CHAPTER V

EXCHANGEABLE CATIONS
(Ca, Mg, Na, K)
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"It is no wonder that cation exchange, next to photosynthesis, is said to be the most important chemical reaction in the whole domain of agriculture." - Marshall-1.

Agriculture is based, to a very important degree on clay and most important and characteristic property of clays is their base exchange capacity (B.E.C.), obviously B.E.C. of soils is most significant in agriculture. As the clay minerals are the dominant constituents of clays, B.E.C. of clays is attributed to these clay minerals. Chemical and physical processes, which are influenced by ion exchange, include weathering of minerals, nutrient absorption by plants, swelling, shrinkage and plasticity etc. and leaching of electrolytes. Ion exchange may, therefore, be considered as the most important of all the processes occurring in soil.

The following four important groups of clay minerals have been distinguished:-

(1) Montmorillonite
(11) Attapulgite
(111) Illite
(iv) Kaolinite

The base exchange capacity of these minerals is as follows:- 2.

<table>
<thead>
<tr>
<th>Clay Mineral</th>
<th>B.E.C. m.e./100 gms. of clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>60-100</td>
</tr>
<tr>
<td>Attapulgite</td>
<td>25-30</td>
</tr>
<tr>
<td>Illite</td>
<td>4-20</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>3-15</td>
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</table>
It has been shown that exchangeable bases are the integral constituents of the lattice. It is also seen that higher the atomic wt. of an ion the more firmly it will be held up by the exchanger.

Obviously the exchange reaction-ns should be in order:-

\[ \text{Li} \ll \text{Na} \ll \text{K} \ll \text{NH}_4 \ll \text{Rb} \ll \text{Cs} \quad (\text{alkalies}) \]

\[ \text{Mg} \ll \text{Ca} \ll \text{Sr} \ll \text{Ba} \quad (\text{alkaline earths}) \]

Thus Marshall and other workers report that in clay particles, having a high b.e.c, calcium would be more firmly held (relative to Na or K) than in clay particles with low b.e.c.

Clay particles are made up of complex negative radical (micelle) and a miscellany of adsorbed cations. The negative radical is made up of complex insoluble alumin and iron silicic acids. Where as \( \text{Ca}^2+, \text{Mg}^2+, \text{Na}^+, \text{K}^+ \), hydrogen and others form the positive radical.

\[ \text{Ca}^{++} \]

\[ \text{Mg}^{++} \]

\[ \text{K}^{+} \]

\[ \text{Na}^{+} \]

complex micelle formed of alumin and iron silicic acids carrying negative charges.

miscellany of cations

The cations are held firmly on the outside of the negative colloid, and only a small portion dissociates into the surrounding solution so forming an ionic atmosphere.

The significance of calcium and hydrogen of the formula are obvious since in a humid region these cations jointly dominate the complex. \( \text{Mg}^{++}, \text{K}^{+}, \text{Na}^{+} \) etc, which are comparatively in smaller amounts,
are usually present in the ionic outer layer. By the adsorption of Ca\(^{++}\), K\(^{+}\), or Mg\(^{++}\) micelle forms a salt like compound similar to CaSO\(_4\) or KNO\(_3\). In the same way, if the hydrogen ions are adsorbed, an acid results. Since a considerable amount of CO\(_2\) is evolved, as the organic matter decomposes, the presence of carbonic acid is inevitable in soil solution. The hydrogen ions thus produced are exceedingly active and will tend to replace exchangeable calcium—(being taken as representative) of colloidal complex, in a representative humid region mineral soil high in replaceable calcium under optimum conditions. The reaction may be expressed as follows:

\[
\text{Ca}^{++} + 2\text{H}^+ \rightleftharpoons \text{H}^+ \text{micelle} + \text{Ca}^{++}
\]

