CHAPTER IV.

General Discussions

(A). Fixation of potassium in soils, soil colloids, clay minerals and primary minerals.

Investigations on potassium fixation in soils, soil colloids, clay minerals and primary minerals of Indian origin are very limited and scanty and are much inadequate to draw any definite conclusions from the data available. The soil samples and minerals of the present study originated from ten localities in five states of the Indian Union.

Out of 13 soils, eleven of them contained K\textsubscript{2}O above 1.7 and only two were below this value. Guntur black cotton soil recorded the highest potash content giving 3.02 per cent K\textsubscript{2}O (vide Appendix Table 69). Distribution of K\textsubscript{2}O in the whole and fractions of the 13 soil samples was as follows:

<table>
<thead>
<tr>
<th>Clay %</th>
<th>Silt %</th>
<th>Sand %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole %</td>
<td>Fanning from</td>
<td></td>
</tr>
<tr>
<td>1.40 to 3.02</td>
<td>2.02 to 3.98</td>
<td>1.40 to 3.60</td>
</tr>
</tbody>
</table>

(vide Appendix Tables 70 and 71)

Percentage potassium distribution amongst minerals analysed by the author, is as follows:

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Whole</th>
<th>Clay Fraction Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muscovite, Bihar</td>
<td>9.5</td>
<td>9.1</td>
</tr>
<tr>
<td>Biotite, Mysore</td>
<td>9.1</td>
<td>8.5</td>
</tr>
<tr>
<td>Illite, U.S.A.</td>
<td>7.1</td>
<td>6.7</td>
</tr>
<tr>
<td>-do- Shale, U.S.A</td>
<td>3.55</td>
<td>3.55</td>
</tr>
<tr>
<td>-do- Underlay U.S. A</td>
<td>4.15</td>
<td>4.15</td>
</tr>
<tr>
<td>Mineral</td>
<td>Whole</td>
<td>Clay Fraction</td>
</tr>
<tr>
<td>------------------------</td>
<td>-------</td>
<td>---------------</td>
</tr>
<tr>
<td>Bentonite, Jhelum</td>
<td>0.28</td>
<td>0.31</td>
</tr>
<tr>
<td>-do- Kashmir</td>
<td>0.32</td>
<td>0.40</td>
</tr>
<tr>
<td>-do- U.S.A.</td>
<td>0.41</td>
<td>0.50</td>
</tr>
<tr>
<td>Vermiculite, Bihar</td>
<td>0.30</td>
<td>0.40</td>
</tr>
<tr>
<td>Kaolin, U.P. (May and Baker)</td>
<td>0.41</td>
<td>0.23</td>
</tr>
<tr>
<td>Kaolin, Bihar</td>
<td>0.61</td>
<td>0.45</td>
</tr>
<tr>
<td>Fauconite, U.S.A.</td>
<td>0.58</td>
<td>0.38</td>
</tr>
<tr>
<td>Halloysite, U.S.A.</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Attapulgite, U.S.A.</td>
<td>0.81</td>
<td>0.81</td>
</tr>
<tr>
<td>Diaspore, U.S.A.</td>
<td>0.26</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Exchangeable potassium in the 13 soils ranged between 0.15 m.e to 0.53 m.e./100 (vide Table 73 - Appendix).

Hydrochloric acid soluble K₂O in soils ranged between 0.23 to 0.483 per cent. Hydrochloric acid soluble potash extracted from minerals were high in case of muscovite, biotite and illite (vide Table 74 - Appendix).

Top soil samples of the 13 soils showed, positive potassium fixation both in wet and dry conditions (vide Tables 10 - 20, 22 and 27).

Mica minerals showed also positive potassium fixation capacity which is high (vide Table 21).

According to this study potassium fixation is dependent upon the following factors:—

1. **Soil reaction, pH**.

Potassium fixation takes place between pH 4.5 to 10.1. Fixation of potassium increases with increase in pH in the wet condition. Fixation is lowest at 4.5 (vide Table 23).
II. Wet and drying conditions:

Soil, soil colloids and clay minerals of 2:1 layer silicate types show greater amount of fixation in dry condition as compared to wet condition (vide Tables 10 to 20). Illite and other miscellaneous minerals fix potassium in wet condition. Montmorillonite and kaolinite show no fixation in wet condition (vide Tables 17 to 22).

III. Equilibrium time:

Potassium fixation equilibrium with exchangeable form reaches to optimum value very quickly and the maximum fixation value reaches in three days time (vide Table 22).

IV. Concentration:

Potassium fixation increases with the increase of K ion in the solution and also on the saturation percentage of K ion on the exchange complex. Colloids fix large quantities of K₂O under high K concentration and in drying condition (Graph II, p.98). Three symmetry concentrations fix largest amount of potassium (vide Tables 10 to 20).

V. Size of particles:

Nature of clay remaining the same potassium fixation increased with the increase of base exchange capacity. In other words, particles of very fine sizes fix potassium in large quantities (vide Tables 17 to 22).

Potassium fixation is greatest in the clay fractions of the soil (vide Tables 20 and 21).

VI. Types of clay minerals:

Different types of clays fix different amounts of potassium in them (vide tables 20 and 21). Kaolinite, halloysite and attapulgite do not show fixation.

