CHAPTER I

FIXATION OF POTASSIUM IN INDIAN SOILS AND CLAY MINERALS

INTRODUCTION

It is a well known fact that a portion of the exchangeable potassium held by the inorganic base exchange silicate material of a soil may go to non-exchangeable forms. Investigators have indicated that this reversion of exchangeable potassium to the non-exchangeable form may be effected by certain conditions to which potassium saturated exchange material may be subjected. The potassium which goes from the exchangeable to non-exchangeable forms as a result of the application of these conditions is commonly known as "fixed" potassium, because it is not extractable with N neutral ammonium acetate.

It is observed that certain soils have been found capable of fixing potassium more readily and in greater quantities than others. It was thought that an investigation of the ability of soils and clays to fix potassium and of the change in the properties of these exchange materials as a result of potassium fixation and also of the reversibility of these reactions might explain the cause of phenomena of fixation and its mechanism, exact nature of chemical weathering of these exchange materials and also might facilitate the study of soil mineralogy.

This study was conducted by chemical methods.

REVIEW OF LITERATURE

(A). Concept of base-exchange reactions with reference to potassium fixation:

Thompson (296) in 1845 observed that leachate from a soil to which ammonium sulphate had been applied contained calcium sulphate instead of ammonia. The first comprehensive
study of power of soils to take up cations from solutions was made by Way in 1850. He observed that anion of the applied salt was not retained and that the cation adsorbed could be replaced by leaching with different cation. He further noted that replacement took place between chemical equivalents of the cation involved.

Numerous investigators have since established the importance of the base exchange material of the soil as a store house from which essential nutrient elements can be taken by the plant.

Kellner (148) in 1887, Dyer (70) in 1894, Frear and Erb (88) in 1918 and Naselschmidt (212) in 1944 noted at their respective places that soils after receiving potash fertilizer retained appreciable amount of potash in them in a difficultly exchangeable form. Bartholomew and Jansen (29) in 1932 and Hoagland and Martin (120) in 1933 claimed that in some experiments fixation of potash occurred during a period of cropping.

Martin (188) in 1929 reported that 12 successive annual barleycroppings on a California soil resulted in a loss of 32% of the original exchangeable potassium contained therein, 82% of this being removed by the crops. The loss of potassium as a result of two crops of barley followed by 10 successive fallow years made up 13% of the original exchangeable potassium content. Of this loss 64% was removed by the crops. Since Ca and Mg made up about 90% of the total exchangeable cations, the potassium removed was in almost every case greater than that shown to be available by chemical test.

Gedrolz (91) in 1931 substantiated the evidence that plants could grow on potassium not shown to be available by chemical tests. He leached a chernozem soil free from potassium and magnesium and obtained a good growth of oats without any additional fertilization. Moreover he got no appreciable response
from applying potassium to the chernozem soil whose exchange material was saturated with Ca and Sr. He thus concluded that plant could feed on the non-exchangeable potassium of a soil.

Hoagland and Martin (120) in 1933 observed that some soils fix potassium readily while others effect fixation only by alternate wetting and drying. They discovered that various soils yielded from 40 to 90% of the applied potassium to the plant growth but there was little correlation between the level of exchangeable and solution potassium in soils and the plant growth.

Magistad (179) in 1934 noted that when the level of exchangeable potassium exceeded 0.40 m.e. per 100 gm. dry soil, no response was observed from potassium fertilizer application. Since 70% of Hawaiian soils show levels of potassium above this figure, the potassium applications have largely been dispensed with in these areas. Volk (311) in 1934 started detailed study of potassium fixation in soils and observed relatively little fixation when soils were kept moist compared to that by drying at 70°C. He found that drying caused greater fixation than moist storage. He showed that clay size particles fixed potassium most. Abel and Magistad (1) in 1935 showed that soils low as well as those high in exchangeable potassium liberated potassium from the non-exchangeable sources for growth of soybeans and sorghum.

Bray and De Turk (43) in 1938 proposed a two phase equilibrium in the soil between the potassium in soil solution and the exchangeable and between exchangeable and non-exchangeable potassium. They declare that a soil tends to attain its inherent "equilibrium level" of exchangeable potassium. For example, leaching a soil of its exchangeable potassium and consequently storing it in a moist condition resulted in a gradual conversion of non-exchangeable form of potassium to exchangeable. Conversely, addition of KCl equivalent to 500 lbs. of potassium per acre resulted in substantial...
decrease in exchangeable potassium during an eight week storage period in moist condition. Heating the soil at 200°C for six days hastened the attainment of the equilibrium. Each soil studied seemed to possess a definite equilibrium level.

