison in 1933 suggested that a reference point of pH 8.4 may be adopted since, at pH 8.4, most of the normal soils of the humid regions, in which calcium is the major soil cation, would be saturated when in equilibrium with surplus of $CaCO_3$ at the partial pressure of CO_2 existing in the atmosphere at a temperature of $25^{\circ}C$. This point of reference though arbitrary seems to be logical in the pedological sense and of practical value. Any calcium in excess of that necessary to saturate the complex would appear as $CaCO_3$ under the conditions defined above. Piper (1936) in Australia has adopted this view and has modified Schofield's method for determining the exchangeable hydrogen accordingly.

Recently Schofield (1939, 1949) has offered a different explanation for the variations in the exchange capacity with pH. He considers that the soil clay minerals (i.e. the inorganic exchange complex) are not weak acids as defined by Bradfield, but that they carry negative charges which arise in the following two ways.

(a) A permanent negative charge carried by the clay minerals due to isomorphous replacements in the lattice structure.

(b) The development of negative charges as a result of the proton transfer from the hydroxyls attached to the silicon atoms at the broken edges of the oxygen sheets of the clay mineral structure. The reaction may be represented as follows -

$$\equiv \mathrm{Si} - \mathrm{OH} + \mathrm{H_2O} \xrightarrow{\text{at pH value of 6 or above}} \equiv \mathrm{Si} - \mathrm{O^-} + \mathrm{H_3O^+}$$

Schofield's views offer an explanation of the observation that the exchange capacity of the soil increases as the pH value increases. Schofield (1949) noted that the exchange capacity between pH range 2.5 to 5 was almost constant; he therefore concluded that the clay minerals have a permanent negative charge, which in that pH range is satisfied by Al ions, and that any further increase in the exchange capacity above pH 6 is due to dissociation of hydrions from the hydroxyls attached to the silicon atoms as previously stated.

Percentage saturation and the titration curves.

In classical chemistry it is accepted that for a weak acid an inflexion point in the titration curve indicates the neutralization of some H^+ ions, present in a definite affinity level, at a given pH value. Bradfield (1927a) noted that the titration curves of electrodialysed soils gave an inflexion at a point which within experimental errors corresponded with the exchange capacity of the soil determined by the NH_4Cl method of Kelley and the saturation of soil with Ba. Baver (1930) confirmed Bradfield's findings and noted that the inflexion with different metal ions occurred at the exchange capacity, determined by the above two methods used by Bradfield, though at different pH values. Subsequently Baver and Co-workers (1931a, b) adopted this procedure for determining the exchange capacity of soils used for studies on buffer capacity and the nature of soil acidity.

Puri and Asghar (1938) adopted quite a different line of reasoning. They did not report the exchange capacity of the soil used for comparison with that found from the titration curve. However they concluded that the point of inflexion occurred at half the saturation capacity, which they designated as T/2, where T was the saturation capacity. This assumption is not always true. In fact more often than not the "dissociation constants" of the acids are so close to each other that the curve looks like that of a monobasic acid and probably part of H_2 is also neutralized before H_1 is completely neutralized. Hence Puri and Asghar's assumption will be true only in those few cases where the two "dissociation constants" are far apart ($\frac{K_1}{K_2} > 16$) (Auerbach & Smolczyk), to give distinct breaks. Thus Puri and Asghar's interpretation will not be applicable for all types of curves.

Caldwell and Marshall (1942), working with nontronite, saponite and altapulgite clay minerals, and Mukherjee, Mitra and Co-workers (1942, 1943, 1946), working with montmorillonite and kaolinite soils, observed that, unlike the findings of Bradfield (1927a), Baver and Co-workers (1931a and b), the inflexion did not occur at the same degree of saturation with different metal ions.

Thus it can be seen that there are three different types of data reported by various workers.

In one case the curves looked like those of monobasic acids and gave an inflexion point corresponding with the exchange capacity determined by the usual analytical procedures.

The second conclusion that inflexion occurred at half the saturation capacity was shown to be unacceptable for all titration curves.

The third conclusion was that at any given pH value the exchangeable metal ion content varied with the metal ion used and the degree of saturation at the inflexion point differed for different metal ions. Mukherjee and Co-workers (1942, 1943, 1946) reported two distinct breaks in the titration of a kaolinite with Na, Ca and Ba. The exchange capacities as determined by Parker's method (1929) and Schofield's method (1933) were equivalent to the cation exchange capacity at the first inflexion point but were very much smaller than those at the second inflexion point. They considered that the second inflexion point indicated the neutralization of hydrogen ions which were present at a high level of affinity and they could only be displaced at high pH values. In the cation exchange capacity methods of Parker (1929) and of Schofield (1933) the exchange capacity was determined at pH 7.0 only.

D. Experimental.

(a) Preparation of the acid soils.

(i) By acid washing. (0.01 N HCl).*

Usually the acid soil is prepared by washing the soil with 0.05 N HCl. In the present investigations the acid soils were prepared by washing the soil with 0.01 N HCl. The reasons for selecting the weaker strength of the acid are discussed in the chapter dealing with results and discussion (p.65).

100-150 gm. of air dry soil were taken in a three litre beaker with two litres of 0.015 N HCl and stirred by means of a motor stirrer for 1 hour. The soil-acid suspension was then transferred to a ten litre bottle and the volume of acid added adjusted so that the strength of the acid was 0.01 N and the total amount of hydrogen ions was twice the symmetry concentration of total exchangeable metal ions. To illustrate: 150 gm. of Urrbrae Loam contained approximately 40 m.e. total exchangeable metal ions. The total volume of 0.01 N HCl in the bottle was 8

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* The abbreviation 0.01 N HCl has been frequently used to designate the acid soil prepared by washing with 0.01 N HCl.

litres which contained 80 m.e. H^+, i.e. twice the symmetry concentration of exchangeable metal ions of the soil. The soil-acid mixture in the bottle was then vigorously stirred by bubbling air through it for four hours. The soil was allowed to settle overnight and after about 16 hours the supernatent liquid was syphoned off. Another lot of 0.01 N HCl containing twice the symmetry concentration of hydrogen ions was then added to the soil. The soil-acid mixture was vigorously stirred for two hours by passing air through it. After about 16 hours the clear supernatent liquid was syphoned off. The operation was repeated once more. The supernatent liquid in at least 33% of the samples was reduced in volume and analysed for Si, Al, Ca, Mg, Na and K to get an idea concerning the quantity of exchangeable metal ions removed from the soils. The analytical procedure adopted was the same as for the analysis of the dialysates. (p.20).

The acid soil thus obtained was washed on a No.50 Whatman filter paper with distilled water to remove all chlorides. The soil was then dried, powdered and used for potentiometric titrations.

(ii) By electrodialysis. (E.D.)[*].

50 gm. of oven dry soil were electrodialysed continuously for 96 hours in the case of Caniaba Clay Loam, Urrbrae Loam, Laffer Sand and Kent Sand, and 120 hours in the case of Tomki Clay, to remove all exchangeable metal ions. The dialysate was analysed to find exactly to what extent the exchangeable metal ions had been removed. The electrodialysed soil was then washed free from chlorides with distilled water on No.50 Whatman filter paper.

(iii) Electrodialysis of NH_4-soils. (E.D. of NH_4-soil)[**].

Ammonium soils were prepared by leaching 50 gm. of soil with 1 litre of N NH_4Cl solution. The soil was washed free from chlorides with 40% alcohol. The acid soil was then prepared by electrodialysis of NH_4-soil. The procedure adopted was essentially the same as in "b" above. However, the time taken to electrodialyse these soils was much less than that taken by the electrodialysis of the untreated soils (48 hours).

(b) Soil pH Values. (See Part I. p.18).

(c) Titration of the acid soils with various metal ions.

The acid soils thus prepared by each method were bulked together and a large sample obtained in each case for the titration of the soils. The acid soils were brought to various degrees of saturation with Na, K, Ca, Mg, or Na + Ca by Veitch's method (1902, 1904) for determining the

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[*] The abbreviation "E.D." has been frequently used to designate the acid soils prepared by electrodialysis.

[**] The abbreviation "E.D. of NH_4-soil" has been frequently used to designate the acid soils prepared by electrodialysis of NH_4-soil.

lime requirement of soils as adopted by Prescott and Stephens (1934). 4 gm. lots of oven dry acid soils were taken in pyrex or silica basins and increasing amounts of a metal ion in the form of a hydroxide or oxide were added to each soil. 20-25 ml. distilled water was also added to each soil. The soil-hydroxide mixtures were kept on a water bath for drying and were stirred with a glass rod at frequent intervals to facilitate the absorption of the metal ion. 0.1 N NaOH, 0.1 N KOH, 0.4 N $Ca(OH)_2$ solutions and M_gO powder were used to bring the soils to various degrees of saturation, with Na, K, Ca and Mg respectively. Soon after the soils were dry on the water bath, they were removed, powdered and transferred to 25 ml. specimen bottles provided with plastic screw caps. 20 ml. of water were added to each sample (1/5 soil/water ratio). The mixture was shaken for 2 hours in a mechanical end-over-end shaker and the pH value determined in duplicate. For each soil the pH values were determined when the amount of metal ion added was equivalent to 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 150 and 200% "exchange capacity"*, to construct a titration curve.

For preparing the triangular graphs to investigate the relationship of soils brought to various degrees of saturation with mixtures of Na and Ca, 66 determinations were necessary at an interval of 10% saturation up to 100% saturation capacity. Out of these 66 determinations, 30 values to construct the sides of the triangle were obtained experimentally. In order to fill the inside of the triangle 36 determinations were necessary out of which 22 values were experimentally obtained, while the remaining 14 values were interpolated from the graphs constructed from the data obtained.

E. Results and Discussion.

(a) Preparation of the acid soils.

Puri and Asghar (1938) suggested that the acid soil could be prepared by washing the soil with 0.05 N HCl until no more Ca came out in the leachate. It was however thought that the 0.05 N HCl acid was probably too strong for the exchange complex and might result in the breakdown of the clay minerals. Consequently an experiment was conducted to study the effect of 0.05 N and 0.01 N HCl acids on soils.

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* In these studies exchange capacity at pH 8.4 is taken as the saturation capacity. When metal ions equivalent to the exchange capacity were added to an acid soil it was taken to be 100% saturated.

TABLE 31.

Preparation of acid soils. Exchangeable metal ions removed by various methods.

TOMKI CLAY.

By 0.01 N HCl acid washing.

Sample No.	m.e. per cent.							
	Si.	Al.	Ca.	Mg.	Na.	K.	Total.	pH.
1	18.61	5.57	26.98	21.91	2.04	0.25	50.46	3.66
2	17.50	5.06	26.63	21.04	2.17	0.22	50.06	3.90
3	18.35	4.28	26.88	22.28	2.12	0.21	51.49	3.84
4	18.79	5.61	26.74	21.90	2.10	0.20	50.94	3.89
5	17.45	5.49	25.58	21.77	2.19	0.22	49.76	3.89
6	18.30	6.63	26.30	21.86	2.19	0.22	50.57	3.90
7	-	5.37	26.06	22.29	2.20	0.22	50.77	3.89
8	17.06	6.04	26.45	22.04	2.15	0.22	50.86	3.92
9	18.01	6.04	27.42	21.84	2.25	0.24	51.75	4.00
10	18.21	6.71	27.40	22.38	2.36	0.23	52.37	3.78
Average	18.03	5.68	26.64	21.93	2.18	0.22	50.97	3.87

By continuous electrodialysis for 120 hours.

Sample No.	Si.	Al.	Ca.	Mg.	Na.	K.	Total.	pH.
1	-	50.01	28.69	16.91	4.36	0.68	50.64	3.48
2	-	49.95	27.00	25.70	3.90	0.93	57.53	3.49
Average	-	49.98	27.85	21.35	4.13	0.80	54.08	3.48

By NH_4Cl extraction.

Sample No.	Si.	Al.	Ca.	Mg.	Na.	K.	Total.	pH.
	1.02	0.16	27.18	24.18	3.04	0.33	54.73	

TABLE 32.

Preparation of acid soils. Exchangeable metal ions removed by various methods.

CANIABA CLAY LOAM.

By 0.01 N HCl acid washing.

Sample No.	m.e. per cent.							
	Si.	Al.	Ca.	Mg.	Na.	K.	Total.	pH.
1	16.17	8.65	21.14	12.48	1.15	0.10	34.87	4.12
2	10.42	7.09	21.34	14.10	1.43	0.10	36.99	3.90
3	18.77	10.40	20.75	13.06	1.26	0.11	35.18	3.92
4	16.55	9.07	21.22	14.81	1.21	0.11	37.35	3.86
5	20.63	9.05	22.27	15.19	1.25	0.09	38.80	4.23
6	24.22	12.65	23.71	15.99	1.32	0.11	41.13	4.23
7	17.94	8.26	21.90	13.68	1.21	0.11	36.90	3.83
8	17.68	7.92	21.87	15.05	1.23	0.10	38.25	3.76
Average	16.55	9.14	21.78	14.29	1.26	0.10	37.43	3.98

By continuous electrodialysis for 96 hours.

Sample No.	Si.	Al.	Ca.	Mg.	Na.	K.	Total.	pH.
1	-	34.87	23.86	11.73	2.20	0.44		4.18
2	-	37.46	20.47	12.82	1.94	0.34		4.25
3	-	37.63	20.57	12.83	1.75	0.51		4.16
4	-	33.92	22.16	15.89		0.41		4.11
5	-	36.99	19.97	13.90		0.41		4.08
6	-	40.44	20.26	16.88		0.44		3.84
7	-	42.26	23.56	19.60		0.34		3.95
8	-	47.02	21.96	19.78		0.50		3.70
9	-	38.56	22.96	16.06		0.32		4.06
10	-	39.19	20.17	16.95		0.41		4.18
11	-	38.64	21.81	17.43		0.40		4.01
Average	-	38.82	21.61	15.81	1.96	0.41	39.79	4.04

By NH_4Cl extraction.

Sample No.	Si.	Al.	Ca.	Mg.	Na.	K.	Total.	pH.
	3.27	0.67	22.82	14.80	1.41	0.11	39.14	

TABLE 33.

Preparation of acid soils. Exchangeable metal ions removed by various methods.

URRBRAE LOAM.

By 0.01 N HCl acid washing.

Sample No.	m.e. per cent.							
	Si.	Al.	Ca.	Mg.	Na.	K.	Total.	pH.
1	9.71	8.21	15.29	6.74	0.92	1.11	24.06	4.16
2	12.20	5.31	16.32	7.88	0.95	1.21	26.35	4.13
3	12.23	8.94	15.63	7.76	0.98	1.21	25.58	4.23
4	12.41	7.16	14.73	7.04	0.94	1.15	23.86	4.25
5	12.05	7.14	15.43	7.45	0.95	1.14	24.97	4.07
6	15.37	7.47	15.55	7.83	0.98	1.14	25.50	4.15
Average	12.33	7.23	15.49	7.45	0.95	1.16	25.05	4.13

By continuous electrodialysis for 96 hours.

Sample No.	Si.	Al.	Ca.	Mg.	Na.	K.	Total.	pH.
1	-	32.24	17.07	7.53	2.06	1.98	28.67	3.99
2	-	32.71	16.03	5.90	1.38	2.06	25.37	4.00
3	-	37.65	16.64	9.10	1.34	1.96	29.04	3.96
4	-	-	16.44	6.39	2.16	1.73	26.72	4.04
5	-	35.30	15.76	6.85	1.86	1.46	25.93	3.97
6	-	30.36	16.23	6.52	1.60	1.36	25.71	3.91
Average		33.65	16.13	7.05	1.73	1.76	26.67	3.99

By NH_4Cl extraction.

Sample No.	Si.	Al.	Ca.	Mg.	Na.	K.	Total.	pH.
	-	0.91	15.87	7.15	1.45	1.26	25.73	

TABLE 34.

Preparation of acid soils. Exchangeable metal ions removed by various methods.

LAFFER SAND.

By 0.01 N HCl acid washing.

Sample No.	m.e. per cent.						
	Al.	Ca.	Mg.	Na.	K.	Total.	pH.
1	7.92	14.91	10.06	2.12	3.00	30.89	4.02
2	7.92	13.57	10.10	2.04	2.72	28.43	3.86
3	12.94	13.82	10.48	1.99	2.75	29.04	4.14
4	16.31	14.21	10.56	2.02	3.09	29.88	4.10
Average	11.27	14.12	10.50	2.04	2.89	29.56	

By continuous electrodialysis for 96 hours.

Sample No.	Al.	Ca.	Mg.	Na.	K.	Total.	pH.
	51.00	14.13	9.00	2.72	3.71	29.56	

By NH_4Cl extraction.

Sample No.	Al.	Ca.	Mg.	Na.	K.	Total.	pH.
	0.35	14.43	9.18	2.50	3.53	29.65	

TABLE 35.

Preparation of acid soils. Exchangeable metal ions removed by various methods.

KENT SAND.

By 0.01 N HCl acid washing.

Sample No.	m.e. per cent.						
	Al.	Ca.	Mg.	Na.	K.	Total.	pH.
1	1.74	nil	2.18	0.30	0.04	2.52	4.59
2	1.32	nil	2.09	0.35	0.04	2.48	4.59
Average	1.53	nil	2.13	0.33	0.04	2.50	4.59

By continuous electrodialysis for 96 hours.

Sample No.	Al.	Ca.	Mg.	Na.	K.	Total.	pH.
	10.98	-	2.20	0.62	0.06	2.88	-

By NH_4Cl extraction.

Sample No.	Al.	Ca.	Mg.	Na.	K.	Total.	pH.
	0.71	nil	2.11	0.34	0.05	2.50	-

TABLE 30.