Although halloysite and attapulgite have base exchange
illite and
capacity more than 20 m.e./100, very near to native/biotite and
latter show positive fixation and in the former the fixation
is absent. Hence it is evident that mud clays possess certain
charges for fixation of potash. Vermiculite, montmorillonite,
illite, biotite and muscovite indicate positive fixation of
potassium in them and show high fixation capacities. Percentage
of potassium fixation when compared to base exchange capacity is
different for each of the clay minerals (vide Tables 19 and 20).
VII). Base exchange capacity:

Results shown in Tables 17 to 25 indicate that K-fixation
runs almost parallel to the base exchange capacity. The
quantity of K₂O fixed is largest in clays with high base exchange
capacity.

VIII). Associating cations: During the study of the influence
of an associating cation on fixation capacity of a clay mineral,
two series of observations relating to two types of clays were
made. First kind of observations were related to montmorillonitic
clays in which fixation was influenced by cations in the decreasing
order of fixation in the series:

\[ K > Na > Ca > H > Mg > NH₄ \]

The second type of observations were related to the
illitic clays, in which fixation was influenced by cations in the
decreasing order of fixation in the series:

\[ K > Ca > H > Na > NH₄ > Mg \]

(Vide Tables 31 and 32).

Calcium ion influences both fixation and release of
potassium, (vide Tables 33, 47-50 and 61.
IX). Percentage of relative humidity:

It was observed that potassium fixation had occurred in
micaceous minerals even at a high relative humidity say as high
as 37 per cent (vide Table 30). This is of significance as the relative humidity of the atmosphere seldom reaches this value during the year.

3). Influence of dehydrating organic liquids

More contact of potassium saturated colloids with dehydrating organic liquids did not cause potassium fixation (vide Table 29) but drying after washing potassium saturated clays with the organic liquids enhanced fixation (vide Table 28) and facilitated redispersion of clays in water.

XI). Liming - addition of lime to a soil or soil colloid suspension

Addition of lime to a soil or soil colloid suspension increased pH of the suspension and also replaced potassium from the complex and so increased its concentration in the solution phase. On giving potassium fixation treatment to the colloid, potassium was fixed in greater amount (vide Table 34).

Under the section of associating cations it was observed that Ca ion influenced potassium to become fixed. In the presence of Ca++, K+ is oriented in preference to Ca to enter itself to region of base exchange charge and thus get itself fixed (Table 33).

Properties of clays which were changed as a result of potassium fixation

1). The first question arises - "Was the silicate structure of clays unstable before the potassium fixation had taken place"? X-ray studies by Bradley (40), Wear and White (323) and several others have definitely established that primary and clay minerals are stable crystalline compounds. Analysis of the silicates after potassium fixation indicated that SiO₂ percent and Al₂O₃ percent were identical under both conditions, that
It was observed that a potassium saturated clay on drying from benzene gave a contracted (001) spacing while calcium saturated clay was relatively expanded. Hence lattice can be contracted by potassium fixation and it could be expanded by saturating the same exchange complex with Ca ions. Effect of movement of plates were studied. It was noted that only 10 to 20 per cent of the fixed potassium could be released by the movement of lattice layer and the remaining 80 to 90 per cent fixed potassium remained non-exchangeable in the clay (vide Table 38). Composition of the clays during these reactions remained constant (vide Table 63). Hence structure of the silicate is quite stable.

3). The second property which was changed as a result of potassium fixation was that of base exchange capacity. Invariably base exchange capacity was decreased as a result of potassium fixation (vide Tables 10 to 24).

In case of minerals like montmorillonite, vermiculite, illite and micas the potassium fixation capacity measured from the decrease in base exchange capacity caused as a result of potassium fixation was equivalent to the amount of potassium fixed in 100 gms. of clay. This equivalence was absent when base exchange capacity was less than 20 m.e. (vide Tables 10 to 25). It was also observed that the per cent of the decrease in the base exchange capacity over the original base exchange capacity of a clay could be used as a good index for its identification. This equivalence was absent, firstly in clays having b.e.e. less than 20 m.e./100 and those clays where fixed already K was in appreciable amount. The present investigation supports the findings of Truong and Jones (290).
4). The changes in the ratios of the competing cations:

From previous paragraph it is noted that 2:1 layer silicate vary in the per cent decrease of the original base exchange capacities as a result of potassium fixation in them. Hence it suggests that there might be a specific type of charge which is responsible for fixing potassium. If this hypothesis is true then one will find the absorption ratios of two competing cations before and after potassium fixation to be different. As a result of this study, absorption ratios between Ba and Ca and K and Ca are found to be different before and after the potassium fixation in these clays. Ratios Ba/Ca and K/Ca are lowered in clays in which fixation had occurred (vide Tables 39 and 40). The ratio is between smaller hydrated ionic radius cation and that of larger hydrated ionic radius cation. Hence it can be concluded from the results that cation of smaller hydrated ionic radius was absorbed in greater quantity as compared to the other larger hydrated cation. After studying the effect of concentration of the solution with respect to both cation ions, the conclusion remains the same as said previously (vide Tables 42 and 43).