Frap and Fudge (87) in 1939 conducted greenhouse experiments with numerous soils on the availability of potassium as measured by the growth of corn. They noted wide differences in potassium supplying power among the soils investigated. They observed that potassium was more available to corn per unit of potassium contained in soils rich in potassium than in those soils low in this element. A high correlation was noted between the amount of potassium taken up by a plant and the amount of exchangeable potassium present before plant growth.

Kolodny and Robbins (155) in 1940 conducted perhaps first experiment using artificial fixed potassium as the sole source of potassium for plant growth. He grew tomato plants on Wyoming bentonite in which potassium was artificially fixed. Their results led them to conclude that fixed potassium was only slightly available to plants. Fine (82) in 1941 had criticized this conclusion on the grounds that "firstly the tomato plant is a poor feeder on potassium and therefore, it is not right that a poor plant be used in an experiment of this kind; secondly the bentonite containing fixed potassium was left saturated with Ca, a condition not favourable to plant growth owing to unfavourable Ca/Mg ratio; thirdly the availability of fixed potassium was compared in part with that of exchangeable potassium in which case approximately eight times as much total potassium was present". After removing all these unfavourable conditions he concluded that practically all of the artificially fixed potassium in bentonite became available to corn and wheat, and only about 25% of this supply to tobacco.
Peach (237) in 1941 reported that increase in pH from 5 to 6 gave rise to an appreciable increase in availability of the bases. Fertilizer applications of potassium salts of weak acids resulted in a greater absorption of potassium by the soil colloids than that of the potassium salts of strong acids. Nandy (214) in 1946 in India reported that potassium release from the non-exchangeable form/soils had occurred only between pH 6.0 and pH 7.0.

Fine, Bailey and Truog (83) in 1941 reported freezing and thawing cycles tended to increase exchangeable potassium in soils of low to moderate fertility and to decrease it in soils of high fertility and they concluded that 2/3 of the soils which were under investigation had effected a considerable potassium release. In certain cases fixation had occurred while in a few cases no change was observed. They further observed that from such clay minerals in which artificial fixation treatment was given there was a release of potassium after freezing and thawing.

Wood and De Turk (333) in 1940 showed that some Illinois soils after receiving heavy dressings of potassium were able to retain potassium in non-exchangeable form and which became available again as the soils were depleted of their exchangeable potassium. They had postulated the following equilibrium systems of soil potassium.

(I). Primary mineral potassium; (II). Fixed potassium (acid soluble potassium - acid insoluble potassium); (III). Replaceable potassium; (IV). Water soluble potassium.

This system under field conditions is displaced to the right, with acceleration under cropping. They also stated that out of the two portions of the fixed potassium, the portion which is soluble in boiling N HNO₃ for ten minutes is most important from the standpoint of crop production. The quantity of potassium
in the latter form seems definitely limited while that of the acid insoluble appears to be restricted. Genetically old soils were found to have a higher potassium fixation capacity and retention power than do the virgin or young soils.

Sauers and Winters (277) in 1944 studied the relationship between potassium fixation, exchange capacity and complementary ions. They suggested that the exchangeable potassium is in equilibrium with the potassium bearing soil minerals and that by fertilizing or cropping potassium tends to be respectively fixed or released.

For a more complete review of early investigations relative to crop response to potassium fertilization treatment references may be made to the work of De Turk (66) in 1943 and Feitmeier (253).

2. Forms of Potassium in Soil

According to Wiklander (328) in 1954, the soil potassium occurs in a variety of forms. Total potassium in a soil depends on mineral composition of the parent material, leaching and type and degree of weathering. Arbitrary division into four categories, namely, Soluble potassium, exchangeable potassium, fixed potassium and lattice potassium have been made.

(1). Soluble Potassium. K\textsubscript{b}t

It is always present as an ion in the soil solution. Its concentration may vary from one soil to another and from season to season. Its contents depend on the amount of exchangeable potassium, type of clay mineral, water content, intensity of leaching, kind and concentration of other cations present, season etc. Its usual range is between 0.002 to 0.02 m.e./100 gms. soil which comes to be about 1% of the exchangeable.