Release of metal ions from soils by 0.05 N and 0.01 N HCl acidr.

Soils.	Strength of acid.	Al.*	Ca.	Mg.	Na.	K.	Total.
Caniaba Clay Loam.	0.01 N	9.14	21.78	14.29	1.26	0.10	37.43
	0.05 N	13.25	21.86	14.83	1.32	0.18	38.34
Urrbrae Loam.	0.01 N	7.23	15.49	7.45	0.95	1.16	25.05
	0.05 N	11.10	15.61	7.01	0.95	1.09	24.66

0.01 N HCl was as effective as 0.05 N HCl treatment in removing the exchangeable Ca, Mg, K and Na. On the other hand 0.05 N HCl seemed to be more drastic in its effects on the exchange complex than 0.01 N HCl treatment as was indicated by the amount of aluminium released. It was therefore decided to prepare the acid soils by washing them with 0.01 N HCl so that the exchange complex could be preserved in as natural a condition as possible.

A large number of samples were subjected to acid washing and electrodialysis treatments to prepare bulk samples of acid soils. At least 33% of the acid extracts and all the dialysates were analysed for exchangeable metal ions to keep a thorough check on the extent of the removal of metal ions from the complex.

Various workers have adopted different techniques for preparing the acid soils. None of them has reported analyses of the acid extracts or dialysate in order to check the extent of removal of metal ions from the complex. During preliminary work it was noted that the reproducibility of metal ions released by acids or electrodialysis was not as good as when the NH_4Cl method was used. Therefore a large number of acid extracts and dialysates were anlaysed to reduce the variability observed and also to obtain good average samples of acid soils. The data obtained are reported in Tables 31, 32, 33, 34 and 35.

The data obtained indicated that acid washing and continuous electrodialysis were equally effective in removing the exchangeable metal ions but were different in their effects on the exchange complex as judged from the quantities of aluminium released.

The date of Table 29 (p.51) show the effect of various treatments on the release of aluminium from the exchange complex. Electrodialysis removed the maximum quantities and it was quite probable that some of the

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* Iron and aluminium were precipitated together as hydroxides and are expressed together as mee. percent. "Al". In the text any reference to mobilization of aluminium includes the very small quantities of iron which were also mobilized.

aluminium may have been released as a result of a break down of the lattice structure, in addition to any exchangeable aluminium released as discussed on p.39 (Part I). On the other hand 0.01 N HCl released smaller quantities of aluminium than electrodialysis. It is quite probable that due to these differences the acid soils obtained by different treatments would differ among themselves (p.72).

(b) Time of equilibrium.

It was shown in the review of the literature that the reaction between an acid soil and hydroxide takes place slowly when compared with the reaction between substances entirely in solution. Usually equilibrium is achieved by allowing the soil-hydroxide suspension to stand for 24 to 48 hours. Prescott and Stephens (1934) on the other hand suggested that the equilibrium could be accelerated and the absorption of the calcium made more effective by evaporating the soil and $Ca(OH)_2$ suspensions to dryness on a water bath. Two soils were titrated by both these methods to investigate a suitable method of titrating the soils.

TABLE 36.
Comparison between two methods of attaining equilibrium between an acid soil and NaOH.

Na, m.e.% added.	pH values. Method 1.	Method 2.
Caniaba Clay Loam (0.01 N HCl).		
0	4.10	4.10
3	5.20	5.07
7	5.64	5.51
15	5.97	5.91
22	6.11	6.03
27	6.35	6.25
29	6.63	6.37
34	7.27	7.06
36	7.92	7.39
44	9.28	8.50
Urrbrae Loam (0.01N HCl).		
0	4.16	4.16
2	5.34	5.06
5	5.82	5.57
10	6.03	5.92
15	6.31	6.22
18	6.63	6.52
20	7.10	6.86
23	8.04	7.48
25	8.66	8.04
30	9.98	9.00
32.5	10.64	9.13

(Vide Figure 9).

Method 1 = Soil + NaOH suspension allowed to stand for 48 hours.

Method 2 = Soil + NaOH suspension dried on water a bath.

Soil/Water ratio 1/5 in both methods.

The pH values obtained by drying of soil + NaOH suspensions were lower at all points than those obtained by the equilibrium method. The differences between the two methods were particularly marked towards the end of the titration, probably due to conversion of hydroxide to

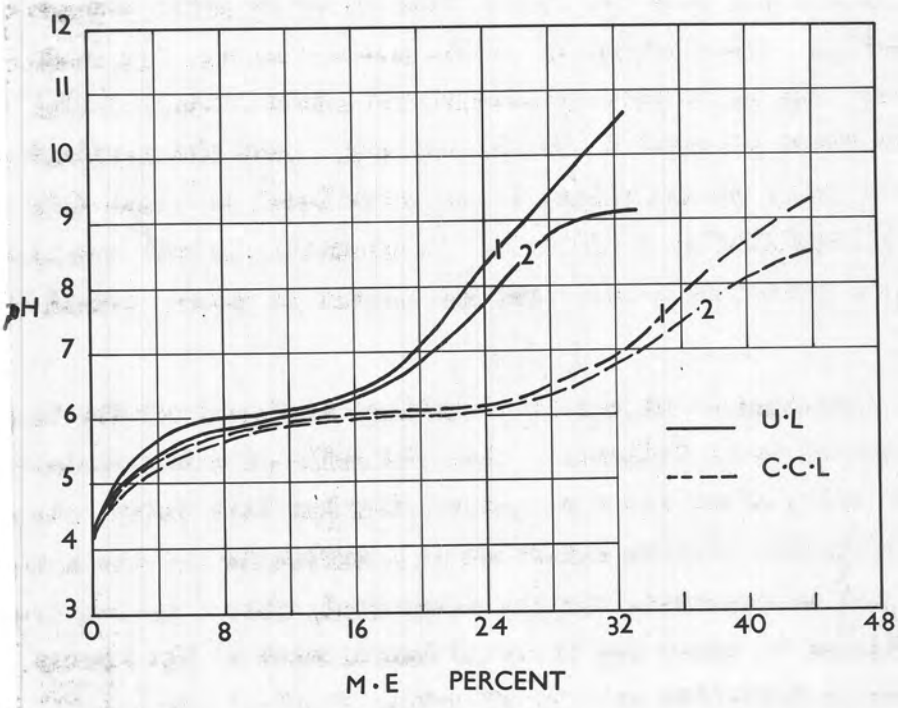


Figure 9.

Illustrating the influence of the method used on the equilibrium pH value of acid soils to which various amounts of NaOH have been added.

(1) Soil + NaOH suspensions allowed to stand for 48 hours.

(2) Soil + NaOH suspension dried on water bath.

carbonate. It is also evident that the reaction was definitely accelerated by the application of heat as is the usual case with all chemical reactions. If the curves reported in Figure 9 are compared with those obtained in connection with the progressive pH values (Figure 8, p.50), it will be seen that at the same percentage saturation points the pH values were much higher in the former case than in the latter case. There are two reasons for this difference. Firstly, in Figure 8 (and Table 27) the soils contained a mixture of exchangeable metal ions, particularly Ca and Mg, while in Figure 9 the soils contained Na as exchangeable metal ion. The Na-soils gave higher pH values than the Ca and Mg-soils. (This cation effect is discussed subsequently). However, the soils in Figure 8 had lower pH values than Ca or Mg soils prepared from the acid soils. This brings us to the second reason, i.e. under natural conditions the soils have approached the state of equilibrium more nearly than those prepared in the laboratory. Even the application of heat could not bring the pH values to the same level as those obtained under the natural equilibrium conditions. Consequently in all the laboratory experiments a procedure which gives the lowest pH values should be adopted.

The second advantage which may be visualized in favour of the "drying on water bath" method is as follows. When the soil-hydroxide mixture is dried on a water bath, after the exchange complex has been fully saturated, all the excess hydroxide will be converted to a carbonate and the natural soil processes will be repeated. On the other hand, when a soil-hydroxide suspension is allowed to stand for 24 to 48 hours, most of the excess hydroxide remains as hydroxide and the pH values obtained are much higher than those obtained under natural conditions. Secondly, it is known that when a large excess of a hydroxide is added to an acid soil and high pH values are attained the exchange complex breaks down. When a 24 to 48 hour equilibrium period is adopted, the pH values obtained when hydroxide is added in excess of the saturation requirements are not really due to interaction between the exchange complex and the hydroxide but between the exchange complex and its decomposition products on the one hand and to hydroxide on the other hand. The third advantage of this method is that it enables us to have 1/5 soil/water ratio for all pH determinations. For these reasons Prescott and Stephens' method (1934) was adopted for obtaining soils at various degrees of saturation.

(c) Presentation of data.

The method of presenting the data of titration curves to investigate the nature of soil acidity is very important. Almost all the workers have drawn the titration curves by plotting m.e. metal ion added along the abscissa and pH along the ordinate. This method of presentation of data does not give a correct picture of the nature of soil acidity. When a number of soils are to be compared and a comparison is made at a point where equal amounts of a metal ion have been added, we are, in fact, not reading the same point on each curve. Each of the soil curves has a

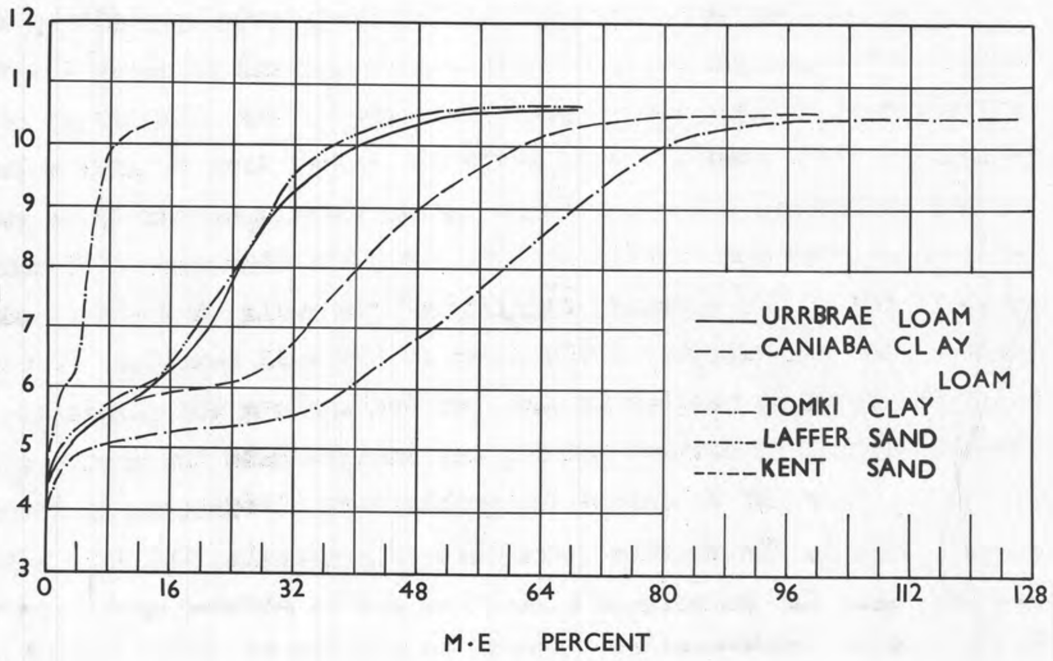


Figure 10.

The Nature of Titration Curves as influenced by the Method of presentation of Data.

(The above curves are drawn by the usual method).

different exchange capacity and when an equal quantity of a metal ion has been added to all the acid soils they have not necessarily reached the same percentage saturation. To take a simple example, let us imagine two acid soils having an exchange capacity of 10 and 50 m.e. per 100 gm. respectively. When 5 milliequivalents of a metal ion have been added, the former soil is 50% saturated (half neutralized), while the other is only 10% saturated. Evidently the pH values at these points are not comparable. Because of this, the curves reported in this fashion are not comparable and show very wide variations. A more logical way of depicting the data for comparing the nature of acidity of soils is to plot the percentage saturation at various points of observation along the abscissa and pH along the ordinate.

Baver and Scarseth (1931a) reported their data by plotting the metal ion added in m.e. per cent. along the abscissa and pH along the ordinate. They reported, "These curves show very clearly that the nature of soil acids is not the same". This statement though true to some extent was not entirely true. Some of their curves were replotted by me according to the suggested modification and it was noted that many differences were smoothed out. The exchange capacity of two soils at the very outset gives us the quantitative differences of the soil acidity. When the metal ion added is plotted in m.e. per cent. along the abscissa a known fact is emphasized without gaining any insight into the nature of soil acidity. In order to obtain the qualitative differences in the nature of soil acidity the modified procedure of presenting the data may be adopted, i.e. the percentage saturation may be plotted along the abscissa. To illustrate, reference may be made to Figures 10, 17(1) (p.77), and 8 (p.50).

In Figure 10 the titration curves with Na are drawn by plotting the Na added in m.e. per cent. to the acid soils along the abscissa. It is evident that all five curves have different shapes, their buffered sections correspond to different amounts of NaOH and they also have inflexions at different amounts of NaOH depending upon the exchange capacity of the respective soils. For example, in Figure 10, the curve for Kent Sand is very steep and pH 10.4 is reached when 13.6 m.e. per cent. Na had been added. On the other hand the curve for Tomki Clay has a flat buffered portion up to about 32 m.e. per cent. Na and attained a pH value of 10.52 when 124.36 m.e. per cent. Na had been added to it. Thus each of the five curves seemed to indicate that the nature of acidity for each soil was quite distinct and that it varied in kind when compared with any other curve. However, when the same data are shown in Figure 17(1), where the percentage saturation is plotted along the abscissa, these wide differences are eliminated, and a general pattern common to all the soils has emerged and they are easily comparable. A reference to this point was made earlier in Part I (Figure 8, p.50). Accordingly all the data in this thesis are reported in the modified form.

TABLE 37.

pH VALUES OF ACID SOILS, PREPARED BY DIFFERENT METHODS, BROUGHT TO VARIOUS DEGREES OF SATURATION WITH Na.

Percentage Saturation.*	Soils. →	Tomki Clay.			Caniaba Clay Loam.			Urrbrae Loam.			Laffer Sand.			Kent Sand.		
	Methods. →	0.01N HCl.	E.D.of NH$_4$-soil.	E.D.	0.01N HCl.	E.D.of NH$_4$-soil.	E.D.	0.01N HCl.	E.D.of NH$_4$-soil.	E.D.	0.01N HCl.	E.D.of NH$_4$-soil.	E.D.	0.01N HCl.	E.D.of NH$_4$-soil.	E.D.
0		4.00	3.90	3.48	4.10	4.10	3.97	4.16	4.18	3.90	4.16	3.93	3.95	4.59	4.53	4.59
10		5.00	4.69	4.40	5.30	5.20	5.08	5.40	5.24	4.96	5.32	5.07	5.00	5.20	5.18	5.20
20		5.20	4.77	4.70	5.70	5.67	5.28	5.80	5.36	5.33	5.50	5.34	5.32	5.50	5.70	5.60
30		5.30	4.83	4.74	5.90	5.79	5.70	5.92	5.47	5.54	5.76	5.66	5.60	6.00	6.02	5.90
40		5.40	5.02	4.86	6.00	5.80	5.82	6.20	5.67	5.79	6.04	5.90	5.92	6.12	6.24	6.10
50		5.60	5.02	5.20	6.20	5.98	5.98	6.45	6.03	6.02	6.65	6.30	6.54	6.17	6.50	6.41
60		6.00	5.13	5.24	6.50	6.22	6.30	6.86	6.53	6.38	7.33	7.11	7.34	6.67	6.97	6.90
70		6.50	5.40	5.58	7.30	6.73	6.95	7.60	7.05	7.28	8.07	7.96	7.97	7.58	7.78	7.80
80		7.40	6.06	6.05	8.00	7.47	7.53	8.35	7.95	8.00	8.77	8.72	8.63	8.20	8.32	8.24
90		8.20	7.11	6.94	8.60	8.08	8.05	9.00	8.67	8.64	9.28	9.20	9.26	8.90	8.85	8.72
100		9.00	8.26	7.86	9.10	8.75	8.60	9.30	9.42	9.24	9.78	9.75	9.75	9.10	9.15	9.10
120		9.95	9.66	9.75	9.88	9.56	9.78	9.94	10.12	10.10	10.24	10.55	10.29	9.90	9.80	9.72
150		10.45	10.42	10.46	10.40	10.32	10.38	10.40	10.33	10.42	10.53	10.58	10.66	10.16	10.22	10.19
200		10.52	10.66	10.56	10.56	10.66	10.54	10.59	10.66	10.57	10.66	10.75	10.66	10.36	10.46	10.33

* 100% saturation = Exchange capacity = Exch. metal ions as determined by NH$_4$Cl extraction + exch. H at pH 8.4

TABLE 38.

pH VALUES OF ACID SOILS, PREPARED BY DIFFERENT METHODS, BROUGHT TO VARIOUS DEGREES OF SATURATION WITH Ca.