Taking a specific example where calcium, hydrogen and other metallic cations \(B\) are present in 40:40:20 ratio, the situation can be expressed as:

\[
\begin{align*}
\text{Ca}_{40} & \quad \text{micelle} + 5\text{H}_2\text{CO}_3 & \quad \text{Ca}_{38} & \quad \text{micelle} + 2 \text{Ca} (\text{HCO}_3)_2 \\
\text{H}_{40} & \quad \text{micelle} & \quad \text{H}_{45} & \quad \text{micelle} & \quad 6 (\text{HCO}_3) \\
\text{O}_{20} & \quad \text{micelle} & \quad \text{O}_{19} & \quad \text{micelle} & \quad \text{O}_{18}
\end{align*}
\]

\((B\ being\ monovalent)\)

If a soil, which is fairly high in calcium, is given a liberal dressing of KCl, assuming that potassium ions replace one hydrogen ion and two each of cations associated with the micelle, the change can be expressed as:

\[
\begin{align*}
\text{Ca}_{40} & \quad \text{micelle} + 7\text{KCl} & \quad \text{Ca}_{32} & \quad \text{micelle} + 2 \text{CaCl}_2 \\
\text{H}_{40} & \quad \text{micelle} & \quad \text{H}_{38} & \quad \text{micelle} & \quad 2 \text{KCl}
\end{align*}
\]

\((B\ being\ monovalent)\)
Thus potassium chloride encourages the loss of calcium in drainage.

The functions of cation exchange may be classified as under:

(i) The nutrients released by the cation exchange accumulate in the outer portion of the soil solution to be taken up by plants and micro-organisms or may be washed out.

(ii) In case of intimate contact between the root hairs and micro-organisms with the soil colloid surface, a direct exchange of cations may take place. In such cases hydrogen ions generated, generally, affect the change.

Factors affecting the exchange may include:

(i) proportion of the cation exchange capacity of soil
(ii) effect of ions held in association
(iii) effect of particular cation on the exchange and its mass-action effect influence upon the rate of displacement.
(iv) difference in the tenacity of holding specific ions by the colloidal micelle.

In soils the most common exchangeable cations are Ca⁺⁺, Mg⁺⁺, H⁺, K⁺, Na⁺ and NH₄⁺; calcium and hydrogen being dominant ions. The capacity of soils to adsorb and exchange cations, chiefly, depends upon:

(i) contents of clay
(ii) organic matter
(iii) mineralogical composition

The relative effect of cationic concentration on one another has been studied by several workers. They conclude that increase in one particular cation in soil affects the uptake of other and thereby influences their concentrations in in plant. Thus potassium concentration is likely to cause Mg-deficiency, large lime dressings
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may cause Mg and K deficiencies. Increasing magnesium may depress calcium.

Several workers have studied the nutritive values of these ions (Ca\textsuperscript{++}, Mg\textsuperscript{++}, K\textsuperscript{+}, Na\textsuperscript{+}).

According to an early hypothesis calcium was required to prevent the concentration of oxalic acid in plants but it is rather doubtful if there existed any danger of oxalic acid toxicity. Calcium as a dehydrating ion influences the water economy and thereby counteracts the hydration of potassium and possibly sodium. Calcium is important in tip-extension and bud formation. Besides several other uses, role of calcium is significant in the formation of middle lamella. Wilson & Staker report that in spite of the high calcium content many peat soils are acid. The possible reason being dissolution of lime and large amount of the exchangeable calcium content (in peat horizons). Loss of exchangeable calcium by leaching causes increase in the acidity of the soil. There is, thus, a definite correlation between the soil pH and its calcium content, both in humid as well as arid regions. According to Truog & the presence of sufficient adsorbed sodium may affect this relationship in arid regions. Lime can affect the soil physically, chemically and biologically. In heavy soils deficiency of lime adversely affects the aeration of water movement. Lime dressing in such arid soil raises the crumb structure. Amongst the chemical effects of lime, the following may be included:

(i) decrease in hydrogen ion concentration
(ii) increase in hydroxyl ions
(iii) decrease in solubility of Fe, Al and Mn.
(iv) increase in phosphate availability
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(v) increase in exchangeable calcium
(vi) decrease in availability of potassium