It is in equilibrium with the exchangeable potassium from which it is difficult to distinguish. As a consequence of the
exchange equilibrium with Ca and Mg, soluble potassium increases at moist conditions. On drying soluble potassium decreases. The phenomenon is known in the ion exchange theory as the valence and dilution effects.

(11). Exchangeable or Adsorbed Potassium, \( K_a \):

The exchangeable potassium is defined as the potassium which is adsorbed on the soil exchange material and is replaceable with neutral salts in a relatively short time. The contents of the exchangeable potassium depend on the mineral composition of the exchange material, soil texture, water content, weathering and leaching conditions, fertilization with mineral fertilizer, liming, kind and concentration of the competing cations etc.

The contents of the exchangeable potassium in mineral soils are usually less than 1% of the total potassium. The usual range is between 0.30 m.e. and 0.35 m.e./100 gm. soil (Wiklander 245). Variations of this form in Indian soils are very great.

Sandy soils usually show lower values for exchangeable potassium than the heavy soils, and it is due to less weathering, low base exchange capacity and stronger leaching.

Drying favours the adsorption of potassium at the expense of Ca and Mg. The same thing happens on the decrease of the exchange capacity.

Exchangeable potassium is completely available to plants either directly by contact exchange or indirectly by the equilibrium \( K_a \rightarrow K_e \). The level of the exchangeable potassium falls during the cropping period but a soil is never deprived of all its exchangeable potassium, because of its weathering or defixation process releasing enough of potassium to keep up the exchangeable potassium at or above a certain minimum level, characteristic of the soil or cropping. The magnitude of this level depends on the rate of removal and mobilization by weathering and defixation.
(iii). Fixed or non-exchangeable Potassium, \( K_f \):

If potassium added to a soil is so firmly bound that it is not immediately replaceable with neutral salts it is said to be fixed. The fixed potassium is assumed to be bound between basal planes of chiefly micaceous minerals in the hexagonal oxygen cavities normally occupied by potassium as a lattice constituent. By leaching and weathering a part of the lattice potassium ions migrates out of their positions between the unit layers, replaced by cations such as \( \text{H}_3\text{O}^+ \), \( \text{Ca}^{++} \) and \( \text{Mg}^{++} \), etc., entering the interior of the particles. As a result of this substitution the mineral becomes somewhat degraded, that is, the content of potassium is decreased and that of water increased and the lattice partially expanded. If potassium is added to such a potassium-deficient mineral, potassium ion migrates in between the unit layers, replace the ions adsorbed on the normal potassium positions and contract the lattice, thus rebuilding the mineral and it becomes fixed. The fixed potassium represents a transition stage between the exchangeable potassium and the lattice potassium from which it is impossible to distinguish sharply. Fixed potassium is plant available only to the extent that it is released by defixation. There exists an equilibrium amongst \( K_s \), \( K_e \) and \( K_f \) which may be expressed as follows:

\[
K_s \xrightarrow{} K_e \xrightarrow{} K_f
\]

The cations competing with potassium for the exchange positions may keep exchangeable potassium low and thus effect low fixation. In soils poor in soluble and exchangeable potassium, a release or defixation from the mineral is likely to take place more or less and plants will feed on potassium released partly in this way and partly by weathering. Other ions having similar size and charge as potassium such as \( \text{NH}_4 \) are also fixed in
potassium deficient micaceous minerals.

Soil materials having potassium fixing power are chiefly illite, montmorillonite, vermiculite and glauconite and primary minerals like, chlorite whereas kaolinite and feldspars do not show this fixation property (328).

The capacity and the rate of fixation and defixation in a soil are influenced by several factors other than the mineralogical composition, fertilization and cropping.

Fixation and defixation work as a good buffering mechanism in the soil. At a high concentration of soluble potassium the level is lowered by fixation, thus minimising the loss by leaching and on the other hand the soil is able to supply plants with more potassium than is possible without the reserve of fixed potassium. (iv). Lattice Potassium:

The largest portion of the total potassium in mineral soils and minerals resides in the potassium bearing primary and clay minerals in non-exchangeable form. The primary minerals are muscovite, biotite and potassium feldspars. Out of the clay minerals only illite has a substantial potassium content, above 4%. The capacity of soil to release potassium by weathering depends on the quantity of potassium bearing minerals and the soil texture. Certain clayey soils release so much potassium that plants do not respond to potassium fertilization. It seems that the primary minerals are less stable than the clay minerals and that the non-expanded illite is less stable than the partially expanded and potassium poor mica-montmorillonite intermediate.