Percentage Saturation.*	Soils. ⟶ Methods. ⟶	Tomki Clay.			Caniaba Clay Loam.			Urrbrae Loam.			Laffer Sand.			Kent Sand.		
		0.01N HCl.	E.D.of NH_4-soil.	E.D.	0.01N HCl.	E.D.of NH_4-soil.	E.D.	0.01N HCl.	E.D.of NH_4-soil.	E.D.	0.01N HCl.	E.D.of NH_4-soil.	E.D.	0.01N HCl.	E.D.of NH_4-soil	E.D.
0		4.00	3.90	3.48	4.10	4.10	3.97	4.16	4.18	3.90	4.16	3.93	3.95	4.59	4.53	4.59
10		4.40	4.00	3.87	4.40	4.58	4.14	4.60	4.30	3.97	4.25	4.26	4.21	4.70	4.77	4.76
20		4.60	4.22	3.94	4.70	4.70	4.34	4.85	4.44	4.18	4.40	4.30	4.39	4.78	5.07	4.97
30		4.90	4.37	4.11	4.90	4.85	4.53	4.98	4.66	4.37	4.63	4.60	4.84	4.89	5.12	5.21
40		5.15	4.40	4.18	5.10	4.96	4.75	5.20	4.84	4.63	5.01	4.94	5.05	5.10	5.44	5.36
50		5.40	4.83	4.41	5.40	5.20	5.00	5.55	5.07	4.87	5.49	5.46	5.74	5.57	5.97	5.90
60		5.60	5.03	4.78	5.80	5.43	5.42	6.42	5.67	5.48	6.34	6.18	6.46	6.54	6.60	6.55
70		6.20	5.27	5.03	6.60	6.09	5.96	7.10	6.50	6.27	7.06	6.81	7.20	7.06	7.35	7.22
80		6.70	5.97	5.60	7.30	6.83	6.64	7.80	7.14	6.89	7.79	7.36	7.56	7.37	7.70	7.60
90		7.30	6.74	6.34	7.70	7.29	7.10	8.18	7.72	7.32	8.01	7.70	8.05	7.74	8.05	7.94
100		7.90	7.21	6.98	8.00	7.65	7.46	8.40	8.16	7.56	8.42	8.03	8.18	7.90	8.20	8.11
120		8.40	7.92	7.50	9.40	8.29	7.80	8.46	8.44	7.92	8.67	8.45	8.42	8.07	8.61	8.52
150		9.00	8.58	8.28	9.36	8.83	8.16	8.70	8.79	8.42	9.05	8.88	8.83	8.51	8.68	8.55
200		9.55	9.14	9.20	9.20	8.96	8.53	8.88	8.96	8.44	9.24	8.94	9.17	8.79	8.82	8.70

* 100% saturation = Exchange capacity = Exch. metal ions as determined by NH_4Cl + exch. H at pH 8.4

TABLE 39.

pH values of acid soils (0.01 N HCl) brought to various degrees of saturation with Mg or K.

Percentage saturation.*	pH values with Mg.				pH values with K.				
	T.C.	C.C.L.	U.L.	L.S.	T.C.	C.C.L.	U.L.	L.S.	K.S.
0	4.00	4.10	4.16	4.16	4.00	4.10	4.16	4.16	4.59
10	4.20	4.30	4.40	4.18	4.50	4.61	4.75	4.65	4.72
20	4.50	4.60	4.70	4.48	4.80	5.00	5.20	5.06	5.04
30	4.70	4.80	4.86	4.75	5.00	5.29	5.40	5.35	5.34
40	5.00	5.00	5.00	5.12	5.20	5.50	5.81	5.65	5.66
50	5.20	5.30	5.41	5.52	5.40	5.82	6.20	6.10	5.90
60	5.50	5.89	6.12	6.34	5.60	6.29	6.83	6.78	6.52
70	5.90	6.70	6.90	7.25	6.03	7.00	7.60	7.38	7.42
80	6.40	7.38	7.60	7.66	6.55	7.80	8.35	7.98	8.38
90	7.20	7.90	8.00	8.08	7.25	8.38	9.00	8.45	8.82
100	7.80	8.18	8.30	8.33	7.90	8.90	9.30	8.80	9.22
120	8.70	8.62	8.71	8.67	9.44	9.70	9.94	9.82	9.74
150	9.26	9.13	9.23	9.03	10.22	10.07	10.11	10.10	10.10
200	9.45	9.41	9.60	9.26	10.31	10.29	10.30	10.22	10.18

* 100% saturation = Exchange capacity = Exch. metal ions as determined by NH_4Cl + exch. H at pH 8.4

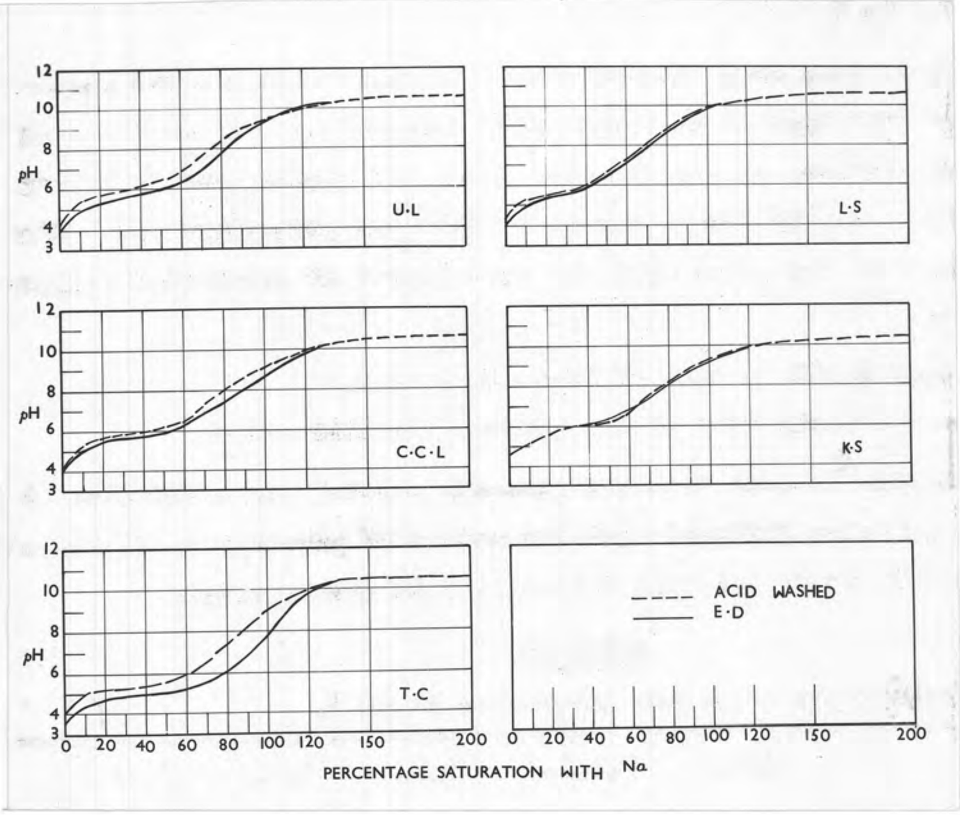


Figure 11.

The Nature of Titration Curves as influenced by the methods of preparation of acid soils.

(d) Nature of titration curves obtained with acid soils prepared by three different methods.

It was shown (p.51) that the ultimate pH of the soil prepared by different methods was in the order -

$$0.01\ N\ HCl > E.D.\ of\ NH_4\text{-soil} > E.D.$$

Titration curves of acid soils obtained by acid washing, electrodialysis and electrodialysis of NH_4-soils of all five soils are shown in Figures 11 and 12. The pH values at various degrees of saturation with Na and Ca are given in Tables 37 and 38.

It can be seen from Figures 11 and 12 that, although the curves obtained by titration of the acid soils prepared by acid washing and electrodialysis have almost the same shape and slopes, yet there are marked differences in the pH values at the same percentage saturation. The pH values at any point with the same degree of saturation followed the order -

$$0.01\ N\ HCl > E.D.\ of\ NH_4\text{-soil} > E.D.$$

This was particularly true of the montmorillonitic soils.

It can also be seen that the percentage metal ion saturation at any particular pH value differed with the method of preparation of the acid soil. To illustrate this the following data are reported.

TABLE 40.

Percentage metal ion saturation at pH 7.

Soils Method	T.C.	C.C.L.	U.L.	L.S.	K.S.
Na.					
0.01 N HCl	75	67	62	55	63
E.D. of NH_4-soil	89	74	69	59	60
E.D.	92	73	67	57	63
Ca.					
0.01 N HCl	86	76	69	69	69
E.D. of NH_4-soil	96	87	79	73	65
E.D.	102	89	84	69	67

At pH 7, the percentage saturation of the montmorillonitic and illitic soils was in the following order, in the case of both Na and Ca.

$$E.D. > 0.01\ N\ HCl.$$

The differences between the two methods of electrodialysis were marked in the case of calcium but were not pronounced in the case of sodium. The general trend of the data obtained indicated that electrodialysed montmorillonitic and illitic soils had lower ultimate pH values, lower pH values at the corresponding degrees of saturations or higher degrees of saturation at a given pH value than the soils prepared by acid washing. With regard to the above differences observed between acid soils prepared by electrodialysis on the one hand and acid washing on the

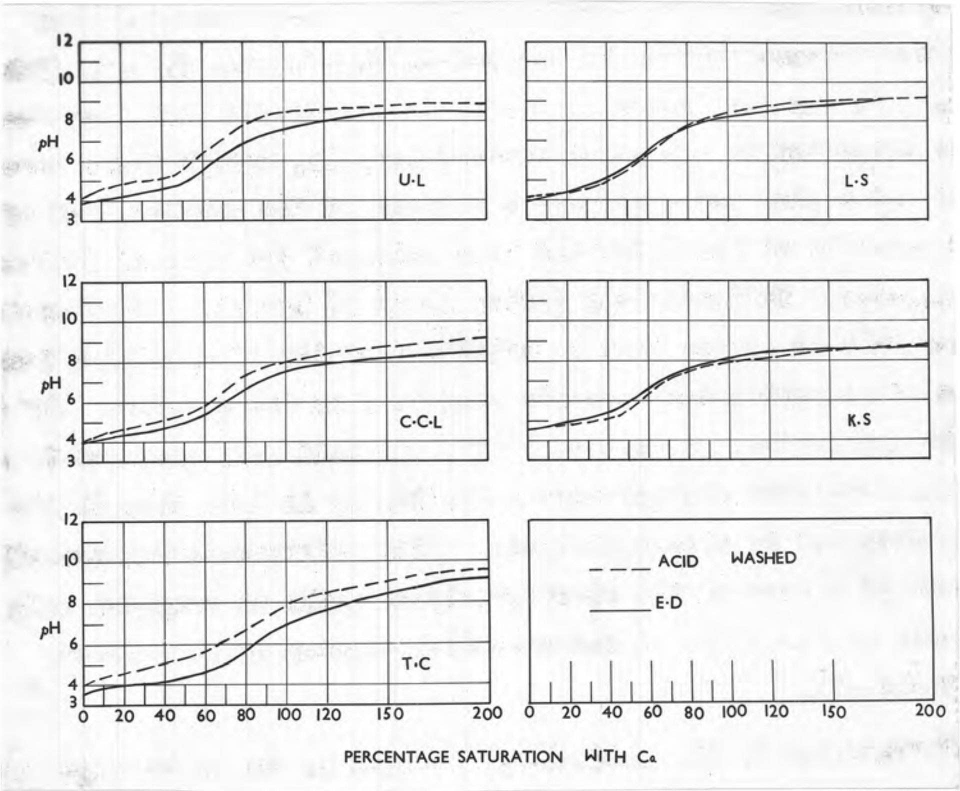


Figure 12.

The Nature of Titration Curves as influenced by the methods of preparation of acid soils.

other, the following explanation is suggested (in respect to montmorillonite and illite).

At present there are two views regarding the nature of the ions balancing the negative charges of an acid soil. The generally accepted view is that in an acid soil negative charges of the exchange complex are satisfied by hydrogen and aluminium. In the light of this theory it may be visualized that the greater the quantity of aluminium removed from the complex the less aluminium will be available to occupy the exchange positions. It was shown earlier that when the acid soils were prepared by acid washing and electrodialysis, larger quantities of aluminium were removed by the latter method than by the former. (Table 29, p.51). It was also shown in Part I of the thesis that when the soils were subjected to prolonged electrodialysis, though there were indications of a slow and continued breakdown of the complex, yet after a certain quantity of aluminium had been released the rate of further release was almost infinitesimal (after about 96 hours). It therefore seems reasonable to assume that a definite quantity of aluminium ions is capable of occupying exchangeable positions on the complex. If this is true, it may further be assumed that in an acid soil prepared by acid washing, more negative charges were satisfied by Al ions than in the acid soils prepared by electrodialysis. This difference may contribute to the lower pH values of the electrodialysed soils as compared with those of acid washed soils at corresponding degrees of saturation. (Tables 37 and 38).

The differences in the ultimate pH values, in the percentage saturation values at pH 7 and in the pH values at the corresponding degrees of saturation as a result of different methods of preparing the acid soils were not significant in the case of kaolinitic soil. This different behaviour of the kaolinitic soil is not surprising in view of the greater stability of kaolinite (p.41) as judged by the quantities of aluminium released (see Table 29).

It may be pointed out that various workers have used different methods to prepare the acid soils for their studies. It is evident that the results obtained will not be comparable unless a uniform method of preparation of the acid soils is adopted.

(e) Effect of different metal ions on the shape of titration curves.

All the acid soils prepared by various methods from various soils were titrated with different metal ions to study their influence on the nature of the titration curves, buffering action, etc. The acid washed soils were titrated with Na, K, Ca and Mg, while the electrodialysed soils were titrated with Na and Ca only. The latter soils were not titrated with K and Mg since the indications were that the acid soils prepared by different methods will show similar variations due to the cation effects. The complete data are reported in Tables 37, 38 and 39 and in Figures 13, 14, 15 and 16a and b.

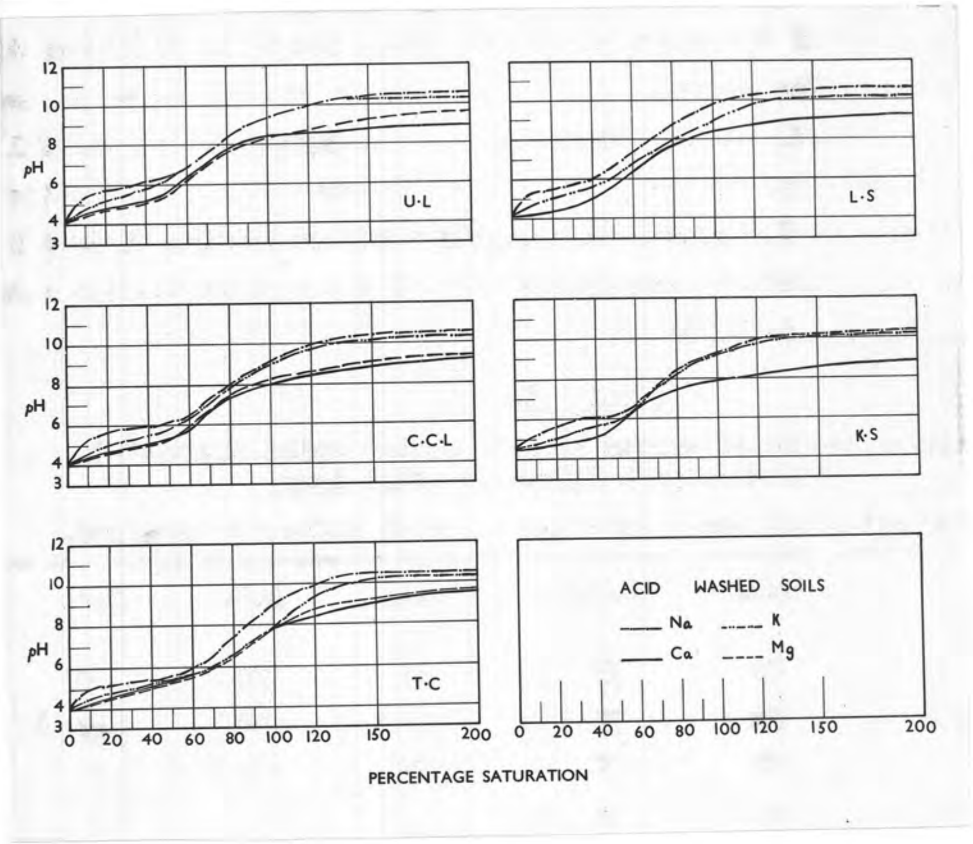


Figure 13.

The Nature of Titration Curves as influenced by the metal ion used.

Note: Ca and Mg curves in Laffer Sand overlap.

Acid Washed soils.

Reference to Figure 13 will show that there were quite distinct differences in the pH values at the same percentage saturation when different metal ions were used. The pH value with different metal ions at any point followed the order -

Na > K > Ca > Mg.

In the initial stages of titration the sodium curve was quite distinct from the calcium and magnesium curves, while the potassium curve was midway between the Na curve on the one hand and Ca and Mg curves on the other. In the initial stages the pH values of the sodium curve were high and the curve had a very steep run up to 20% saturation followed by a buffer region. In the case of Ca and Mg the pH values did not rise abruptly in the beginning and the curves had an initial flat run. The potassium curve was midway between these two distinct types of curves. The curves were highly buffered between 20 to 50% saturation and inflexions occurred almost at the same percentage saturation, as is shown in Table 41.

TABLE 41.

Inflexion points of curves of acid washed soils obtained by titration with different metal ions.

Percentage metal ion saturation at which inflexion occurred.

Soil Metal ion	T.C.	C.C.L.	U.L.	L.S.	K.S.
Na	85	75	75	70	70
K	90	75	70	70	73
Ca	85	75	70	70	65
Mg	85	75	70	70	-

In the case of Caniaba Clay Loam and Laffer Sand the inflexions occurred at the same percentage saturation for all the metal ions. The K curve in the case of Tomki Clay and the Na curve in the case of Urrbrae Loam had inflexion points at 5% higher saturation than the other curves. In the case of Kent Sand the inflexion occurred at 70 ± 5% saturation. The above data very clearly indicate that in the case of each soil the inflexion occurred at the same point with various metal ions. These findings were in accord with the results of Bradfield (1927a) and Baver (1929, 1930).