5). Altering the water contents of the crystal: It was noted that there was always a loss of water of hydration from the silicate as a result of potassium fixation (vide Table 44). It was thought that if dehydration would occur as a result of potassium fixation then properties related to water holding by the clays would also change. In support of this hypothesis Atterberg's plastic limit values and ethylene retention values were found to be affected. They decreased after potassium fixation which means potassium ion is difficult to hydrate when it has once entered the layer lattice (vide Tables 44, 45 and 46). The decrease in Atterberg's limit constants and ethylene glycol
Retention values as a result of potassium fixation can be explained due to two causes. Firstly, surface area of a silicate colloid may be decreased as a result of this fixation or secondly electric charges on the colloid present as a result of isomorphous replacement of Si<sup>+++</sup> by Al<sup>+++</sup> were neutralised by the K ion on fixation.

b) Inhibition of K-fixation in presence of big cation: 

Fare and Paver (243) in 1939 showed that a big cation, if saturated on exchange complex, would inhibit fixation in silicates. White (325) and Wear and White (323) in 1951 reported from X-ray studies of the clays that the lattice plates were drawn together after the potassium fixation treatment. It was thought perhaps drawing together of the lattice plate during the potassium fixation probably aids in fixing potassium. Fixation of potassium occurred in presence of large organic radical (vide Table 37) showing that drawing together of lattice plate is not essential for potassium fixation. The present investigation did not find total inhibition in K-fixation in presence of big cation on the complex. In presence of diethylamine cation, K<sup>+</sup> is preferentially absorbed by those charges which are capable of K-fixation. On drying diethylamine was either distorted or decomposed.

(R) Release of fixed and native potassium:

Previous investigations on release of potassium from Indian soils and minerals are very meagre. For a very long time it was believed that Indian soils had high potassium supplying powers and hence there was no need of adding any potassic fertilizer to them.

In order to obtain adequate data on the release of potassium
from soils and their fractions under certain specified conditions, this investigation was undertaken. The whole investigation was divided under two subdivisions:

(1). Physical methods of potassium release:

   (i). Air and oven drying: It was observed that drying in air and in oven at 105°C of soils liberated potassium from them (vide Table 47, 48 and 49).

   (ii). Freezing and thawing: Calcium saturated clays suspensions were frozen and melted. After twelve cycles of freezing and thawing, the samples were found to have released potassium from the clays (vide Table 51).

   (iii). Moist storage: Soils and their fractions saturated with cations other than potassium, release potassium on keeping them moist for several months (vide Table 50).

   Results shown in Tables 47, 48, 49, 50 and 51 indicate that fixed potassium can be mobilised by physical conditions cited above. It is further noted that illitic material, release potassium in large amounts than the montmorillonitic materials.

   Potassium supplying powers of minerals is in the order of biotite > illite > muscovite. The potassium supplying power of soils and their fractions is of the following order:

   Bihar, Black soil > Delhi, TC > Delhi M4
   Karnal > Delhi, R > Palampur > Srinagar
   Sirsa, Heavy > Sirsa, light > Madras, lateritic
   Bihar, Lateritic > Fusa 2 > Fusa 1
   (vide Tables 56 and 57).

   Potassium was artificially fixed in certain clays and then the clays were treated with 3/20 solutions of various cations and the release of potassium obtained after shaking for 108 hours
was found as below:

Montmorillonite

\[ \text{Cu}^{++} > \text{Ca}^{++} > \text{H}^+ > \text{Mg}^{++} > \text{Mn}^{++} > \text{Na}^+ > \text{Ba}^{++} > \text{Fe}^{+++} > \text{NH}_4^+ > \text{Li}^+ \]

\[ \text{as NO}_3^- \]

Ililitc

\[ \text{Cu}^{++} > \text{Ca}^{++} > \text{H}^+ > \text{Na}^+ > \text{Mg}^{++} > \text{Mn}^{++} > \text{Fe}^{+++} > \text{Ba}^{++} > \text{Li}^+ \]

\[ \text{as NO}_3^- \]

It is also noted that \( \text{NaNO}_3 \) and \( \text{Ca(NO}_3^-)_2 \) are more effective in liberation of potassium than their chlorides (vide Tables 58 and 53-a).

The results shown in Tables 56, 57, 58, indicate that potassium is released more by boiling \( \text{N HNO}_3 \) from illitic soils than from those soils poor in that mineral. It is also clear that cations play a good role in liberating potassium from soils and clay minerals.

As a result of the release of fixed potassium it is noted that initial properties relating to base exchange were returned to the original values (vide Table 60 and 64).

Digestion of biotite with \( \text{HgCl}_2 \) solution several times on water bath liberates about 80.9 m.e. of \( \text{K}_2\text{O} \) and the resultant mineral has all the characteristic and also composition of vermiculite (vide Table 64).

(2). Liberation of fixed potassium by chemical methods:

Under this heading, influences of cations in the liberation of fixed potassium by leaching, extraction and digestion procedures were examined. The cations employed were \( \text{H}_2\text{O}^+, \text{Li}^+, \text{Na}^+, \text{Ca}^{++}, \text{Fe}^{+++}, \text{Mg}^{++}, \text{Mn}^{++}, \text{Cu}^{++} \) and \( \text{Fe}^{+++} \). Their solutions employed were either neutral or acidic.