(Ca and Mg are also essential in the nutrition of soil micro-organisms/

The activity of the organic matter and nitrogen of the soil is
favourably affected by lime which may be due to the stimulating effect
of lime on microbial flora (specially heterotrophic type). There are
plants which thrive most in excess of lime (alfalfa, cauliflower etc).
others growing in moderate acid conditions respond favourably to
lime dressing. There are some which grow much better in soils with
low exchangeable calcium or exchangeable magnesium (e.g. cranberries).
The reasons for lime responses are obvious. These may be summed as
follows:

(i) direct nutritive or regulatory action.
(ii) removal or neutralisation of toxic compounds both
organic and inorganic.
(iii) retardation of plant disease.
(iv) increase in the availability of plant nutrients.
(v) encouragement of microbial activity favourable
to nutrition.

Many workers have noticed that over liming adversely affects the
plant growth. Thus over liming may cause deficiency of iron, mangan-
ese, copper and zinc. Drastic changes in soil pH may not be favourable
to the plant growing in the soil. Some times complex calcium
phosphates are formed thereby reducing the availability of phosphates.

McMurtry has reported on the recognition of magnesium as
an important constituent of fertilizer for a long time. Magnesium
is a component of chlorophyll and thus important in photosynthesis.
It is helpful in transport of phosphates. Probability of its

114
playing some role in enzymatic reactions is also not bleak. Plants take up magnesium from the soil solution which is in equilibrium with exchangeable magnesium. Most of the total soil magnesium is not exchangeable, but the presence of non-exchangeable form is important which might be helpful in replacing exchangeable magnesium lost in leaching or removed by crops. According to Othaus and other workers, the decomposition of illitic clays varies with acidity and temperature; and release of magnesium depends on the nature, composition and particle size of the minerals. According to McMurtry, magnesium deficiency is rather more prevalent in deep sandy soils and excess of rainfall accelerates such deficiency. Gamman had found some correlation between magnesium and organic matter in sandy soils.

Role of potassium is possible in almost all the physical and biochemical processes in plants. It is related to the process of photosynthesis and starch formation or digestion. According to Richards & others, potassium, although not essential to protein synthesis, is necessary to maintain the protoplasmic complex. Anderson and co-workers believed that potash functioned in all plants as a catalyst in the synthesis of carbohydrates and possibly proteins. Agronomists have known for some time that adequate potash is necessary for the maintenance of legume stands on soils with low available levels of potassium. Jackson and co-workers have observed that there is a continual need for potassium as a top dressing on established forage stands to maintain high proportion of legume to grass. It is a well known fact that potash may be adsorbed by the clay minerals in a difficultly exchangeable state. The occurrence of the potassium fixation has been demonstrated and it has been, generally,
observed that when heavy doses of potash fertilizers are given to the soils potassium fixation is noticed in certain soils but not in others. Volk-19 attributed this fixation to the development of mica. Potassium fixation in hydrated, and moist soils (without drying) has been studied by many workers-20. From these studies it can be concluded that two distinct type of inorganic fixation of potassium take place, one brought about by drying and other taking place in continuously moist conditions. Replacement of potassium by other cations has been studied by William and Jenny-21. According to them all cations except ammonium can replace non-exchangeable potassium and the order of replacement would be \( H > Na > Ca > Mg \). There is a possibility of transference of non-exchangeable potassium into soil solution (by exchange process) and probably non-exchangeable potassium is not directly absorbed out of the soil particles by plant roots. According to Reitemeir-22 potassium fertilizer residues increase both readily exchangeable and also potentially useful (but non-exchangeable) potassium reserves in many soils. The quantity of non-exchangeable or 'fixed' potassium in some soils is quite large. The fixed potassium in such soils is continually released to the exchangeable form in such amounts large enough to be of great practical importance-23.