TABLE 42.

pH values at the inflexion points of curves of acid washed soils titrated with different metal ions.

Soil Metal ion	T.C.	C.C.L.	pH U.L.	L.S.	K.S.
Na	7.80	7.60	8.00	8.10	7.60
K	6.90	7.45	7.60	7.40	7.80
Ca	6.90	7.00	7.10	7.10	6.80
Mg	6.80	7.10	7.00	7.00	-

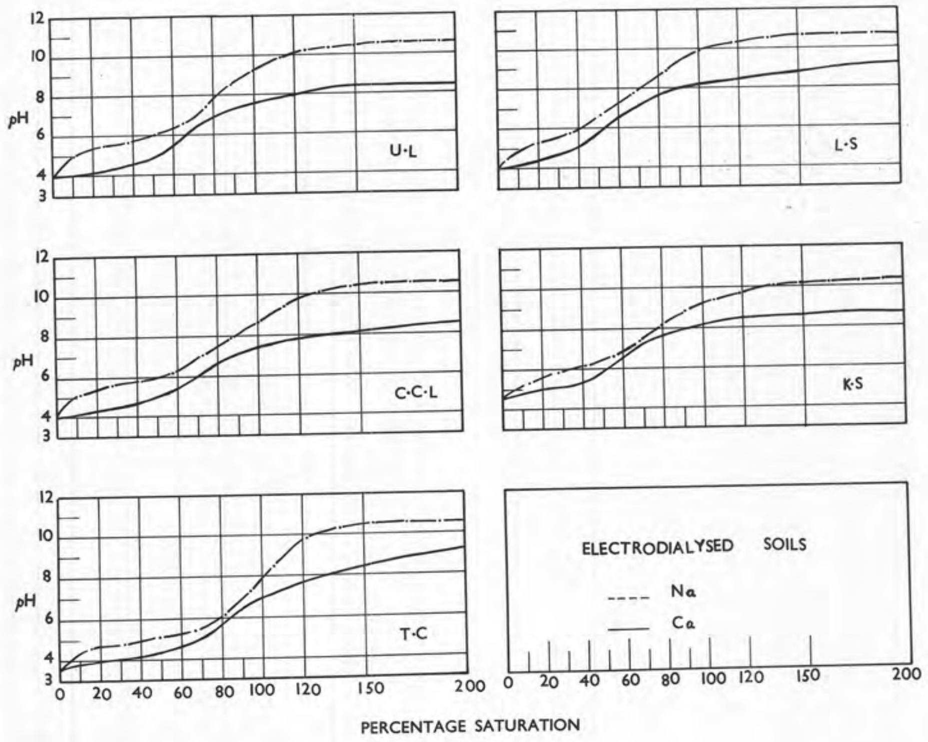


Figure 14.

The Nature of Titration Curves as influenced by the metal ion used.

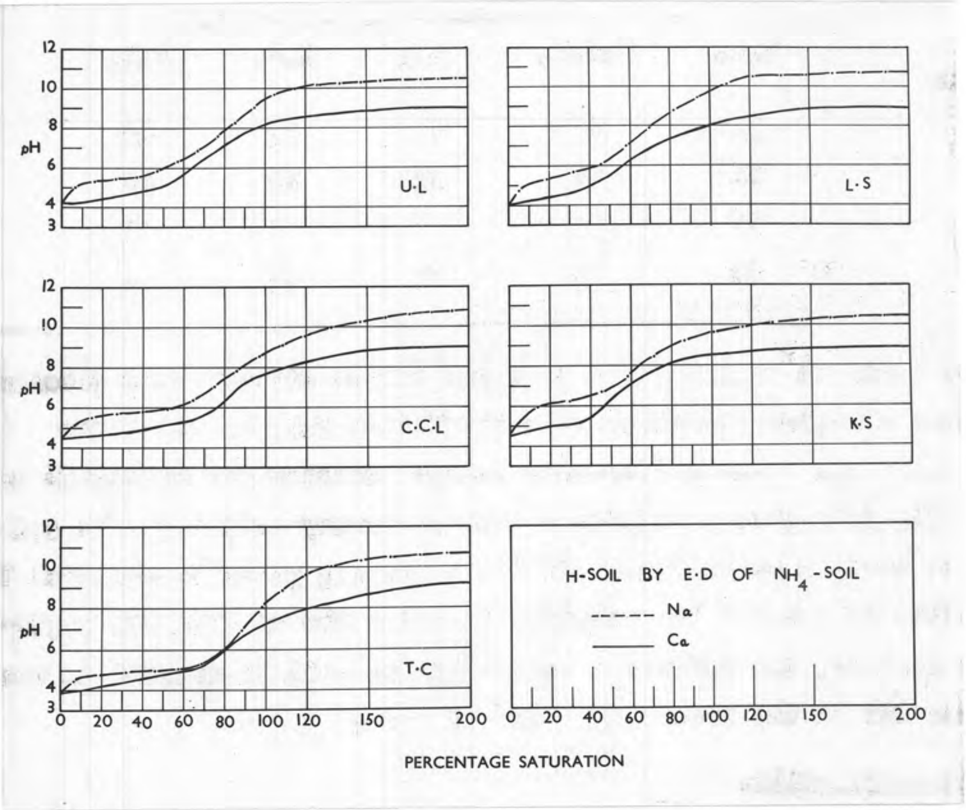


Figure 15.

The Nature of Titration Curves as influenced by the metal ion used.

Though the inflexions occurred at the same percentage saturation, yet the pH values at the inflexion points were quite different for various metal ions. The pH values at the inflexion points were in general agreement with the influence of different metal ions on the soil pH, i.e. the pH value followed the order Na > K > Ca > Mg. It should be noted that the differences between Ca and Mg were very small.

TABLE 43.

Percentage metal ion saturation at pH 7 when acid washed soils were titrated with different metal ions.

Soils Metal ions	Percentage saturation. T.C.	C.C.L.	U.L.	L.S.	K.S.
Na	75	67	62	55	63
K	86	70	62	63	65
Ca	86	76	69	69	69
Mg	89	75	71	69	-

Once again it will be seen that the cation effects were pronounced. At the same pH value the percentage saturation fell in the order Na < K < Ca < Mg. The differences between calcium and magnesium were small. The data give a measure of the buffering action of the soil in respect to various metal ions. If the buffering power is measured by the quantity of a metal ion required to raise the pH from one particular value to another, the buffering action of the soil in respect to various metal ions was in the order Mg > Ca > K > Na.

Electrodialysed soils.

In Figures 14 and 15 are shown the Na and Ca titration curves of the acid soils prepared by the electrodialysis of normal and NH_4-soils respectively. The cation effects on the various characteristics of the titration curves, discussed above, were the same as noted in the case of the acid washed soils.

The differences in the influence of various metal ions on the pH values and the shape of the titration curves are determined by the energy of absorption of the cations and their hydration values. The data in the present studies are in agreement with the findings of Hissink (1919, 1920) that the energy of absorption of various ions was in the order Mg > Ca > K > Na, and that the differences between Mg and Ca were small. Anderson (1929) also reported that the pH value of the soils treated with different metal ions were in the same order as obtained in the present studies. Wiegner (1931) on the other hand reported that Ca had a higher energy of absorption than Mg. The cation effects were the same in the case of all clay minerals examined, namely montmorillonite, illite and kaolinite. Similar results were reported by Mukherjee, Mitra and Coworkers (1942, 1943, 1946) for montmorillonitic and kaolinitic soils and by Caldwell and Marshall (1942) for saponite and nontronite clay minerals.

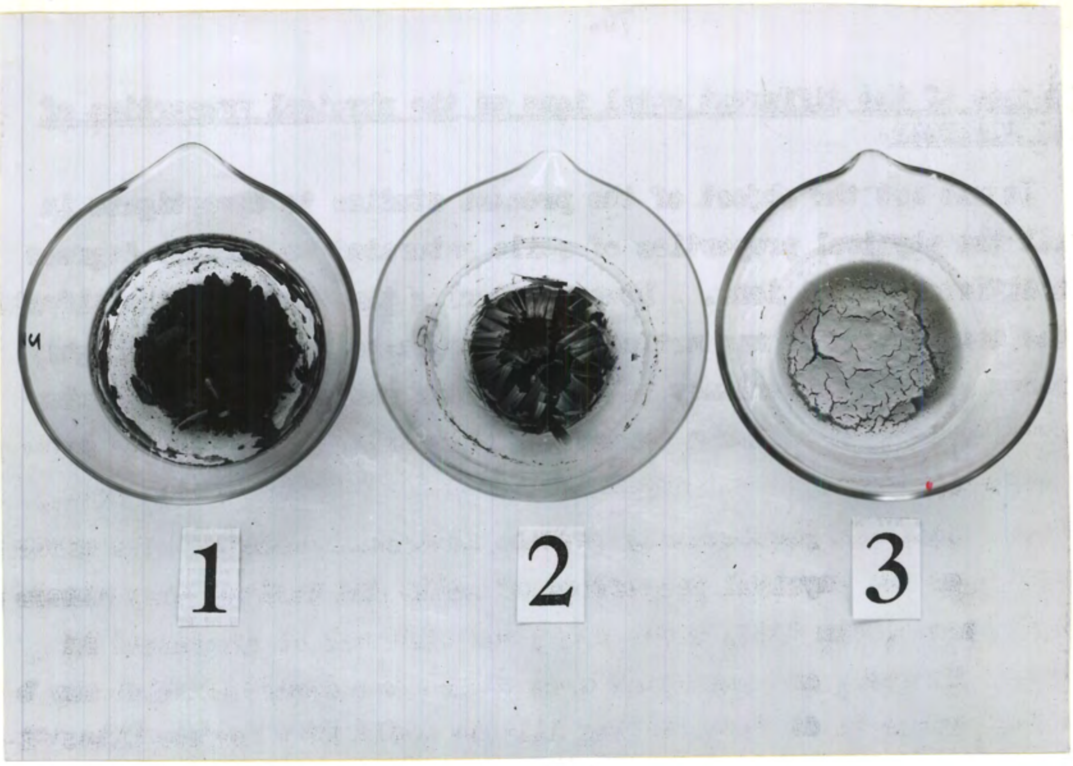


Figure 16a.

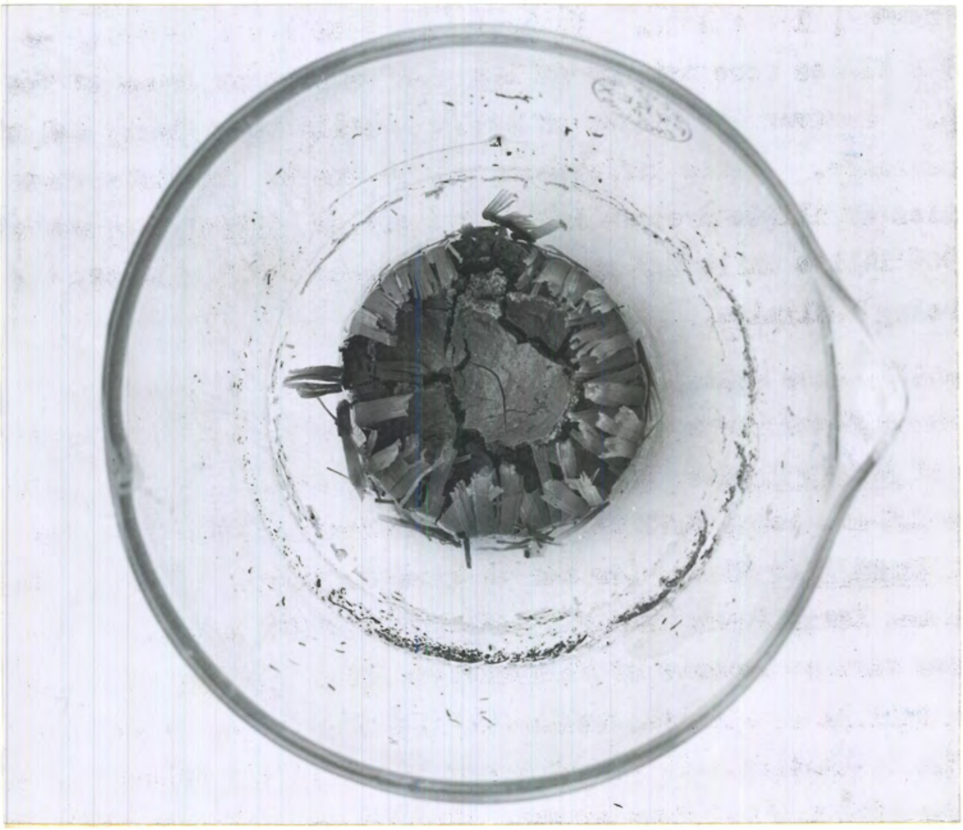


Figure 16b.

Characteristic flaking of Illitic Soil when 30% saturated with sodium.

Figure 16a: (1) Montmorillonite - Tomki Clay.
(2) Illite - Laffer Sand.
(3) Kaolinite - Kent Sand.

Figure 16b: Illite soil - Laffer Sand.

(f) Influence of the different metal ions on the physical properties of clay minerals.

It was not the object of the present studies to investigate in detail the physical properties of soils saturated to various degrees with different metal ions. However, during the course of the titration of the acid soils, it was noticed that the Na-soils were very highly dispersed and had a tendency to form a thick paste in 1:5 soil-water suspension even at as low a percentage saturation as 20. When hydroxide was added in excess of the saturation capacity the soils were freely moving. This was particularly true of montmorillonites. This effect of sodium on the physical properties of soils and various clay minerals is well known (Grim 1942, Baver 1948) and will not be discussed in detail. However, one important observation was recorded which may be of practical value in differentiating illitic soils from montmorillonitic and kaolinitic soils. It was noticed that when sodium or potassium soils were dried on a water bath, Laffer Sand (illite) dried in a peculiarly characteristic way. From the sides of the basin fine, glassy flakes, mica-like in appearance, separated out. These flakes stuck to the sloping walls of the basin, forming a complete circle and were vertically split into rectangular sheets. Urrbrae Loam also had a tendency to flake but the flakes were neither as long nor as fine as those of the Laffer Sand. However the flakes of both the soils were glassy and mica-like in appearance. These differences may be due to the differences in the quantities of illite present in the two soils. Laffer Sand contained more than 90% illite while Urrbrae Loam contained 65 ± 5% illite, the remainder being kaolinite.

Montmorillonitic soils also had a tendency to flake formation at the edges but their flakes were smaller, thicker and wider and more curved than those of Laffer Sand or Urrbrae Loam. For example, Laffer Sand flakes were 7.5 mm. long, 0.12 mm. wide and extremely thin. On the other hand, Tomki Clay flakes (or curved irregular lumps of soil? Figure 16a) were 4 mm. long, 2 mm. wide and more than 1.0 mm. thick. (The above figures were an average of 16 measurements). Montmorillonitic flakes were dull in appearance, unlike the illitic flakes which were glassy. The kaolinitic soil formed a cake which firmly adhered to the bottom of the dish and had fine cracks. Kaolinitic soil cake never broke into pieces. The illitic flakes were well pronounced from 20 to 100% saturation. When the hydroxide was added in excess of the exchange capacity, this characteristic behaviour of illite was not noticed. The differences in the flake formations are shown in Figure 16a and 16b. This flaking property of illite was noticed with potassium soils as well. However, no flakes were produced when calcium or magnesium were used to prepare the soils.

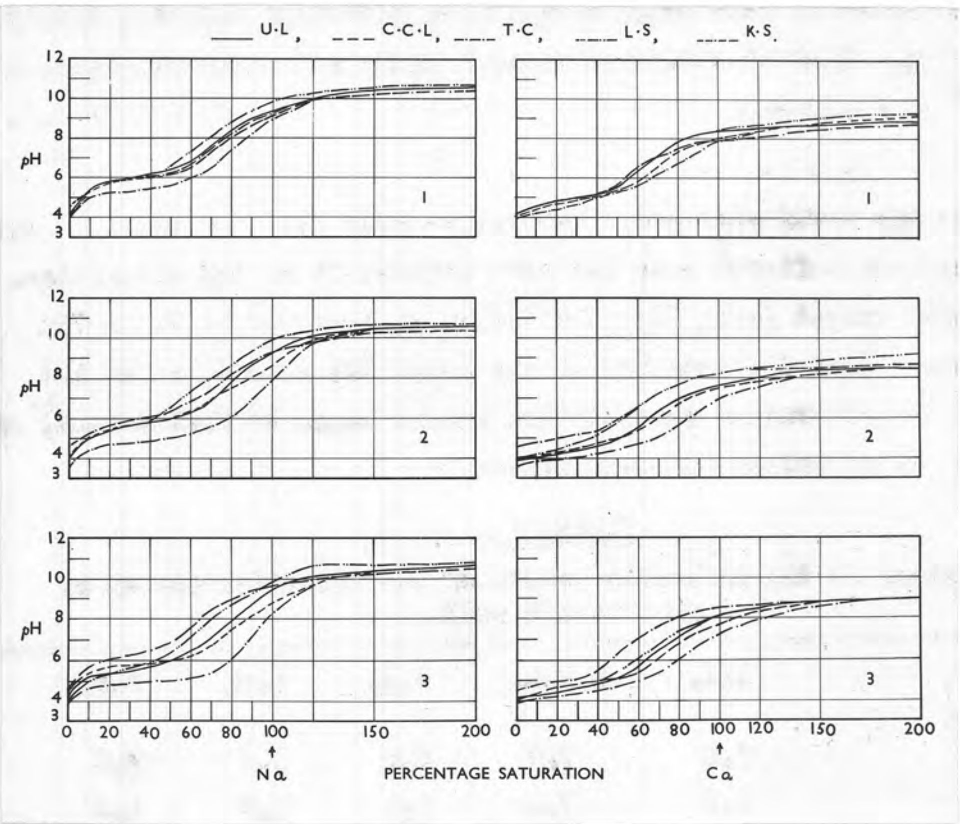


Figure 17.