Acid solutions of \( \text{N/10 HCl} \), acetic acid and saturated solution of \( \text{CO}_2 \) liberated \( \text{K}_2\text{O} \) in the order of \( 0.1 \text{ N HCl} > 0.1 \text{ N acetic acid} > \text{H}_2\text{CO}_3 \) by leaching procedure (vide Table 53).
Extraction method also removed potassium by the similar types of solutions in the same order but in greater magnitude (vide Table 54). Same order was observed under release of fixed potassium by N/10 acids (vide Table 55). Extraction procedure is more effective in securing release of potassium than leaching method. The present investigation agrees with the findings of Beitamur et al (256) in 1951.

Results of Beitamur et al (256) and House and Bertramson (262) showed that extraction of potassium from soils, their fractions and minerals by digestion with boiling N HNO₃ for ten minutes, indicated good correlation with the uptake of potassium by Italian clover in 740 days. According to them, correlation coefficient was 0.938. Boiling N HNO₃ for exactly 10 minutes is sensitive to time but insensitive to dilution. Ratio of acid to soil was 10:1. The present work in relation to release of potassium from soils, soil fractions and minerals by boiling normal solutions of mineral acids like HCl, H₂SO₄, HNO₃ and 5 N HNO₃, showed the order of release of potassium to be 5 N HNO₃ > N H₂SO₄ > N HCl > N HNO₃. Liberation of potassium by N HNO₃ using extraction method at room temperature gave lower values than obtained by boiling for 10 minutes (vide Table 56). Hence boiling N HNO₃ for 10 minutes method was adopted to record potassium supplying powers of soils.

Potassium release is largest from the clay fractions and decreased with the increase of size of particles (Table 57). This is in the same order as was found in fixation of potassium namely, fixation was greatest in fine fractions and it decreased as the size of the fractions increased (vide Table 24).

The present investigation agrees with the findings of
Fama Murthy, et al (251) in 1952 that soils containing illitic and montmorillonitic minerals in which potassium fixation had occurred would release potassium in large amounts. The present work confirms that soils classified by them in group I, are rich in illitic minerals, (vide Tables 17-24 and 54).

Since in potassium fixation mechanism it was shown that 2:1 type of expandible lattice clays were responsible for the fixation phenomenon, so it is considered that the release of potassium and also its fixation are transverse processes. Potassium bearing clays, in which there is a fixed potassium, will be expected to contribute potassium to the crop by its release. Fixed potassium particularly from illite and micas, is highly available compared to the native potassium of the soil (vide Tables 56 to 60).

It is revealed (vide Table 57) that out of 13 soil samples those containing dominant illite mineral, possess high K-supplying power.

It is noted from the present work that fixed potassium is released in sufficient amount by boiling N HCl, both from illite and biotite minerals and clays containing them. N MgCl₂ and N NaNO₃ are good extractants for K₂O from these minerals (vide Tables 58, 58-a, and 59). The present work confirms the conclusion of Farahad (24), that potassium from biotite can be released in large amounts by leaching with MgCl₂ solution and that the amount of water gained by biotite was proportional to the K-ion replaced. The present work also puts NaNO₃ as a good agent to release potassium from the lattice place of biotite (Table 62-64).

The present investigation supports the views of Walsh and Sullivan (316) that fixed potassium is mobile. It also
confirms the views of York and Roger (539), Ayres (15) and Perrin (193) that Ca-saturated soil and clay liberate fixed potassium faster than Na-saturated. (vide Tables 58 and 58-a)

Conversion of one type of clay minerals to another type by potassium fixation and depotassification processes:

Potassium fixation and depotassification occurs in potassium bearing minerals only. Hence to understand the conversion of one type of clay mineral into another, will require a precise conception of structures of various silicates involved in these chemical reactions. These reactions involve a movement of K-ion under the processes of hydroxylation, dealumination, desilication, depotassification and potassium fixation. The first four reactions belong to chemical weathering in which potassium moves out of the parent mineral whereas the fifth reaction represents in which movement of potassium ion is in the reverse order.

During the present investigation, chemical reactions involving movement of K ion from the outside to the structure of clay mineral and from the structure of silicate to outside were studied. To comprehend these reactions in the conversion processes, a short reference to the modern conception of structural units of silicates are essential.

(1). Structure of Micas (Odim - 102).

The fundamental structural unit is a layer composed of two silica tetrahedral sheets with a central octahedral sheet. The tips of each tetrahedron in the silica sheet point towards the centre of the unit and are combined with the octahedral sheet in a single layer with suitable replacement of OH by O.

The unit is identical with montmorillonite except that some of
the Si atoms are always replaced by Al atoms and the resultant charge deficiency is balanced by K ion. In many well-crystallised micas, one-fourth of the silicon atoms are replaced by aluminium atoms. The site of the potassium ion is the space between the two unit layers where they just fit into perforations in the surface O (oxygen) layers. The adjacent layers are stacked in a manner that the K ion is equidistant from twelve oxygens—six of each layer.