Competition for the available potassium between the plant\'s species has been reported by Blaser and others-24,25. According to Jenny and Shade-26 several factors may affect this competition and availability of potassium including the possible competition for potassium in micro-organisms, which might reduce, at least temporarily, the availability of potassium to plants.

Although the exact nature of potassium fixation or its release
are not very clear, it is known for definite that there are factors like, i-

(i) nature of the soil colloids,
(ii) wetting and drying,
(iii) freezing and thawing and
(iv) amount of lime present, which markedly influence the phenomenon.

Deficiency of potassium may retard such metabolism for which it is essential. Potassium deficiency may also cause winter killing of grain, yellow and narrow leaves -27.

Recent work-28 has shown that growth of beets and some vegetable crops is increased by the application of sodium chloride or sodium sulphate. Different crops respond differently to exchangeable sodium. Thus Bernstein and Pearson-29 observed that tolerance to exchangeable sodium with different plants is in order beets> alfalfa> clover> beans. Puri and Uppal-30, on the formation of Na-soil, report that sodium carbonate reacts almost quantitatively with the Ca-soil and precipitates whole of the exchangeable calcium as CaCO3. High exchangeable sodium content may adversely affect water penetration, aeration or physical resistance to root growth. It may cause sodium toxicity and Ca or Mg deficiency. Rather-31 had observed calcium deficiency associated with high levels of sodium.

Supplementing of potassium with sodium has often been suggested. Brown-32 had observed that when lower amounts of potassium were supplemented with sodium the adsorption of potassium was not appreciably influenced when sodium chloride was added. On the other hand comparatively much less amount of sodium was found in alfalfa than potassium. That, effect of sodium may be of indirect nature in
increasing the efficiency or economy of potassium has been suggested by different workers. 33

Sodium or potassium treatments may affect calcium or magnesium or both. Brown 34 had observed that when NaCl or KCl treatments were given the Ca-content was not much influenced but Mg-content in forage decreased with increased NaCl or KCl fertilization. Perkin & Stelly 35 had found that application of potassium or sodium, or mixture of both, reduced the percentage of calcium and magnesium in oats. The same treatment failed to affect any changes in the percentages of calcium and magnesium in crimson clover, with the exception of percentage of magnesium which was reduced significantly by potassium. Brown Bower and Wadleigh 36 have noted that accumulation of calcium and magnesium by roots and tops of various species of plants tended to decrease, and that of sodium to increase as soil was subjected to increasing degree of sodium saturation. Thorne 37 had observed that potassium or sodium contents of plants increased and calcium content decreased with increasing proportion of exchangeable potassium or sodium in soils. It has also been reported by several workers 38, 39 that when ammonium salts are added to the soil it results in marked reduction of exchangeable calcium and also corresponding increase in the soil acidity in absence of free calcium carbonate.

Several workers thought it possible that slat also played some part in ion-exchange. Joffe and Kunin 41 found that slat fractions separated from soil profiles exhibited a cation exchange capacity. Karim and Islam 42 have also observed that slat exhibits ion-exchange capacity. Base exchange is not, as was assumed for long time, limited to inorganic cations, organic cations can be introduced just as well, if they are hydrophyllic 43;
Experimental

Methods, as described in the chapter II., pp. 34, were followed for the determination of E-Ca, E-Na, E-K and E-Mg for the various soil samples in every month.
RESULTS AND DISCUSSION

Experimental results on the exchangeable cations in case of various soil samples containing inorganic fertilizers (NH₄NO₃ and NH₄Cl) alone or in combination with organic matter (neemleaf and cowdung) show that there is not any remarkable difference of the added substances on the b.e.c. of the soil. It is observed that ammon for the first 30 days calcium and potassium show an increase in their exchangeability followed by more or less a regular decrease during rest of the period of exposure. On the otherhand sodium and magnesium show an increase in their exchangeability throughout the period of exposure. Almost similar trend of changes is exhibited in all the soil samples. Although there is a slight increase in or decrease in exchangeability of cations with increased doses of fertilizers, the difference is not significant. Added organic matter with fertilizers do not affect appreciable changes in the b.e.c. of this soil, and the exchange values are not very much different from those obtained with fertilizers alone.