The Nature of Titration Curves as influenced by Clay Mineral Type.

(1) Acid Soil prepared by Acid Washing.
(2) " " " " Electrodialysis.
(3) " " " " Electrodialysis of NH_4-soil.

(g) Titration curves of various clay minerals.

The titration curves of montmorillonitic, illitic and kaolinitic soils are shown in Figure 17. Curves for sodium and calcium have been reported in Figure 17, while curves for potassium and magnesium are reported in Figure 13. The nos. 1, 2 and 3 in Figure 17 indicate the titration curves of acid soils prepared by different methods, namely, acid washing, electrodialysis of natural soils and electrodialysis of NH_4-soils respectively.

All the titration curves in Figure 17 obtained by any particular method and any particular metal ion had roughly the same shape. All the curves were buffered over the zone between 20 to 50% saturation. In all cases except Tomki Clay the inflexion occurred at 70 to 75% saturation. When the quantity of the metal ion added was 10% in excess of the saturation capacity the curves began to flatten out, and the change in pH values was very slight.

TABLE 44.

pH values at the inflexion points of the titration curves of acid washed soils.

Soil Metal ion	T.C.	C.C.L.	U.L.	L.S.	K.S.
Na	7.8	7.6	8.0	8.1	7.6
Ca	6.9	7.0	7.1	7.1	6.8

It can be seen that, although there were differences in the pH values at the inflexion points, no relationship between various clay minerals could be established. On the one hand the pH values at the inflexion points of sodium curves of Caniaba Clay Loam and Kent Sand were the same, while those of Urrbrae Loam and Laffer Sand were almost the same. The pH values at the inflexion points of the calcium curves were almost the same for all the clay minerals; the range of variation being only ± 0.2 pH units from pH 7. This was true for the other titration curves obtained with acid soils prepared by different methods.

A study of all the 40 titration curves indicated that whatever the method of preparation of the acid soil, or whatever the metal ion used for titration, the general shape of the titration curve was the same for all clay minerals. On the other hand, there were quantitative differences and similarities in the behaviour of various clay minerals which would not, however, justify any hard and fast relationship that could be used to distinguish one clay mineral from the other by means of titration curves. The above conclusion is in conformity with the findings of Marshall and co-workers (1942a, 1942b, 1942d, 1946 and 1949) and Sen and Deb (1941). Marshall and co-workers, by studying the titration curves of montmorillonite, beidellite, illite and kaolinite, have shown that the qualitative behaviour of various clay minerals was similar even though the quantitative measurements were different. However, by measuring the activities of various ions (Ca, Na, K, NH_4), they have shown that the exchangeable ions of kaolinite were more extensively ionized than those of montmorillonite; the exchangeable ions of illite were least ionized. Sen and Deb, by studying the titration curves of laterite and red soils whose SiO_2/R_2O_3 ratios varied from 1.25 to 2.15, concluded that though there were quantitative differences there were no qualitative differences in the titration curves.

On the other hand, the findings of the present investigations do not support Jones and Hoover's views (1950). Jones and Hoover, from a study of two titration curves for montmorillonite and kaolinite, suggested that pH values at various degrees of saturation could be used to distinguish clay minerals. They were of the opinion that if the titration curve of a clay of unknown mineral composition fell close to that of kaolinite it could be classed as a kaolinite clay and if the curve was close to that of the montmorillonite the clay could be classified as a 2:1 crystal type mineral. The chief objection to Jones and Hoover's work is that their conclusions were based on a study of only two titration curves. In the present studies, where only five soils have been used, it can be seen at the outset that the quantitative differences were so small that it would be difficult to establish a relationship of the type suggested by Jones and Hoover.

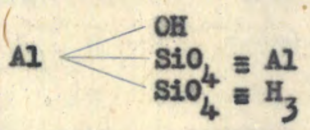
(h) The Nature of soil acidity.

As was pointed out on p.58, Bradfield (1923a and b) concluded that the "soil colloidal" complex behaved like a weak acid and that soil acidity could be due to alumino-silicic acids which ionized to give a definite hydrogen-ion concentration in the suspension. Subsequent work by Baver (1929), Kelley and Brown (1926), Page (1926), Oden (1927) and Kerr (1928a) supported Bradfield's views.

That an acid soil was essentially the result of hydrogen taking the place of metal ions in the exchange positions was a view generally accepted by soil scientists until quite recently. It has always been conceded that aluminium could, if present in an exchangeable form, produce the results ascribed to exchangeable hydrogen, but no good evidence had been published in support of aluminium as the major cation in acid soils until recently Schofield (1949) devised a method to test the rival hypothesis of hydrogen and aluminium. He concluded that his results support aluminium as the dominant cation in acid soils. Schofield's work will be discussed more fully later (p.86).

Kerr (1928a and b), Truog and Chuka (1930) and Chuka (1932) were of the opinion that all soils contained one inorganic acid of the formula $H_2O.\ (Al_2O_3.\ 6\ SiO_2).\ 8\ H_2O$, which was responsible for soil acidity. They considered that the differences in the acidity of various soils was one of degree and not of kind. Data reported by Anderson and Byers (1936) could neither strongly support nor entirely disprove this theory. They found that as silicon increased in the complex the exchange capacity increased out of proportion to the relative increase of silicon, suggesting that a stronger acid occurred rather than a greater quantity of the same acid. A colloid having a SiO_2/R_2O_3 ratio of 4 had a lower pH and had more than twice the exchange capacity of a colloid having a ratio of 2.

Puri (1930a) was of the opinion that the alumino-silicic acid responsible for the soil acidity was of the composition, $Al_2O_3 . 2\ SiO_2 . 2\ H_2O$, which could have the following structural formula -



$$\mathrm{Al}\left<\begin{matrix}\mathrm{OH}\\ \mathrm{SiO_4 \equiv Al}\\ \mathrm{SiO_4 \equiv H_3}\end{matrix}\right.$$

The structural formula suggests that the soil acid was tribasic.

Brown and Byers (1932), Byers (1933) and Byers, Alexander and Holmes (1935), extended Puri's hypothesis and concluded that the soil acids had a characteristic nature according to the type of weathering under which they had formed. They visualized the following four types of inorganic clay acids -

(1) $3\ H_2O .\ Al_2O_3 .\ 6\ SiO_2$. Montmorillonitic Acid.
(2) $3\ H_2O .\ Al_2O_3 .\ 4\ SiO_2$. Pyrophyllic Acid.
(3) $3\ H_2O .\ Al_2O_3 .\ 2\ SiO_2$. Halloysitic Acid.
(4) $3\ H_2O .\ Al_2O_3 .\ SiO_2$. Allophanic Acid.

The names of clay acids were derived from the names of clay minerals of approximately similar composition. Byers, Alexander and Holmes (1935) were of the opinion that the montmorillonitic acid with SiO_2/Al_2O_3 ratio of 6 would rarely exist in nature since the weathering conditions which contribute to their formation from the parent rocks would be strong enough to carry the reaction one step further to pyrophyllic acid. All these acids in their opinion are tribasic in nature but they grow weaker and weaker from montmorillonitic acid down towards allophanic acid as silicon is progressively lost. It can easily be seen that no single colloid, particularly from the surface horizons, would contain only one acid but will contain a mixture of acids, usually one of them predominating.

It is difficult to reconcile these acid formulae suggested by Puri (1930a) and Byers and co-workers (1932, 1933 and 1935) with the modern knowledge of clay minerals. The structural formula of the clay acid suggested by Puri (1930a) was discussed earlier and it was shown that it was tribasic in nature. It will also be noted that the chemical formula of the suggested acid is the same as kaolinite. The kaolinite structure as worked out by Gruner (1932) is electrically neutral as shown by the following structural formula -

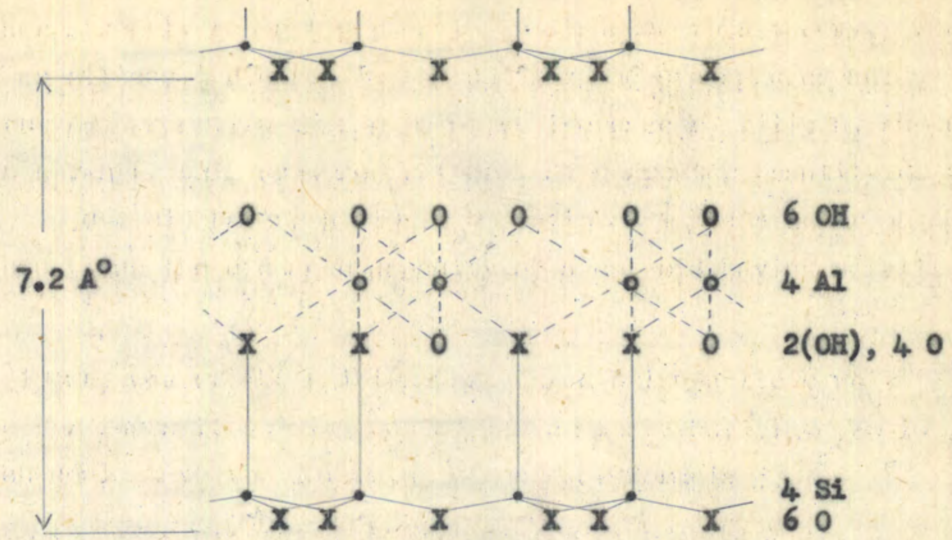


FIGURE 18.

Structural formula of Kaolinite after Gruner (1932).

The sequence of the atomic planes in the kaolinite is as follows -

	charges.	
6 OH	- 6	
4 Al	+ 12	- 28
2(OH); 4 O	- 10	+ 28
4 Si	+ 16	
6 O	- 12	

Since the charges of the lattice are electrically balanced, external cations are not attracted to it except by the negative charges due to the broken bonds of the terminal oxygens or the hydrogens of the hydroxyls on the lattice edges. The broken O or OH bonds at the edges are not large in number since the kaolinite does not break down into very thin sheets and consequently comparatively few broken bonds are exposed for cation exchange. Kaolinite is known to have a very low exchange capacity of 3 to 15 m.e. per 100 gms. On the other hand, it is known that the exchange capacity of some soil clays may be as much as 100 m.e. per 100 gms. In view of these considerations it is difficult to accept Puri's version of the nature of soil acid responsible for the acidity of all the soils.

Byers and co-workers suggested chemical formulae for hypothetical acids which were derived from various clay minerals. One clay acid characteristic of each clay mineral would explain the differences in the exchange capacity. However, all the clay acids suggested by Byers and Co-workers are tribasic in structure while on the other hand the modern views on clay mineral structure and the literature dealing with the basicity of acid soils do not give any definite indication that they are tribasic in nature.

The halloysitic acid of Byers and co-workers has the same chemical composition as kaolinite except that the proposed acid contains one molecule of water more than that present in the kaolinite. Thus, though the halloysitic acid has low exchange capacity like kaolinite, yet in the light of the modern concept of kaolinite structure discussed above, it is difficult to visualize the acid to be tribasic.

The pyrophyllic acid has the same chemical composition as that of the clay mineral pyrophyllite (Pauling 1930), except that the former contains 2 molecules of water more than the latter. The pyrophyllite structure is electrically neutral as will be seen from the following structural formula.

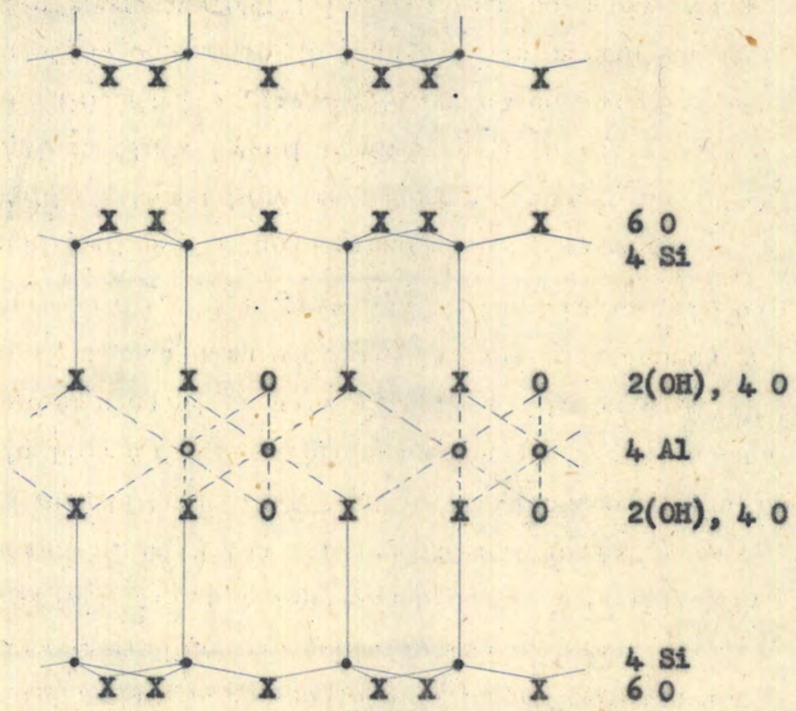


FIGURE 19.

Structural formula of pyrophyllite after Pauling (1930).

The sequence of atomic planes in a lattice layer is as follows -

		Charges.	
Si-Tetrahedron	$6\ O^{-2}$	- 12	
	$4\ Si^{+4}$	+ 16	
	$4\ O^{-2}\ 2(OH)^{-1}$	- 10	
Gibbsite layer	$4\ Al^{+3}$	+ 12	- 44
	$4\ O^{-2},\ 2(OH)^{-1}$	- 10	+ 44
Si-Tetrahedron	$4\ Si^{+4}$	+ 16	
	$6\ O^{-2}$	- 12	

Since the charges carried by the lattice are electrically balanced, pyrophyllite is unable to attract external ions except by weak Van der Wall forces and it has a low exchange capacity.

Hofman, Endell and Wilm (1933) suggested a structural formula for the clay mineral montmorillonite which was essentially the same as that of the pyrophyllite except that the former is distinguished from the latter by the presence of essential magnesium in the crystal composition, water between the layers in the "C" axis and a large quantity of exchangeable cations. The differences in the physical and cation exchange properties of montmorillonite and pyrophyllite are a result of metal ions other than Al which characterize the members of montmorillonite group but are absent in pyrophyllite.

Edelman and Favejee (1940) proposed a modified structure for montmorillonite which differed from the one suggested by Hofman, Endell and Wilm in having every other tetrahedron of silicon sheet inverted and the substitution of (OH) for the inverted O positions, which as a consequence would not be balanced.

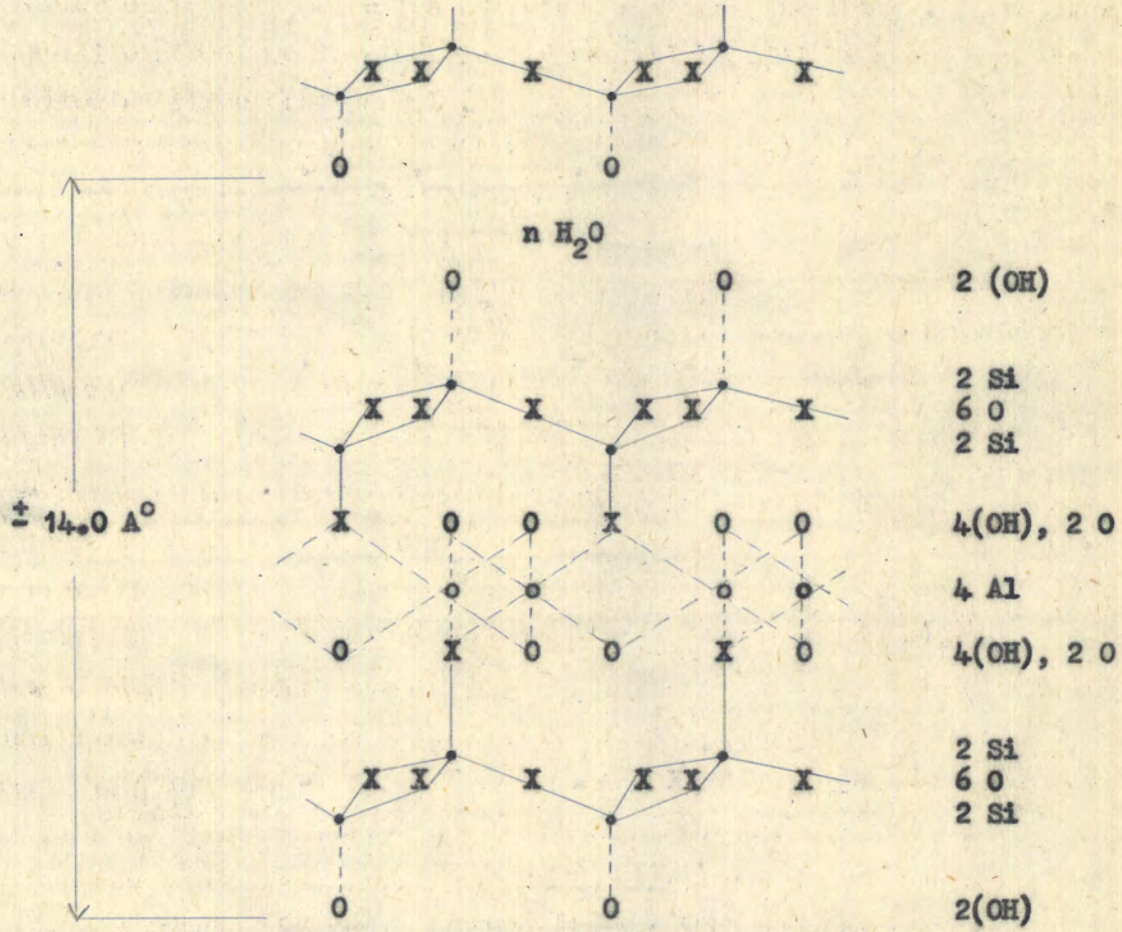


FIGURE 20.