Grim (102) gives structure of micasite as

\[(\text{OH})_2\text{Al}_2\text{Si}_2\text{O}_5\cdot\text{H}_2\text{O}\]

giving composition as \(\text{SiO}_2\) 45.2 per cent, and \(\text{Al}_2\text{O}_3\) 38.5 per cent, \(\text{H}_2\text{O}\) 4.5 per cent, \(\text{K}_2\text{O}\) 11.8 per cent/Molecular ratio \(\text{SiO}_2/\text{Al}_2\text{O}_3\approx 2.0\).

K-ion may be partially replaced by other cations possibly by Ca\(^{++}\), Mg\(^{++}\) and H\(^{+}\) from its seat in the unit layers. 
di-
Muscovite is called/catahedral mineral.

Trioctahedral micas are trioctahedral. Grim (102) assigns structural formula for it – \((\text{CH})_4\text{K}_2\text{Si}_2\text{Al}_2\) (Mg\(_{\text{Fe}}\))\(_6\text{O}_20\).

Illite: Grim (102) assigns structural formula –

\[(\text{CH})_4\text{K}_y(\text{Al}_4\text{Fe}_2\text{Mg}_6\text{Mg}_6\text{Al}_y)\text{Si}_2\text{Al}_2\text{O}_20\] where \(y = 1\) to 1.5.

In illite 1/6 of the Si atoms are replaced by Al atoms isomorphously. It differs from muscovite in the isomorphous replacement of Si\(^{+++}\) ions by Al\(^{+++}\) ions.

Montmorillonite: The structural formula given by Grim (102) is: \((\text{OH})_4\text{Al}_4\text{Si}_8\text{O}_20\cdot\text{nH}_2\text{O}\) – \((\text{CH})_4\text{Si}_8(\text{Al}_{3.34}\text{Fe}_{0.66})\text{O}_20\)

Vermiculite: The structural formula assigned by Grim (102) is:

\(-(-\text{CH})_4(\text{Mg}\cdot\text{Ca})_x(\text{Si}_{8-x}\text{Al}_x)(\text{Mg}\cdot\text{Fe})_6\text{O}_20\cdot\text{yH}_2\text{O}\) where \(x = 1\) to 1.4 and \(y = \) about 8.

Mg\(^{++}\) and Ca\(^{++}\) are largely exchangable cations.

Kaolinite: Grim's (102) structural formula is:

\((\text{CH})_8\text{Al}_4\text{Si}_4\text{O}_10\)
Conversion as revealed by fixation study

Volk (311) in 1934 postulated that montmorillonite was converted into mica as a result of potassium fixation. Roll (215) in 1931 reported that illite was formed from the interaction between potassium salt and montmorillonite in the alkaline medium. Bray (49) in 1937 and Jackson et al (131) in 1948 postulated that illite and mica intermediate weathered into montmorillonite in soils. Walker (314) in 1950 stated that the apparent alteration of biotite/illite mica into vermiculite or montmorillonite in soils. Similar kind of alteration in phlogopite was reported by Caillere et al (49) in 1949 by boiling mica in 40 per cent of NaCl solution for 135 hours. Chatterjee (57 and 58) in 1953 and 1954 attempted to study conversion of montmorillonite into illite by fixation of potassium. He has shown that montmorillonite after fixation of potassium in it gave certain properties which indicated the presence of illite in the so treated bentonite, and he concluded that montmorillonite was converted into illite as a result of potassium fixation. He did not find any fixation in kaolinite and thus there was no reported conversion of kaolinite into any 211 type silicate.

The present investigation has established that changes do occur in properties of silicates as a result of potassium fixation. These properties in which changes have been noticed are related to base exchange reactions and water content.

Grim (102) has assigned values of base exchange capacities to various minerals as follows:

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Base Exchange Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>3</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>80</td>
</tr>
<tr>
<td>Illite</td>
<td>30</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>100</td>
</tr>
</tbody>
</table>

The values are given in meq/100 g of mineral.
<table>
<thead>
<tr>
<th>Chlorite</th>
<th>10 to 40 m.e./100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halloysite</td>
<td>40 to 50</td>
</tr>
</tbody>
</table>

The values obtained in the present study, conform to the base exchange capacity values of minerals cited by Grim (102). The present investigation has noted changes in base exchange capacity, competitive action absorption ratios, Atterberg's constants and specific chemical retention values. Potassium content of the resultant silicate increases by 1.42 per cent whereas illite contains potassium about 5.0 per cent and that only a small amount of montmorillonite must have been changed to illite. This indicates that about 30 per cent mineral montmorillonite could be converted into illite. From the chance in base exchange capacity the same conclusions are apparent. Hence the present work indicates a slightly higher value of conversion (vide Table 27) in comparison to the findings of Satterfield (57, 58). The difference in values is due to the different unit basis. In the present study, calculation is based on chance of base, whereas Satterfield based his calculation on the K₂O content.