Rewa soil contains exchangeable bases in moderate quantities. Free calcium carbonate is present and the soil is towards alkalinity. Of the exchangeable bases, calcium is present in dominant quantity, thereby, showing that it is a Ca-soil. Addition of ammonium fertilizers, ammonium nitrate and ammonium chloride, alone or with neemleaf and cowdung influence the bases. As has already been mentioned that for the first month an increase in calcium and potassium is observed followed by, more or less, a regular decrease in later stages. Magnesium and sodium show a regular increase which
which is connected, more or less, with increase and decrease in soil pH. The results are in accordance with the work of Ahmad and Rahman-44. Similar results have been obtained by Awasthi-45 and other workers at Saugar University, India.

As has already been mentioned (pp-118) that when ammonium salts are added to the soil marked reduction in exchangeable calcium and increase in acidity of soil are noticed provide free calcium carbonate is not present.

\[
\text{Ammonium salt} + \text{Ca-soil} \rightarrow \text{Ca}^{\text{++}} + \text{ammonium soil}
\]

\[
\text{Ammonium soil} \xrightarrow{\text{O}_2} \text{Nitrite} \rightarrow \text{Nitrate}
\]

\[
\text{Nitrate} + \text{Ca} \rightarrow \text{Calcium nitrate}\left\{ \begin{array}{c}
2\text{NO}_3^- + \text{Ca}^{\text{++}} \rightarrow \text{Ca(NO}_3\text{)}_2 \\
\end{array}\right\}
\]

If \(X\) represents the exchangeable and \(\text{NH}_4\) \(Y\) denotes the anion part of the ammonium salt, the situation can be expressed as follows:

\[
\text{Ca}X + (\text{NH}_4)Y \rightarrow \text{CaY} + (\text{NH}_4)X
\]

When nitrification takes place the situation becomes:

\[
2\text{NH}_4X + 4\text{O}_2 \rightarrow 2\text{HNO}_3 + 2\text{H}X + 2\text{H}_2\text{O}
\]

\[
2\text{HNO}_3 + \text{Ca}X \rightarrow \text{Ca(NO}_3\text{)}_2 + 2\text{H}X
\]

Nitrification results nitrate ions which are neutralised by calcium. Now, if the nitrate is taken up by plant, the calcium ions thus freed may re-enter the exchange complex. There is other side of the picture as well; thus if nitrate ions are leached out an equivalent amount of calcium would be lost. So long as the soil contains free \(\text{CaCO}_3\) the loss falls on this substance and not on the exchangeable calcium-46. This might be a possible reason as to why decrease in calcium observed in these results is not very marked, which is due to the presence of free calcium carbonate in the soil.
Addition of neemleaf and cowdung follow the general trend i.e. increase in calcium and potassium for the first month is observed followed by a decrease. On the otherhand increase in sodium and magnesium is observed. This may be, to some extent, due to the action of organic acids formed during the decomposition of the organic matter, on exchange complex. Slight increase in the exchange activity (both ways), when heavier doses of fertilizers are applied, may be attributed, besides other factors, to the changes in soil reactions. Specific changes in base exchange reactions may also be attributed to the specific property of soil.

CONCLUSIONS

1. Rewa soil contains exchangeable bases in moderate amounts.
2. Amongst the four cations determined the calcium is in dominant amount.
3. Addition of inorganic fertilizers (NH₄NO₃ and NH₄Cl) and organic matter (neemleaf and cowdung), alone or in combination, show an increase in Ca and K for the first 30-days and then decrease. Sodium and magnesium increase through-out the period of exposure.
4. Ammonium nitrate and ammonium chloride have an increasing influence on the exchangeable cations.
5. Addition of organic matter (neemleaf and cowdung) does not bring any appreciable change in the exchange reactions.