Structural formula of montmorillonite after Edelman and Favejee (1940).

This structural formula explains satisfactorily the various properties and high exchange capacity of montmorillonite which otherwise could not be explained (Bragg, 1937; Garrison, 1938; Holzner, 1935; and De Lapparent, 1938) from the electrically neutral arrangement proposed by Hofman, Endel and Wilm (1933). It will be seen that the chemical composition of the montmorillonite suggested by Edelman and Favejee on the one hand and that of pyrophyllic acid suggested by Byers and co-workers is the same, though there is no evidence of the tribasicity of the clay mineral structure. If we accept the lattice layer structure of the clay minerals and also subscribe to the view that the negative charges arise due to the isomorphous replacements in the lattice structure and the presence of the broken oxygen and hydroxyl bonds near the flake edges, it will be difficult to accept the formulae of hypothetical clay acids suggested by Byers and co-workers. It has now been definitely established that various clay minerals are the chief constituents of the inorganic exchange complex. Their chemical composition and structural formulae are well established and they can easily be accepted in lieu of the hypothetical formulae suggested by various workers. The question of basicity value of the acid clays is discussed in the next chapter.

(i) Basicity of the acid clays.

Reference to titration curves in Figures 11, 12, 13, 14, 15, and 17 shows that, irrespective of the method adopted for preparing the acid soils, the nature of the acidity, as deduced from the titration curve, was determined by the metal ions used. The sodium curves looked like curves of weak monobasic acids characterized by an initial steep rise in the pH followed by a buffered section. The calcium and magnesium curves were characteristic of strong monobasic acids because they had a flat run at the beginning. Potassium curves were midway between these two types of curves.

A number of workers (Bradfield, 1927a; Bradfield and Cowan, 1927; and Baver and Scarseth, 1931a), in their efforts to arrive at the basicity value of acid soils have noted that usually a single break occurs in the region of pH 6 to 8, indicating the presence of weak monobasic acids.

TABLE 45.

pH at the inflexion point of titration curves.

Soil Method	T.C.	C.C.L.	U.L.	L.S.	K.S.
Na Curves.					
Acid washed	7.8	7.6	8.0	8.1	7.6
E.D. of NH_4 soil	7.1	7.1	8.0	8.0	7.78
E.D.	6.9	7.2	7.8	8.2	7.8
Ca Curves.					
Acid washed	6.9	7.0	7.1	7.1	6.8
E.D. of NH_4 soil	6.7	5.9	6.5	6.8	7.35
E.D.	6.4	6.3	6.3	7.2	7.2

In view of the fact that all the curves reported in Figures 11, 12, 13, 14, 15 and 17 had one inflexion in the region of pH 6 to 8, and in general looked like the curves of monobasic acids, one could conclude that all the clay minerals behave like monobasic acids, if it were not for the fact that the percentage saturation values at the inflexion points do not confirm this.

TABLE 46.

Percentage metal ion saturation at the inflexion points.

Soil Method	T.C.	C.C.L.	U.L.	L.S.	K.S.
Na Curves.					
Acid washed	85	75	75	70	70
E.D. of NH_4 soil	90	75	80	70	70
E.D.	90	75	75	70	70
Ca Curves.					
Acid washed	85	75	70	70	65
E.D. of NH_4 soil	90	75	70	70	70
E.D.	90	75	70	70	70
Mg Curves.					
Acid washed	85	75	70	70	-
K Curves.					
Acid washed	90	75	70	70	73

If we assume for the purpose of discussion that the Bradfield concept of soil acidity is correct the following observations follow.

It can be seen from Table 46 that in four soils up to 75% of the exchange positions were neutralized at the inflexion point and the maximum quantity of them neutralized at the inflexion was 90% in the case of Tomki Clay. Best and Prescott (1929) also noted that in the case of Waite Institute soil the inflexion occurred at 60% saturation. This is an indication that all the clay minerals under investigation were not monobasic in nature. At the same time the shape of the curves did not throw any light on the basicity value of the acid soils. The fact that one inflexion occurred before the acid soil was fully saturated is good evidence that the hydrogen ions in the acid soils are present in two different degrees of reactivity, the major portion of which has been neutralized at the inflexion point.

The data obtained by different workers in connection with the basicity value of the acid soils vary widely.

Bradfield (1923b) wrote as follows: "The curves obtained by the hydrogen electrode were also of the type usually obtained with weak acids. There are not sharp breaks but the slope changes gradually showing the least buffer action between pH 9.5 and 7. At the latter point there is a slight flattening of the curve with all clays studied. It seems to be as pronounced as that observed in the titration of weak crystalloidal acid and would seem to be evidence that at least a dibasic acid is involved."

In the same year he (1923a) advanced the theory that though the soils gave curves similar to a monobasic acid still the ionization of that acid represented a series of mass action relations as expressed by the equation:

$$\frac{[H^+]\,[X^-]}{[H\,X]} = Ka,\ Kb,\ Kc \quad \ldots \quad \ldots \quad Kn.$$

where Ka, Kb, Kc ... ... Kn represented the dissociation constants of a series of acids. Bradfield's explanation of obtaining a titration curve without sharp breaks is based on the fact that a mixture of acids with unlike dissociation constants may give a curve resembling that of a monobasic acid if their respective dissociation constants are close enough together so that their individual curves overlap.

Puri and Asghar (1938) obtained curves similar to those of a weak monobasic acid but their interpretation was inconsistent. In one case they treated the curves as weak monobasic acid curves and suggested that, since it was difficult to determine the neutralization point, the method developed by Harris (1923a and b) for finding the end point of a potentiometric titration may be employed. According to this method, the pH interval between the beginning and the end point of a titration curve of a monobasic acid is 4 (Britton, 1929, 1942). They therefore were of the opinion that the pH at the neutralization point was -

= initial pH + 4.

Continuing, they further argued that since the titration was not complete at the inflexion point the curves were dibasic in nature. It is difficult to reconcile these two different interpretations for the same type of curves. If we accept that the curves were of dibasic acids, the suggestion that the first hydrogen is neutralized at 4 pH units higher than the initial pH is not always valid. Puri and Asghar compared their titration curves with weak dibasic acids like succinic acid, tartaric acid, oxalic acid and malonic acid and in none of them did the neutralization of the first hydrogen occur at 4 pH units higher than the initial pH.

It is also known (Auerbach and Smolczyk) that before one equivalent of a dibasic acid is neutralized the second half enters the reaction unless the dissociation constant of the second hydrogen is well removed from the first (i.e. $\frac{K_1}{K_2} > 16$). Due to these considerations it seems difficult to accept Puri and Asghar's suggestion for calculating the neutralization of the first hydrogen ion of a dibasic acid by a method which is essentially applicable to a monobasic acid.

Puri and Asghar (1938) in their paper do not make any reference to the exchange capacity of the soil determined by any standard method. However, when they mention that at the inflexion point the neutralization was not complete evidently they were making a reference to some data obtained by a standard method. If that was the case their data are in agreement with those obtained in the present investigations, which indicated that the neutralization at the inflexion point was not complete. However, the agreement is not complete. Puri and Asghar (1938) were of the opinion that at the inflexion point only 50% of the acidity was neutralized. This assumption is once again not always true as discussed above. (Bradfield; Auerbach and Smolczyk).

The variations in the shape of titration curves of clays and various clay minerals obtained by Mukherjee, Mitra and Co-workers (1942, 1943, 1946) have been discussed previously (p.60). Their data did not show any relationship between the clay mineral type, SiO_2/R_2O_3 ratio and the nature of the titration curves. For example, they state that curves characteristic of weak monobasic acids were given by clays having SiO_2/R_2O_3 ratios of 1.88 to 2.51 and the curves characteristic of dibasic acids were given by clays having SiO_2/R_2O_3 ratios of 1.94 to 2.47. In the case of dibasic curves they obtained two distinct breaks for kaolinite and beidellite. Two distinct breaks in the curves have also been reported by Bradfield (1931) for beidellite. Puri (1930a) reported three breaks in the titration curve. In his subsequent work (1938) he has evidently adopted the view that the acid soils are dibasic in nature.

Anderson and Byers (1936) noted that the titration curves of dibasic tungstic and mucic acids of very low solubility were similar to those of strongly soluble monobasic acids, with little or no evidence of dibasicity. They therefore concluded that the existence of polybasicity was not necessarily detectable from the character of the titration curve, while, when two or more breaks occurred in the curve, their presence was strong evidence of the polybasicity.

All the above discussion is based on the assumption that acid soils are weak acids. However, recently Schofield (1949) has brought forward evidence to suggest that acid soil is not a weak acid as described by Bradfield. According to his hypothesis when the exchangeable metal ions (Ca, Mg, Na and K) are removed the negative charges are satisfied by Al^{+++} ions and not by H^+ ions as is usually supposed. Whether the soil acidity is due to hydrogen or aluminium or both has been an open question for many years. As late as 1948, almost 9 years after Schofield's first paper on this matter (1939) was published, Kelley was of the opinion that it is almost impossible to prove whether Al is exchangeable or not. He also makes an unequivocal statement in his monograph on the cation exchange in soils (1948, p.69) that "Base unsaturated soils contain H ions". It may be noted that no reference is made to any prominent part played by the aluminium ions. Thus even at present there is no unanimity of opinion on this question.

However, the new contribution of Schofield to this problem makes it desirable to discuss further our own results in relation to his conclusions.

The fact that all the titration curves of all the clay minerals reported in this thesis were buffered between 20 to 50% saturation (Figure 17) could be explained according to Schofield's hypothesis.

Schofield (1946) suggested that the exchangeable aluminium ions will be present in 6 co-ordination with water such as $Al(H_2O)_6^{+++}$. When NaOH is added to an acid soil the following reaction may take place -

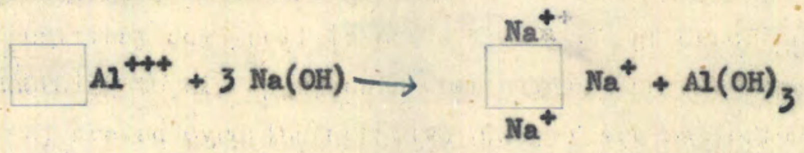
$$(1)\quad Al(H_2O)_6^{+++} + 2(OH)^- + 2\,Na^+ \longrightarrow \left[Al(H_2O)_4\ (OH)_2\right]^+ + 2\,H_2O + 2\,Na^+.$$

On the addition of NaOH as the pH value rises, 2 hydrions dissociate from two molecules of water surrounding the Al^{+++} ion and neutralize the hydroxyls of NaOH with the formation of water and the positive charge is reduced by 2. The unit $\left[Al(H_2O)_4\ (OH)_2\right]^+$ is unstable since it is surrounded by two hydroxyls; it consequently combines with another Al^{+++} ion unit by sharing the two hydroxyls; in this process two more molecules of water are released.

$$(2)\quad Al(H_2O)_6^{+++} + \left[Al(H_2O)_4\ (OH)_2\right]^+ + 2\,H_2O + 2\,Na^+ \longrightarrow \left[Al_2(H_2O)_8\ (OH)_2\right]^{++++} + 4\,H_2O + 2\,Na^+.$$

It will be noted that as the second stage in the reaction is completed, the 2 Al^{+++} ions which carried 6 positive charges carry 4 positive charges only, with the result that 2 negative charges are left unsatisfied on the acid clay. These two negative charges could then be satisfied by the 2 Na^{+} ions which remain in the system (equation 2). As the pH value continues to rise these Al^{+++} ion units continue to lose their positive charges until in the range of pH 5 to 6 they are precipitated as $Al(OH)_3$. The nett reaction may then be represented as follows.

(3)



$$\boxed{}\,Al^{+++} + 3\,Na(OH) \longrightarrow \overset{Na^{+}}{\underset{Na^{+}}{\boxed{}}}\,Na^{+} + Al(OH)_3$$

Aluminium hydroxide precipitate remains stable until pH 9 is reached when it changes to aluminium in 4 co-ordination giving rise to aluminate anion, $Al(OH)_4^-$ (Russell, 1950). It will be noted that all the titration curves with Na in Figure 17 were buffered between pH 5 and 6 which could be due to a buffering exerted by aluminium ions satisfying the negative charges on the clay anion. When the stage, at which all aluminium ions are precipitated as $Al(OH)_3$, is reached, there would be a sudden rise in the pH value, i.e. an inflexion would occur in the titration curve.

Schofield's work suggests two types of negative charges which are active in two different pH regions. It may be expected that the bulk of the permanent negative charges (p.58) will be neutralized before the negative charges arising from the proton transfer enter the reaction.

In the present studies the inflexion of the titration curves was obtained at 70 to 85% saturation when the exchange capacity was determined at pH 8.4; thus there was evidence that the remaining 15 to 30% of the negative charges were at a different degree of reactivity and it is possible that these charges may have arisen largely as a result of proton transfer (p.58). This is in conformity with other data reported by Schofield (1939). In the following table data interpolated by the author from Schofield's graphs are set out in a way to facilitate comparison with the author's results.

Clay mineral.	Permanent negative charges. (a)	Charges developed as a result of proton transfer at pH 8.4. (b)	(b) expressed as percentage of the total charge (a+b) at pH 8.4. (c)
Montmorillonite.	95	18	16
Red clay loam from Natal (kaolinite).	5	2.5	33

To sum up, the present studies indicate that the titration curves of all the clay minerals was highly buffered between 20 to 50% saturation and that there was strong evidence for the presence of negative charges in two degrees of affinity. It could also be reasonably supposed that the 70 to 85% charges neutralized at the inflexion point were probably mainly due to the permanent negative charge on the clay minerals and the remainder, 15 to 30%, were developed largely as a result of proton transfer.

(j) Buffer capacity of clay minerals.

If any solution resists change in the pH value when H^+ or OH^- ions are added to it, it is said that the solution is exerting buffer action. In soil chemistry many soils are known to resist change in pH while others undergo wide variations in pH value when treated with an acid or a hydroxide; the former soils are said to be well buffered.

Baver (1930, 1931) and Maiwald (1928) have discussed in detail the various explanations of the nature of buffer action. Baver (1931) reviewing the literature has concluded that, though various workers (Bradfield, 1923; Wiegner and Gessner, 1926; Maiwald, 1928; Kappen, 1929; Behrens, 1930) have offered different explanations of the buffer action, they have all attributed the buffer action in soils to reactions involving the exchange complex.

TABLE 47.

Amount of metal ions required (m.e. per 100 gm. soil) to increase the pH value of acid washed soils by one unit.

pH range soil	4.5-5.5	5.5-6.5	6.5-7.5	7.5-8.5	8.5-9.5	9.5-10.5
Na Curves.						
T.C.	26.75	14.93	7.46	6.84	10.57	20.53
C.C.L.	5.87	21.52	6.85	6.85	10.27	25.43
U.L.	3.28	13.12	5.58	4.26	7.54	16.73
L.S.	6.23	9.69	5.19	4.50	6.58	15.57
K.S.	1.09	2.65	0.95	0.82	1.84	-
Ca Curves.						
T.C.	24.88	14.31	9.31	12.44	46.65	-
C.C.L.	20.05	7.34	6.85	20.54	-	-
U.L.	12.80	4.57	4.26	11.48	-	-
L.S.	11.07	4.84	4.15	10.73	-	-
K.S.	3.20	0.88	1.36	4.76	-	-

It will be seen that Tomki Clay required the maximum quantity of metal ions and Kent Sand required the least quantity of metal ions to effect a change of one pH unit. The buffering power of the soils as judged from the quantity of metal ions required to bring about a change of one pH unit was in the order -

T.C. > C.C.L. > U.L. = L.S. > K.S.

It will be noted that in respect to their buffering power the soils fell in the order of their exchange capacities, namely -

T.C. > C.C.L. > U.L. = L.S. > K.S.

It may be mentioned at this stage that the clay content and the exchange capacity of Tomki Clay were higher than those of Caniaba Clay Loam (Tables 1 and 2, p.21 and 22); hence the differences in the buffering power of these two soils. If the data in Table 47 are calculated on the clay content of the soils, the following data are obtained.

TABLE 47a.

Amount of Na or Ca required (m.e. per 100 gm. of Clay) to increase the pH value of the acid washed soils from pH 4.5 to 7.5 (3 pH units) in the case of Na curves and 4.5 to 6.5 (2 pH units) in the case of Ca curves, these being the pH ranges in which the Na and Ca curves were most strongly buffered respectively.

	Na.	Ca.
T.C.	60.5	48.3
C.C.L.	59.3	47.5
U.L.	36.9	29.2
L.S.	36.1	28.3
K.S.	8.7	7.6

It will be seen that the wide differences in the buffering power of Tomki Clay and Caniaba Clay Loam have been accounted for and the importance of the clay content and exchange capacity in influencing the buffer capacity of soils has been brought out.

In relation to the clay mineral type it may be said that the buffering power was in the order -

Montmorillonite > illite > kaolinite.