Regarding the fixation in illite, K₂O increased by 0.5 per cent any from 6.7 per cent to 7.2 per cent. Base exchange capacity changed from 36.2 m.e. to 25.5 m.e./100. The molecular ratio H₂O/al₂O₃ remains nearly 3.7. Since there is no difference in the structure of muscovite and illite except that illite has replace most of 1/6 of Si⁺⁺⁺ ions for Al⁺⁺⁺ and in muscovite replacement is of 1/4 Si⁺⁺⁺ ions with Al⁺⁺⁺. Contents of K₂O and base exchange capacity show that conversion might have taken place (vide Tables 19, 21 and 26).

Vermiculite fixed large amounts of potassium and its base
exchange capacity was reduced to the equivalent amount of fixation. Maximum fixation is about 4.1 per cent K₂O and base exchange came to be about 46.0 which shows that vermiculite could be converted into biotite only to the extent of 40 per cent as a result of potassium fixation (vide Table G2).

The numerical value of per cent decrease in base exchange capacity in case of illite is similar to the value calculated for conversion from illite to muscovite, i.e. 30 per cent.

From the release of potassium the conversion of muscovite to illite, illite to montmorillonite and biotite to vermiculite were attempted.

Results obtained in this investigation as shown by K-release, indicate a certain amount of conversion of high potassium bearing clays into low potassium bearing clays by chemical weathering under cationic influences. This conversion of illite to montmorillonite works out only a fraction, a major portion remains unaffected under the specified conditions. Moreover in case of biotite, NaCl₂ removes potash in large amounts and a change in properties indicate conversion to the extent of 45 per cent to vermiculite. This conversion took place under vigorous treatment with NaCl₂ solution directed on water-bath, (vide Tables 59 and 60).

Combined action of NaCl₂, NaOH and Ca(NO₃)₂ increased conversion of illite to montmorillonite to about 30 per cent, muscovite to illite about 50 per cent and biotite was able to release larger amount of potassium and it changed to almost 49 per cent into vermiculite (vide Table G4).

The results of this investigation are now in agreement with Volk (311), Roll (215), Bray (47), Jackson (131), Walker (314), Cailler (49) and Shaterjee (57 and 58), indicating that
conversion of micas to clay minerals of the 2:1 type of layer mineral takes place by mobilization of potassium under cationic reactions. 2:1 type clay minerals become mica partially by fixation. Kaolinite remained unaffected.

**MINERALOGICAL STUDY**

The most important fraction of the soils is clay fraction. This fraction contains extremely small crystalline particles of members of the clay minerals. Analyses of clays by X-ray, optical, Chemical and dehydration methods have evolved certain techniques by which mineralogical composition of the clay fraction can be determined. Since the three clay minerals differ amongst themselves appreciably in their potassium fixation capacities so it was thought to study if the potassium fixation treatment combined with other chemical methods could be employed to find out mineralogical composition in the clay fraction of a soil. Roy (263) in 1951 showed that black cotton and Delhi soils had contained both illite and montmorillonite minerals, the black cotton soil was rich in montmorillonite but Delhi soil was rich in illite.

The present investigation with a study of potassium fixation in clay minerals confirms the conclusion of Roy (263). The chemical analyses of clay fraction of the soils under this investigation give high potassium content showing that it contains K-bearing minerals. Results shown in Table 16 to 25 indicate that soils of Pusa, lateritic soils of Bihar and Madras acid soils of Palampur and Srinagar and black cotton of Guntur are-
rich in montmorillonite mineral containing illite ranging from 20 to 30 per cent. On the other hand, soils of Karnal, Delhi and Sisar are rich in illite mineral. The present investigation confirms the work and findings of Roy (283), Raychaudhuri, Sulaiman and Phuiyan (240), Mukherjee and his associates (209, 210 and 211), Serelcneimt, Desai and Puri (212, 213) and Raschi (18) relating to dominant clay mineral in black cotton soil. Hence by determining base exchange capacity, potash content, K-fixation capacity of clay fractions of soils and also calculating the per cent decrease in base exchange capacity, a definite information as to which clay mineral was dominant, could be arrived at.

Explanations of mechanism of potassium fixation in silicate!

Present theories relating to mechanism of potassium have explained some of the facts.

The following observations were made during the course of the investigation, and an attempt to give explanation of each cause was made:

1). Each type of clay mineral exhibited a decrease in per cent of the original base exchange capacity. For example — montmorillonite 24 to 27 per cent; illite about 30 per cent and vermiculite 60 to 65 per cent (vide Tables 17 and 25).

2). Maximum potassium fixation that took place in clay mineral was — illite 0.6 per cent K₂O; montmorillonite 1.42 per cent K₂O and vermiculite 4.2 per cent K₂O (vide Tables 17, 20, 21 and 62).

3). Maximum releases of fixed K₂O obtained using extraction process were as follows: Results are of one extraction only.

(a) Montmorillonite — 25 per cent (vide Tables 58 and 58-a
(b) Illite — 60
Maximum release of native K₂O under the influence of cations in dilute solutions.

1. Muscovite - 30 per cent (vide Table 64)
2. Fissile - 40 "
3. Illite - 31 "

4. Fixation of potassium was not inhibited by saturating exchange complex with big cations or organic radicals (vide Tables 35 and 37).