It was shown above that the two illitic soils, Urrbrae Loam and Laffer Sand had the same buffering power. However, Urrbrae Loam and Laffer Sand differed in their mineral composition (p.12) since illite constituted more than 90% of the clay of Laffer Sand while Urrbrae Loam clay consisted of 65 ± 5% illite and 35 ± 5% kaolinite. One would therefore expect that Urrbrae Loam would be less buffered than Laffer Sand. The fact that they were equally buffered suggested that the illite present in the former soil had a high exchange capacity than that present in the latter soil. This is supported by the recent work carried out by the C.S.I.R.O. Division of Soils which shows that the calculated exchange capacity per 100 gm. of illite of Urrbrae Loam is 73 m.e. and that of Laffer Sand is 58 m.e. at pH 8.4; it also shows that these differences are related to the K_2O content of the two illites which is 3.6 and 4.3% respectively. These calculations are based on the assumption that the minerals present in Urrbrae Loam are illite and kaolinite. The undetected presence by X-rays of undescribed minerals of high exchange capacity could modify these conclusions.

The variations in the buffering power of the members of the same clay mineral group thus depend on their cation exchange capacity which in turn is influenced by the extent of the isomorphous replacements taking place in the lattice and the number of broken bonds near the edges.

A reference to Table 47 will show that in the case of NaOH the soils were highly buffered in the region of pH 5.5 to 6.5. As the inflexion point was getting nearer and nearer the buffering action of all soils gradually decreased in the pH range of 6.5 to 7.5. The soils were least buffered in the pH range of 7.5 to 8.5 since the inflexion point occurred there. In the more alkaline regions (pH 9.5 to 10.5) there was very little change in the pH value of soils on addition of NaOH and the curves flattened out. In this region one may visualize the presence of free $Al(OH)_4^-$, OH^-, HCO_3^-, CO_3^{--} and Na^+ ions. The flat portion of the curve is quite likely to represent the pH due to the presence of these free ions and the clay system may not make any significant contribution, particularly when it is remembered that $NaHCO_3$ is buffered in the pH region of 9 to 11 and Na_2CO_3 in the region of pH 10 - 10.5.

In the case of Ca curves (Table 47) it will be seen that the soils exerted buffering action from the beginning of the titration. The soils were highly buffered in the pH range of 4.5-5.5 and were least buffered in the region of pH 6.5-7.5. The maximum and minimum buffering took place at pH values which were one pH unit less than those in the case of Na curves. This was due to differential cation effects which were discussed earlier. It was shown that the titration curves exhibited more buffering action when the hydroxides of the divalent metal ions were used. The buffering capacity was influenced by metal ions in the following order :

$$Mg > Ca > K > Na.$$

It was also shown that the differences between Mg and Ca were very small.

(k) Soil acidity (including pH values) as influenced by various proportions of Na and Ca in the exchange complex.

The effect of individual metal ions on the pH value of the soil, on soil acidity and other related properties has been discussed earlier. However, in the natural soils a mixture of metal ions, namely, Ca, Mg, Na and K are present in the exchange complex. So far no worker has investigated the influence of a mixture of metal ions present in the exchange complex on pH values of the soil. In order to investigate the influence of a mixture of metal ions on the soil pH values and the soil acidity, the acid soils prepared by acid washing and electrodialysis were brought to various degrees of saturation with Na and Ca and pH values were determined. Na and Ca were selected deliberately. It is well known that in most natural soils Ca and Mg are the predominant exchangeable metal ions while Na and K are present in very small

TABLE 48.

pH VALUES OF SOILS AT VARIOUS DEGREES OF SATURATION WITH MIXTURES OF Na AND Ca.

TOMKI CLAY - Acid Washed

Percentage saturation with

Ca Na	0	10	20	30	40	50	60	70	80	90	100
0	4.00	4.40	4.60	4.90	5.15	5.40	5.60	6.20	6.70	7.30	7.90
10	5.00	5.10	5.30	5.40	5.60	5.93	6.20	7.37	8.12	8.51	
20	5.20	5.37	5.40	5.60	6.00	6.30	7.37	8.10	8.45		
30	5.30	5.39	5.63	6.10	6.40	7.40	8.10	8.51			
40	5.40	5.60	6.00	6.43	7.46	8.10	8.52				
50	5.60	5.98	6.44	7.50	8.13	8.53					
60	6.00	6.50	7.50	8.10	8.50						
70	6.50	7.46	8.20	8.62							
80	7.40	8.20	8.87								
90	8.20	9.00									
100	9.00										

Note: Figures underlined were interpolated.

Exchange capacity at pH 8.4 was taken as 100% saturation.

TABLE 49.

pH VALUES OF SOILS AT VARIOUS DEGREES OF SATURATION WITH MIXTURES OF Na AND Ca.

CANIABA CLAY LOAM - Acid washed.

Percentage saturation with Ca / Na	0	10	20	30	40	50	60	70	80	90	100
0	4.10	4.40	4.70	4.90	5.10	5.40	5.80	6.60	7.30	7.70	8.00
10	5.30	5.40	5.71	5.90	6.14	6.56	7.00	7.63	7.93	7.95	
20	5.70	5.85	5.95	6.18	6.60	7.10	7.77	8.20	8.50		
30	5.90	6.00	6.20	6.55	7.10	7.75	8.37	8.59			
40	6.00	6.20	6.60	7.02	7.69	3.40	8.69				
50	6.20	6.64	7.02	7.80	8.48	3.62					
60	6.50	7.20	7.89	8.50	8.96						
70	7.30	8.02	8.71	9.02							
80	8.00	8.61	9.00								
90	8.60	9.32									
100	9.10										

Note: Figures underlined were interpolated.

Exchange capacity at pH 8.4 was taken as 100% saturation.

TABLE 50.

pH VALUES OF SOILS AT VARIOUS DEGREES OF SATURATION WITH MIXTURES OF Na AND Ca.

URRBRAE LOAM - Acid Washed.

Percentage saturation with

Ca / Na	0	10	20	30	40	50	60	70	80	90	100
0	4.16	4.60	4.85	4.98	5.20	5.55	6.42	7.10	7.80	8.18	8.40
10	5.40	5.50	5.80	6.00	6.31	6.70	7.40	7.98	8.18	8.44	
20	5.80	5.92	6.05	6.43	6.90	7.40	8.33	8.60	8.80		
30	5.92	6.10	6.41	6.95	7.40	8.40	8.65	8.76			
40	6.20	6.45	6.90	7.47	8.41	8.70	8.83				
50	6.45	6.86	7.54	8.43	8.68	8.96					
60	6.86	7.60	8.42	8.70	8.95						
70	7.60	8.40	8.80	8.98							
80	8.35	9.00	9.01								
90	9.00	9.06									
100	9.30										

Note: Figures underlined were interpolated.

Exchange capacity at pH 8.4 was taken as 100% saturation.

TABLE 51.

pH VALUES OF SOILS AT VARIOUS DEGREES OF SATURATION WITH MIXTURES OF Na AND Ca.

LAFFER SAND - Acid Washed.

Percentage saturation with Ca/Na	0	10	20	30	40	50	60	70	80	90	100
0	4.16	4.25	4.40	4.63	5.01	5.49	6.62	7.10	7.79	8.01	8.42
10	5.32	5.40	5.60	5.80	6.22	7.12	7.50	8.06	8.57	8.84	
20	5.50	5.73	6.00	6.65	7.20	7.93	8.13	8.70	9.10		
30	5.76	6.11	6.65	7.27	8.00	8.50	8.92	9.13			
40	6.04	6.60	7.30	8.07	8.51	9.00	9.20				
50	6.65	7.37	8.08	8.60	9.03	9.26					
60	7.35	8.10	8.65	9.10	9.25						
70	8.07	8.70	9.10	9.40							
80	8.77	9.20	9.56								
90	8.28	9.70									
100	9.78										

Note: Figures underlined were interpolated.

Exchange capacity at pH 8.4 was taken as 100% saturation.

TABLE 52.

pH VALUES OF SOILS AT VARIOUS DEGREES OF SATURATION WITH MIXTURES OF Na AND Ca.

KENT SAND - Acid Washed.

Percentage saturation with Ca / Na	0	10	20	30	40	50	60	70	80	90	100
0	4.59	4.70	4.78	4.89	5.10	5.57	6.54	7.06	7.37	7.74	7.90
10	5.20	5.30	5.44	5.60	5.90	6.50	7.10	7.50	7.75	8.10	
20	5.55	5.82	5.90	6.00	6.60	7.07	7.46	7.90	8.10		
30	6.00	6.00	6.19	6.83	7.40	7.80	7.95	8.10			
40	6.12	6.20	6.80	7.62	8.00	8.30	8.64				
50	6.17	6.79	7.60	8.00	8.32	8.81					
60	6.67	7.60	8.04	8.50	8.90						
70	7.58	8.13	8.60	8.86							
80	8.20	8.65	9.09								
90	8.90	9.10									
100	9.10										

Note: Figures underlined were interpolated.

Exchange capacity at pH 8.4 was taken as 100% saturation.

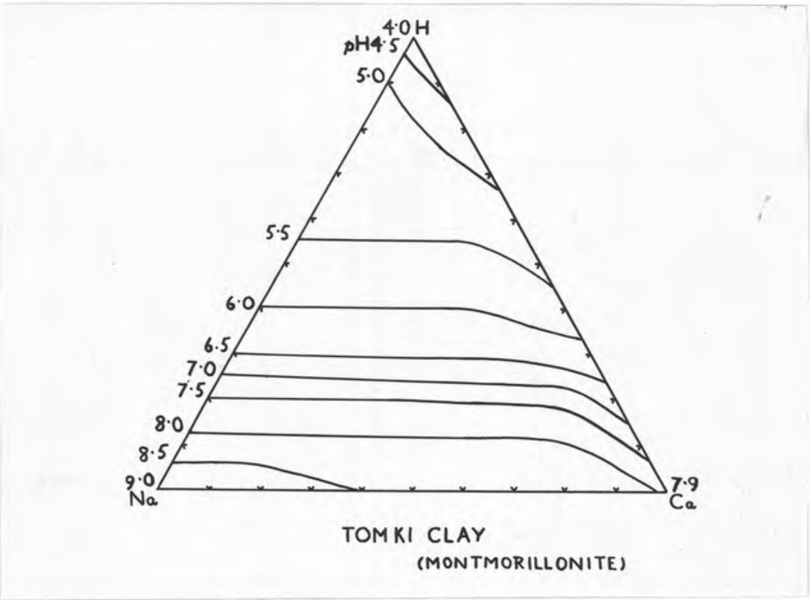


Figure 21.

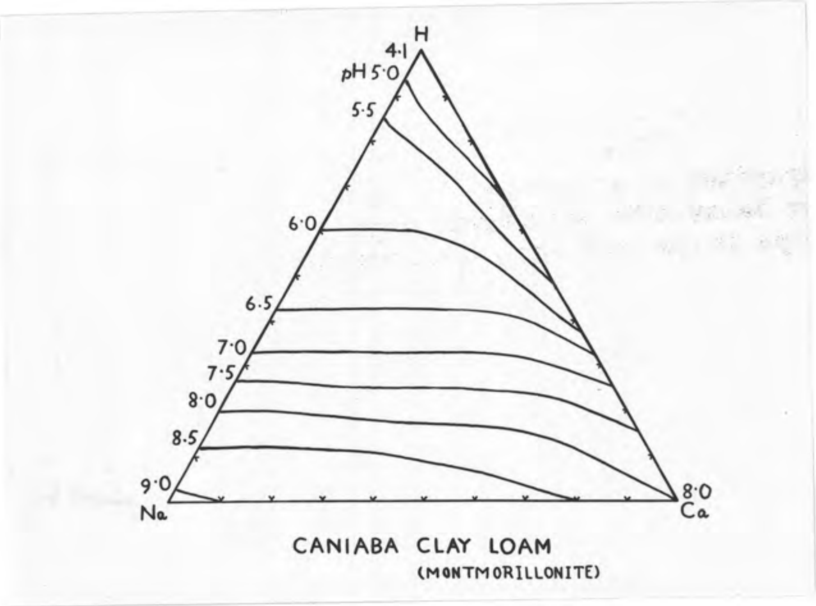


Figure 22.

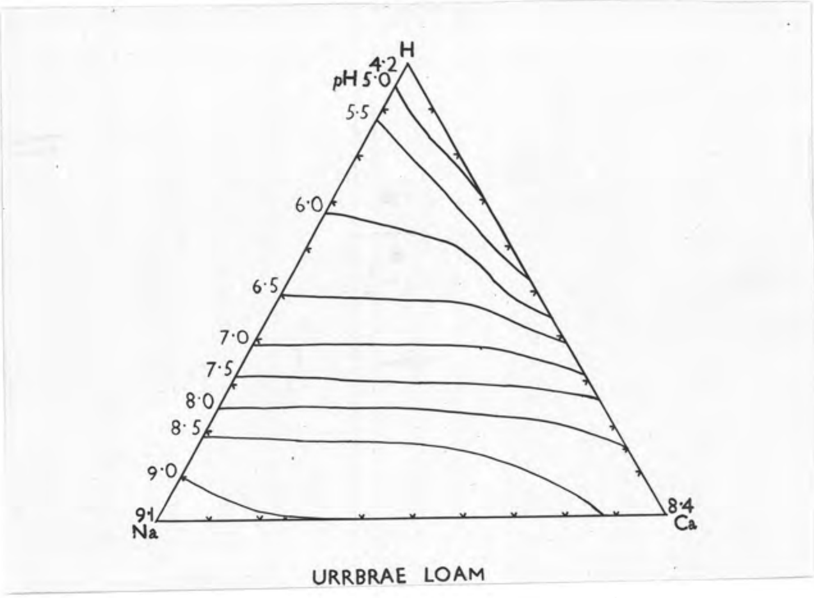


Figure 23.

Triangular graphs indicating the relationship between pH and percentage saturation with different mixtures of Na and Ca.

Note: According to Schofield (1949), H in the above diagrams could include Al.

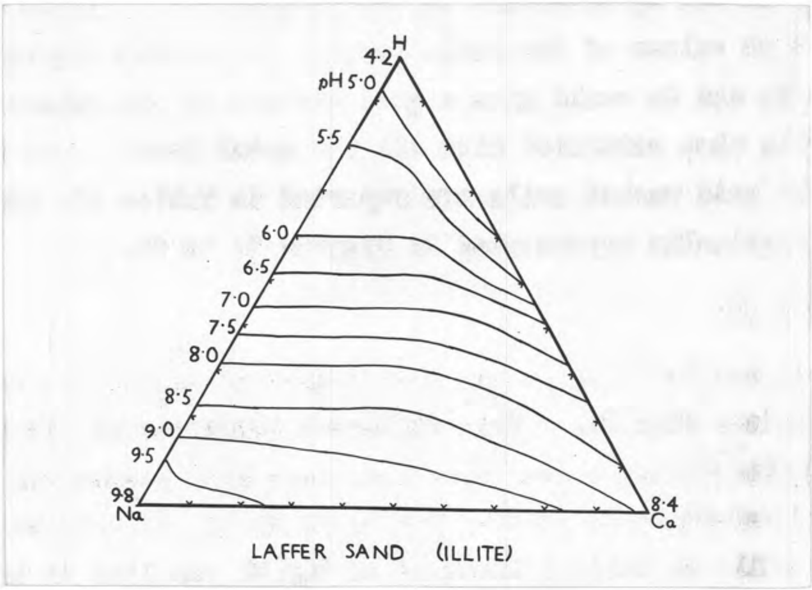


Figure 24.

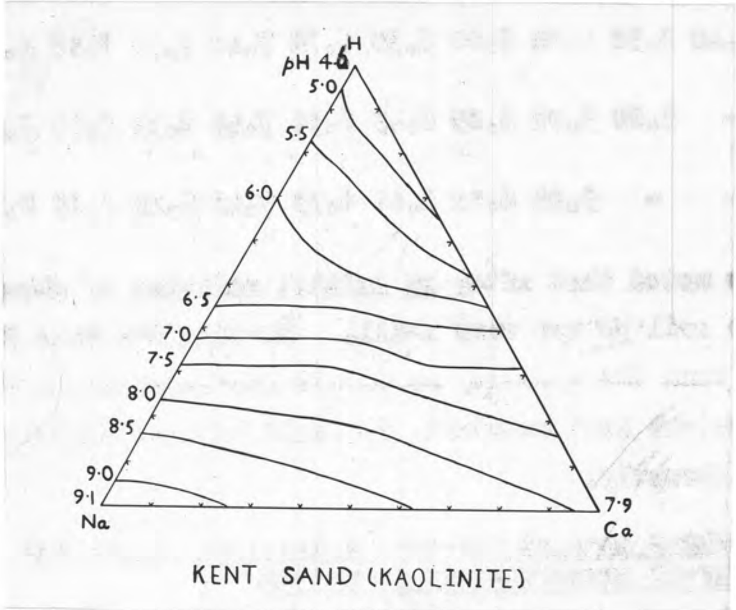


Figure 25.

Triangular graphs indicating the relationship between pH and percentage saturation with different mixtures of Na and Ca.

Note:- According to Schofield (1949) H in the above diagrams could include Al.

quantities; it was also shown that there was not much difference in the behaviour of Ca and Mg titration curves (Figure 13). Hence it was thought that pH values of the soils brought to various degrees of saturation with Na and Ca would give a good picture of the general behaviour of soils when saturated with all the metal ions. The data obtained with the acid washed soils are reported in Tables 48, 49, 50, 51 and 52 and graphically represented in Figures 21 to 25.

Influence on soil pH.

It was shown earlier that at the same degree of saturation Na gave higher pH values than Ca. This different behaviour of the two metal ions was quite definite even when they were both present in various proportions. If reference is made to Tables 48 to 52, it will be seen that in all the soils an initial increase of 10% Na resulted in high pH values as compared with soils at the same percentage saturation. As an example, the following data for Urrbrae Loam may be cited.