5. Competitive cation absorption ratios decreased as a result of fixation (Table 39 and 40).

6. Clays lose water of hydration as a result of potassium fixation. This is evident from (i) loss on ignition (ii) decrease in clay content and (iii) decrease in liquid limits (vide Tables 44, 45 and 46).

7. Clays gain in hydration during the release reactions (vide Table 64).

8. Clays change in certain properties as a result of potassium fixation (vide Tables 37 to 46).

9. About 1 to 3 per cent artificially fixed potassium comes out on shaking with distilled water (vide Table 58).

10. Base exchange capacity of any clay does not reduce to zero as a result of potassium fixation.

11. Composition of clays practically remains constant after potassium fixation (vide Tables 63 and 64).

12. The properties of clays which change as a result of potassium fixation are retained after release of fixed potassium (Table 64).

Observation No. 9 can be explained by Senin’s theory showing fixation by floc of colloidal precipitation.
Observations 2, 3 and 4 invalidate the ionic theory of
Pane and Raver (223). According to ionic theory the site of
entrainment of potassium is "void" in the tetrahedron. Theoret-
ically fixation of potassium in montmorillonite can occur up to
21.6 per cent but in practice maximum potassium fixed is 1.42
per cent. From the structural formula of muscovite, illite and
montmorillonite, it is noted that muscovite could be changed to
illite and the latter to montmorillonite. Maximum reelease
from muscovite and illite have been affected were to the extent
of 30 per cent (vide Table 64).

The facts stated in observation No. 1 and also noting of
limits of maximum fixation, suggest that there might be certain
type of charges on the complex directing potassium fixation.
Observation No. 5 indicates that the nature of charges giving
rise to base exchange has been altered as a result of potassium
fixation. On examining Tables 39, 40, 42 and 43, it may be noted
that the amount of each competitive ion retained on the clay
after the potassium fixation as compared to that retained before
fixation treatment is in favour of the cation having greater
hydrated ionic radius. Applying Coulomb's law which states
that the attraction between two charges varies inversely with
the square of the distance between the seat of the two charges,
it is clear that a strong charge on a clay would exert a greater
force of attraction on the ion of smaller radius than on the
ion of the larger radius, because the distance between the seat
of the charge on the clay and that of the smaller ion is less
than in the case of the larger ion. It is proposed that if
certain charges in the clay lattice occur near to the surface
of the lattice plate than others, they are able to exert their
force at closer range and thus are stronger charges than those occurring at a greater distance from the surface. In case these strong charges are satisfied as a result of potassium fixation, the smaller ions would not be attracted by as many strong charges as previously. Therefore, the absorpotion ratio after fixation treatment would be expected to shift in favour of the ion of greater ionic radius as is found to be the case.

According to Grim (102), inorganic base exchange charges can arise from three sources, namely (i) broken bonds, round edges charges are exhibited by kaolinite and halloysite; (ii) H+ of the exposed OH; and (iii) substitutions within the lattice structure.

The present investigation supports all three causes of base exchange charges and fixation. The most important cause is the third one. According to this two types of substitutions arise, namely, (1) replacement of Mg for Al atoms in the gibbsite layer of the crystal lattice giving rise to excess charge, (2) replacement of Al for Si atoms in the silica tetrahedral sheets of the crystal lattice giving rise to an excess charge. Grim (102) says of the Al for Si type replacement "This replacement provides an excess charge originating near the surface of the 9 A units and therefore, is stronger than the charge resulting from the other replacement".

From Tables 17, 20, 21, 24, 25 and 27 it is noted that illite and illitic clays have higher per cent of their original base exchange capacities decreased as a result of potassium fixation than do montmorillonite. Hence it is postulated that strong charges resulting from Al for Si replacements are at least partially responsible for potassium fixation.

If it is considered that cations for fixation would go
only into those "voids" occurring adjacent to an Al for Si replacements then a suitable explanation for the fact as to why ions smaller than potassium are not appreciably fixed is to be found.

The difficult task is to explain why does illite fix potassium next from amongst the clay minerals. Grim (102) reported that illite has approximately 15 per cent of the Si atoms replaced by Al. Fixed potassium will occupy the "voids" of excess charge.

In montmorillonite the major part of the exchangeable capacity is believed to be due to the replacement of Al by Mg atoms in the gibbsite sheet of the lattice. Each replacement by an ion of lower valency gives rise to an unsatisfied negative charge which acts in the base exchange.

In illite Al replaces 1 for Si in the silicon sheet of the tetrahedral layers are create than in montmorillonite. This replacement in illite alone occurs much nearer the surface of the plate making up the crystal lattice than the other type of replacement. Force residing charge in illite exerts its force at closer range with greater intensity to the surrounding cations than the smaller charge in the gibbsite layer.

Secondly total number of charges on tetrahedral positions in illite and montmorillonite are 18 and 18 to 17 respectively, (137). Out of these total charges, specific charges responsible in illite for K-fixation are in greater number and possess greater force of attraction on cations surrounding the illite exchange.

According to Jackson and Neal (137) the distances between the centre of K-ion to the centre of the charges in the tetrahedral and octahedral positions are 2.99 and 4.99 Å respectively. This clearly indicates that charges on tetrahedral position will exert
greater force of attraction over K-ion and hence greater K-fixation would take place in it.