Percentage saturation.	pH values.										
	0	10	20	30	40	50	60	70	80	90	100
Ca only	4.16	4.60	4.85	4.98	5.20	5.55	6.42	7.10	7.80	8.18	8.40
10% Na and rest Ca	-	5.40	5.50	5.80	6.00	6.30	6.70	7.40	7.98	8.18	8.44
20% Na and rest Ca	-	-	5.80	5.92	6.05	6.43	6.90	7.40	8.33	8.60	8.80
30% Na and rest Ca	-	-	-	5.92	6.10	6.41	6.95	7.40	8.40	8.65	8.76

It will also be noted that after an initial addition of about 20% Na the change in the soil pH was very small. Viewing the data from another angle, i.e. when the quantity of Ca was increased while the percentage saturation was kept constant, it would be seen that the pH values did not fall abruptly.

pH values of Urrbrae Loam at the same percentage saturation points but different proportion of Na and Ca.

Percentage saturation.	0	10	20	30	40	50	60	70	80	90	100
Na only	4.16	5.40	5.80	5.92	6.20	6.45	6.86	7.60	8.35	9.00	9.30
10% Ca and rest Na	-	4.60	5.50	5.92	6.10	6.45	6.86	7.60	8.40	9.00	9.06
20% Ca and rest Na	-	-	4.85	5.80	6.05	6.41	6.90	7.54	8.42	8.80	9.01
30% Ca and rest Na	-	-	-	4.98	6.00	6.43	6.95	7.47	8.43	8.70	8.98
40% Ca and rest Na	-	-	-	-	5.20	6.31	6.90	7.40	8.41	8.68	8.95

It will be seen that an abrupt fall in the pH value occurred only when 10 to 20% of Na was left to the complex.

The behaviour of Na and Ca is quite evident from the nature of the curves shown in Figures 21 to 25. Starting from the Na line on the left hand side of the triangle, it can be seen that the pH lines from

TABLE 54.

pH VALUES OF SOILS AT VARIOUS DEGREES OF SATURATION WITH MIXTURES OF Na AND Ca.

CANIABA CLAY LOAM (E.D.)

Percentage saturation with $\frac{Ca}{Na}$	0	10	20	30	40	50	60	70	80	90	100
0	3.97	4.14	4.34	4.53	4.75	5.00	5.42	5.96	6.64	7.10	7.46
10	5.08	5.20	5.56	5.70	5.87	6.18	6.90	7.40	7.84	8.06	
20	5.28	5.72	5.80	6.00	6.30	6.96	7.52	7.90	8.18		
30	5.70	5.80	6.02	6.32	7.00	7.50	8.00	8.44			
40	5.82	6.00	6.30	7.03	7.52	8.00	8.60				
50	5.98	6.30	7.01	7.50	8.10	8.55					
60	6.30	7.00	7.50	8.10	8.55						
70	6.95	7.55	8.10	8.60							
80	7.53	8.10	8.60								
90	8.05	8.60									
100	8.60										

Note: Figures underlined were interpolated.

Exchange capacity at pH 8.4 was taken as 100% saturation.

TABLE 55.

pH VALUES OF SOILS AT VARIOUS DEGREES OF SATURATION WITH MIXTURES OF Na AND Ca.

URRBRAE LOAM (E.D.)

Percentage saturation with

Ca Na	0	10	20	30	40	50	60	70	80	90	100
0	3.90	3.97	4.18	4.37	4.63	4.87	5.48	6.27	6.89	7.32	7.56
10	4.96	5.20	5.34	5.50	5.76	6.22	6.70	7.26	7.77	8.17	
20	5.33	5.47	5.70	5.90	6.40	6.99	7.54	8.10	8.51		
30	5.54	5.87	6.00	6.43	7.10	7.60	8.15	8.60			
40	5.79	6.00	6.40	7.23	7.75	8.25	8.70				
50	6.02	6.40	7.29	7.80	8.35	8.82					
60	6.38	7.30	7.90	8.50	8.87						
70	7.28	8.00	8.50	9.00							
80	8.00	8.59	9.10								
90	8.64	9.10									
100	9.24										

Note: Figures underlined were interpolated.

Exchange capacity at pH 8.4 was taken as 100% saturation.

TABLE 56.

pH VALUES OF SOILS AT VARIOUS DEGREES OF SATURATION WITH MIXTURES OF Na AND Ca.

LAFFER SAND (E.D.)

Percentage saturation with

Ca / Na	0	10	20	30	40	50	60	70	80	90	100
0	3.95	4.21	4.39	4.84	5.05	5.74	6.46	7.20	7.56	8.05	8.18
10	5.00	$\underline{5.10}$	5.18	$\underline{5.60}$	6.00	6.67	$\underline{7.50}$	7.80	8.18	8.50	
20	5.32	5.52	$\underline{5.90}$	6.66	$\underline{7.10}$	7.62	8.26	$\underline{8.40}$	8.56		
30	5.60	5.92	6.51	7.16	$\underline{7.80}$	$\underline{8.30}$	8.62	8.89			
40	5.92	$\underline{6.50}$	$\underline{7.30}$	7.90	8.40	$\underline{8.80}$	9.06				
50	6.54	7.30	8.00	$\underline{8.60}$	8.94	9.23					
60	7.34	$\underline{8.00}$	8.60	$\underline{9.00}$	9.30						
70	7.97	8.60	9.16	9.46							
80	8.63	9.20	9.50								
90	9.26	9.62									
100	9.70										

Note: Figures underlined were interpolated.

Exchange capacity at pH 8.4 was taken as 100% saturation.

TABLE 57.

pH VALUES OF SOILS AT VARIOUS DEGREES OF SATURATION WITH MIXTURES OF Na AND Ca.

KENT SAND (E.D.)

Percentage saturation with

Ca Na	0	10	20	30	40	50	60	70	80	90	100
0	4.59	4.76	4.97	5.21	5.31	5.90	6.55	7.22	7.60	7.94	8.11
10	5.20	5.40	5.64	5.80	6.07	6.55	7.30	7.80	8.03	8.20	
20	5.60	5.90	6.00	6.32	6.80	7.50	8.00	8.20	8.42		
30	5.90	6.10	6.40	6.94	7.60	8.10	8.28	8.55			
40	6.10	6.40	6.90	7.76	8.20	8.42	8.72				
50	6.41	6.92	7.80	8.20	8.63	8.83					
60	6.90	7.80	8.20	8.70	9.00						
70	7.80	8.20	8.70	9.11							
80	8.24	8.70	9.10								
90	8.72	9.10									
100	9.10										

Note: Figures underlined were interpolated.

Exchange capacity at pH 8.4 was taken as 100% saturation.

pH 6.00 onwards ran almost parallel to the base until there was a sharp downward break when about 10 to 20% Na was left in the complex. In the top portion of the triangles the pH changes were very marked due to the fact that a change of 10% Na or Ca was relatively a big change since in that region the percentage saturation of the complex was only 30 to 40%.

TABLE 53.

Percentage metal ion saturation at the inflexion points of the curves obtained by titrations with mixtures of Na and Ca.

Soils	T.C.	C.C.L.	U.L.	L.S.	K.S.
Increasing Na and decreasing Ca.					
0% Na and rest Ca	85	75	70	70	70
10% Na and rest Ca	80	75	75	65	65
20% Na and rest Ca	80	75	75	70	65
30% Na and rest Ca	80	75	75	70	65
40% Na and rest Ca	80	80	75	70	70
Increasing Ca and decreasing Na.					
0% Ca and rest Na	85	75	75	70	70
10% Ca and rest Na	80	80	75	65	70
20% Ca and rest Na	80	80	75	70	70
30% Ca and rest Na	80	80	75	70	70
40% Ca and rest Na	80	80	75	65	70

It is evident from the above Table that irrespective of the proportions of Na and Ca used for titrations the inflexion in all cases occurred at the same percentage saturation within the experimental error. All the above curves also gave a clear indication of the presence of more than one type of neutralizable negative charge.

Though there were minor differences in the behaviour of various clay minerals, yet the differences were of such a small magnitude that it is not possible to put forward any general conclusion with regard to any relationship between clay minerals and the pH values at various degrees of saturation.

Similar studies were conducted with the electrodialysed soils and the data obtained are reported in Tables 54 to 57. Except that the electrodialysed soils had lower pH values at comparable points than those of acid washed soils (particularly in the case of montmorillonite), the general behaviour of sodium and calcium mixtures was the same. The triangular diagrams of the electrodialysed soils were exactly similar to those obtained with acid washed soils; hence they have not been reported.

SUMMARY AND CONCLUSIONS.

Five heavy clay subsoils, very low in organic matter and free from carbonates were subjected to electrodialysis to investigate the behaviour of clay minerals characterizing them. Each soil was characterized predominantly by one clay mineral. Two were montmorillonitic, two illitic and one kaolinitic in nature. The following conclusions were arrived at.

(1) The quantity of current required to electrodialyse the soil was closely associated with the nature of the clay mineral and the quantity of exchangeable metal ions. The quantity of current passing through different clay minerals was in the following order :

Montmorillonite > illite > kaolinite.

(2) The maximum current passed through the cell in the beginning of electrodialysis in all the soils; the quantity of current then fell off very sharply and after about 24 hours of electrodialysis it was almost constant.

(3) The temperature of the anode chamber was related to the type of clay mineral and the quantity of exchangeable metal ions. The temperature of the anode chamber was in the following order with respect to various clay minerals :

Montmorillonite > illite > kaolinite.

(4) The general tendency of the temperature curve was to rise gradually to a maximum between 8 to 12 hours of electrodialysis and then to fall off gradually as the electrodialysis progressed.

(5) The rate at which different ions were transported to the cathode chamber was in the following order :

Na > K > Ca > Mg > Fe and Al.

There was no difference in the behaviour of various clay minerals.

(6) In all the clay minerals all the metal ions (Ca, Mg, Na and K) were electrodialysed in a similar way, i.e. each metal ion appeared at maximum rate in the first hour of electrodialysis and the rate subsequently fell off very quickly.

(7) In all the clay minerals all the exchangeable calcium was electrodialysed in about 24 hours and sodium and potassium in 8-12 hours.

(8) In all the clay minerals -

(a) The quantity of calcium electrodialysed was the same(within the experimental error) as determined by NH_4Cl extraction.

(b) During fractional electrodialysis magnesium was incompletely electrodialysed. During continuous electrodialysis of soils variable quantities of magnesium were released, sometimes more and sometimes less than that obtained by NH_4Cl-extraction. The reason for this difference is not understood.

(c) More sodium and potassium were released by electrodialysis than by ammonium chloride extraction, thus indicating reserves of these ions not normally revealed by salt extraction.

(9) Relatively large quantities of iron and aluminium (expressed as Al) were mobilized from all the clay minerals during electrodialysis. The quantities of iron and aluminium mobilized from various clay minerals were in the following order :

Montmorillonite = illite > kaolinite.

(10) When the soils were subjected to prolonged electrodialysis the major portion of the exchangeable metal ions and iron and aluminium had been released in the first 96 hours; after that the rate of appearance of the metal ions and the release of iron and aluminium from the exchange complex was exceedingly small. Aluminium mobilized in the first 96 hours of electrodialysis was probably mainly present in the exchangeable form; subsequent slow but continuous release of aluminium was probably due to slow but progressive decomposition of the complex.

(11) Clogging of the porcelain cell with iron and aluminium hydroxide precipitates resulted in slower and incomplete electrodialysis.

(12) A regression equation to establish a relationship between the exchangeable metal ions obtained by the titration and the analysis of dialysate was worked out.

$$Y = 1.1568 + 0.9123\,'X'$$

where Y = exchangeable metal ions by analysis
and X = exchangeable metal ions by titration.

(13) The ultimate pH of various clay minerals followed the order :
Montmorillonite = illite < kaolinite.

(14) The ultimate pH depended on the method used for preparing the acid soil. Electrodialysed acid soils had lower pH values than those of acid soils prepared by leaching with 0.01 N HCl.

(15) The pH of the soil fell very rapidly during the first 4 hours of electrodialysis; after that it was almost constant. This was shown to be related to the percentage saturation of the complex. The pH fell very rapidly when the percentage saturation with metal ions was reduced from 90 to 60%. Below 60% saturation all the soils were highly buffered. All the clay minerals behaved alike.

(16) The five heavy clay subsoils used for electrodialysis studies were used to investigate the nature of the acidity and other related properties of various clay minerals. The acid soils were prepared by three methods:-

(a) By acid washing (0.01 N HCl).
(b) Electrodialysis of NH_4-soil (E.D. NH_4-soil).
(c) Electrodialysis (E.D.).

The acid soils obtained by the above three methods were titrated with hydroxides or oxides of Ca, Mg, Na, K and mixtures of Na and Ca to investigate the nature of soil acidity.

(17) It was shown that when the same quantity of hydrogen ions was used to remove the exchangeable metal ions from the complex 0.05 N and 0.01 N acids were equally effective. On the other hand, 0.05 N HCl removed more aluminium than that removed by 0.01 N HCl; hence the latter strength of the acid was used to prepare the acid soils by acid washing, with the idea of reducing possible lattice breakdown.

(18) The three methods adopted for the preparation of the acid soils released quantities of Al from the complex in the following order :

$$\text{E.D.} > \text{E.D. of } NH_4\text{-soil} > 0.01N\ HCl.$$

(19) A modified method of presentation of the titration curves was suggested. It was shown that the usual method of plotting the exchangeable metal ions (expressed as m.e. per 100 gm. soil) along the abscissa and pH along the ordinate emphasized the quantitative differences (which were already known from the variations in the cation exchange capacity) without bringing out the qualitative relationships. It was therefore suggested that in order to obtain titration curves, which are easily comparable, percentage saturation instead of the exchangeable metal ion content should be plotted along the abscissa.

(20) The pH values at similar degrees of saturation on the titration curves of acid soils prepared by different methods were in the following order :

$$\text{E.D.} < \text{E.D. of } NH_4\text{-soil} < 0.01\ N\ HCl.$$

The percentage saturation at the same pH value was therefore in the reverse order. The differences between the two methods of electrodialysis were small.

The above conclusions refer particularly to the montmorillonitic and the illitic soils. The kaolinitic soil was not differentially affected by various methods of preparing the acid soils.

The above differences in the acid soils prepared by various methods and from different clay minerals were attributed to the differences in the quantities of aluminium mobilized by each method or from each clay mineral.

It was suggested that a more uniform method of preparing the acid soils should be adopted by all workers to obtain comparable data.

(21) The pH values at the same degrees of saturation were in the following order for the metal ions used :

$$Na > K > Ca > Mg.$$

The differences between Ca and Mg were very small. These differences were ascribed to differences in the energy of absorption and the hydration values of different metal ions.

(22) The differential metal ion effects on soil pH value were evident even when mixtures of Na and Ca in various proportions were used to

titrate the soils.

(23) With different metal ions or various mixtures of Na and Ca the inflexion occurred at the same percentage saturation in the case of each soil.

(24) It was shown that when acid soils from Laffer Sand (illite) were dried in the presence of Na or K (present to the extent of 20% or more of the cation exchange capacity) they formed characteristic mica-like glassy, vertical rectangular flakes which may be of use to distinguish illitic soils from montmorillonitic or kaolinitic soils.

(25) A study of 40 titration curves of montmorillonitic, illitic and kaolinitic soils indicated that, irrespective of the method of preparation of the acid soil or the metal ion used for titrations, all the titration curves had almost the same shape and were highly buffered between 20 to 50% saturation. This buffering could be due to Al^{+++} ions (according to Schofield) or due to H^+ ions (as suggested by Bradfield).

(26) The titration curves with Na looked like those of weak monobasic acids while those of Ca and Mg looked like those of strong monobasic acids. These differences were explained in terms of variations in the energy of absorption of the metal ions.

(27) Although the titration curves had an apparent shape of monobasic acid curves, yet all the exchangeable positions as determined by the summation of the exchangeable metal ions obtained by the NH_4Cl extraction method and the exchangeable hydrogen obtained by the metanitrophenol method at pH 8.4 were not neutralized at the inflexion points; the inflexion occurred at 70 to 85% saturation. This was an indication that the exchangeable positions were present in two degrees of affinity. It was also shown that it is quite possible that the exchangeable positions neutralized at the inflexion point were mainly associated with "the permanent negative charge" as defined by Schofield and the remaining 15 to 30% charges were largely due to the "proton transfer", i.e. hydrogen dissociated from the Si-O-H groups at the crystal edges (1949).

(28) It could not be shown conclusively from the above studies whether the negative charges of acid soils were satisfied by H^+ or Al^{+++} or both. However, it was shown that the quantities of aluminium which could be removed by electrodialysis were definite and it was quite possible that the aluminium which was thus mobilized was largely exchangeable.

(29) The buffering power of the soils was shown to be influenced by :

(a) the exchange capacity of the soils. In relation to the exchange capacity (of the whole soil) various soils were buffered in the following order -

T.C. > C.C.L. > U.L. = L.S. > K.S.

(b) the clay content of the soils. When the buffer capacity was calculated on the clay content the soils were buffered in the order -

T.C. = C.C.L. > U.L. = L.S. > K.S.

(c) the metal ion used for titration in the following order -

Mg > Ca > K > Na.

The differences between Mg and Ca were very small.

(30) With respect to the clay mineral type, it was concluded that the buffering power was in the order -

Montmorillonite > illite > kaolinite.

It was also shown that the differences in the behaviour of clay minerals of the same group (e.g. illites in Urrbrae Loam and Laffer Sand) could be due to the extent of isomorphous replacements taking place in the lattice and the number of broken bonds near the edges.

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