After examining total amount of potassium fixed in the crystal lattice (including previously coupled K₂O in the crystal structure), both in illite and montmorillonite it is observed that this value increases with the amount of specific charges available by substitution in the tetrahedral position. The present study agrees with the findings of Pearson and White (323).

It was noted that the absorption ratios of two competing cations by various clays shifts after K-fixation towards the absorption of cation of larger hydrated ionic radius and of ionic potential value - 0.71. The charge acting at closer range would be expected to absorb preferentially the cation of smaller hydrated ionic radius. Hence the fact that a ratio shifts in favour of absorption of large ion shows that there are proportionately less charges acting at closer range after K-fixation, some of these charges having been satisfied by fixed potassium.

It was also observed in present study that the treatment of clay with a solution of 0.25 N with respect to CaCl₂ and KCl on drying caused greater per cent of exchangeable potassium to become fixed than when it was entirely saturated with potassium. On substituting cation diethylamine in place of Ca similar results were obtained. This clearly indicates that during saturation of the clays, potassium in preference to Ca or diethylamine was absorbed by those base exchange charges capable of effecting K-fixation (vide Table 35).

On the evidence cited above it seems that the charge arising from the Si - Al sheets are largely responsible for the K-fixation. Hence the potassium fixation capacity of the base exchange is believed to depend largely upon the number of this type of base
exchange charges possessed by the material. This view explains as to why the total base exchange capacity of clays cannot be measured with the fixed potassium, a much discussed problem but unexplained so far.

To explain the specificity of potassium cation toward its fixation in the clays it was thought to take into consideration values of ionic sizes, ratio of cation and anion radii and ionic potential (valency) and to study why this property was limited to certain cations only. Cations that can fit tightly into the space in the surface occurring in the oxygen tetrahedra of the clay lattice and thereby becoming inaccessible to replacement by other cations, must have ionic size very near to the "void". Application of the ionic size hypothesis and coordination compound formation theory explains the specificity of potassium fixation. According to this, cations which can form twelve or fourteen coordination with oxygen in muscovite and even less in montmorillonite and those having ionic potential (valency) 0.71 and Pa 0.73 to 1.0, can form stronger complexes than the water of hydration and they are the ones which are involved in this kind of specific fixation phenomenon. K-ion possesses all properties to enter the "void" and become non-exchangeable in the clay.

Grim (102) showed that muscovite has potassium 11.8 per cent K₂O which is half of what montmorillonite structural formula suggests if the latter could be changed to muscovite by K-fixation. He also says that illite has 1/6 substitution of Al for Si whereas muscovite has 1/4 i.e., the latter has two Al atoms more substituted than illite has. Maximum fixation in montmorillonite has been found to be 1.42 per cent K₂O which is only about 6.6 per cent of the 21.6 per cent theoretical value of montmorillonite if "voids" could fully be saturated with K-ion and 12.0 per cent of the value given by Grim (102) for native muscovite.
Further calculations show that for every molecule of montmorillonite only a fraction of the atom weight is fixed.

Bradley (40) and Kane and White (323) show that the stable configuration is formed with each positive ion in fourteen coordination when potassium is fixed in a 2:1 layer mineral. They have also shown that potassium fixation is in the "voids" of the tetrahedral layer.

From the chemical analysis it is clear that all "voids" do not attract in potassium ions. Potassium enters only in a few lattice "voids". Hence it is a clear indication that some strong charges are neutralised by K-ions after fixation and that the lattice "voids" which retain fixed potassium are from amongst those where Al has replaced silicon.

Contracted and expanded conditions of lattice:

Observations made by Jackson and Fellman (130) and Bailey (20) showed that if potassium saturated montmorillonite was dried at 110° C the spacing (001) was 10 Å. Invariably workers in this field have reported that lattice plates contracted as a result of potassium fixation. The present investigation has shown that drawing together of the lattice plate condition was not essential for fixation to occur. This is evident (vide Table 37) from the fact that even when lattice plates were kept apart with casein some fixation had occurred.

The same findings were obtained in another form. Montmorillonite was given potassium fixation treatment. The latter was washed with Ca chloride solution to expand its contracted lattice. It was noted that major part of the fixed potassium was retained even though lattice was moved apart by making it Ca-saturated (vide Table 38). Hence contraction of lattice may be the result
of potassium fixation but is not a cause of fixation.

Role of Ca-ion

Liming causes great fixation in clay minerals. Ca-clays also show more fixation than the H-clay (vide Tables 32 and 34). Conversely, the results shown in Tables (37 to 53, 58, 58-a, and 61) indicate that Ca can release fixed potassium. The results, therefore, lead one to the conclusion that Ca ion is playing a part of Dr. Nyki and Mr. Hyde of Stevenson's famous novel. At one time it induces fixation and at another time it liberates fixed potassium (vide Tables 32, 34 and 57). Which of these effects are dominant, probably depends upon the nature and condition of the soil and upon the relative proportion of Ca to K in that soil. Harris (100) in 1937 also observed the same.

The absorption of Ca and K on the soil exchange complex is much influenced by the rate of application of fertilizers containing these ions.