The colloid fraction generally contains more stable clay minerals. A fine textured soil rich in primary potassium bearing minerals possesses a great potassium supplying power by weathering. This capacity diminishes with the progress of the clay
mineral formation resulting in a slow and gradual decrease of the soil potassium and increasing response to potassium fertilization.

The potassium release by weathering is partly held by the exchange adsorption on the clay, partly lost by leaching and partly taken up by plants. To some extent the weathering is counterbalanced by the formation of potassium bearing clay minerals and by fixation of potassium.

With respect to the availability of potassium to plants all forms of potassium have been emphasized at different times by various soil chemists, namely, soluble, exchangeable, fixed and also lattice total as in primary and clay minerals. The amount of moderately mobile potassium in any one form at a particular time is not independent of other forms, but instead the distribution of the mobile form tends to be governed by an equilibrium by which a change in the level of one component is reflected in corresponding changes in the other parts of potassium system.

It is important to stress that the practice of unbalanced use of mineral fertilizers and intensive method of cultivation both lead to an increasing impoverishment of the soils and is particularly in potassium which is withdrawn from the soil in large quantities by the crops.

Potassium deficiency is frequently observed on virgin light sandy or peat soils.

3. Chemical Weathering of Minerals

Russel (267) in 1954 reported that in the study of availability of potassium from soils two important factors are to be kept in view. The first factor was the weathering of soil material and the other was the ability of crop plant to absorb potassium under certain favourable conditions.

Herr Gentili (245) stated that weathering of rocks is
continually increasing potassium in the soil. There are relatively few soils in which potassium supply is so low that cropping is entirely dependent on potassium manuring.

Availability of potassium in a soil depends on the amounts and types of potassium bearing primary and secondary minerals present therein. For the old extensively cultivated soils secondary minerals play the main role. Principal potassium bearing primary rocks are feldspars which includes orthoclase and microcline with some plagioclases containing important amounts of potassium and the micas (both black biotite and white muscovite).

According to Jackson et al (132) in 1952 and Russell (245) in 1954, potassium bearing silicates weather in the soils and potassium in various available forms is liberated. Russell (245) reports that under hot humid conditions biotite and andesine could yield 150 to 250 kgm/ha of potassium per year to crops like sisal and sugarcane, and a considerable amount of potassium was lost in the drainage water.

He describes the products of weathering of primary minerals as secondary products which weather further and yield hydrated oxides of iron and aluminum, silica and clay minerals. The latter products are silicates of well defined structure, grouped into two great classes, (a) potassium bearing clay minerals known as illites and (b) non-potassium bearing minerals, like kaolinites, halloysites and montmorillonites.

Jackson et al (132) in 1952 gave the mechanism of chemical weathering of micas as expressed in the equation:

\[
\text{Micas} \rightarrow \text{illite} \rightarrow \text{intermediate} \rightarrow \text{vermiculite} \rightarrow \text{montmorin}
\]

They declare that during weathering of micas defixation of potassium is the main reaction. They advocate two main chemical reactions involved therein. First reaction is liberation of
-12:-

Potassium ion under the influence of water and cations like H+, Mg++, and Ca++. 

\[ [\text{Al}_2\text{O}_2(\text{OH})_2][\text{Al Si}_3\text{O}_8] K = [\text{Al}_2\text{O}_2(\text{OH})_2][\text{Al Si}_3\text{O}_8] + K^+ \] (I).

Here a decrease in layer charge takes place. This layer charge in mica arises from substitution of \( \text{Si}^{4+} \) by \( \text{Al}^{3+} \), \( \text{Si}_{4+} + \text{Al}^{3+} = [\text{Al Si}_3\text{O}_8] + \text{Si}^{4+} \) in the tetrahedral layer. Oxidation of tri-octahedral ferrous to ferric compensates the negative tetrahedral charge and permits rapid expansion and potassium defixation from biotite micas. Dioctahedral layer charges are destroyed by two chemical processes, namely hydroxilation and dealumination.

(i). Hydroxilation results in neutralization of the charge once held by K+ in mica. In this H+ replaces K+. The reaction is:

\[ [\text{Al Si}_3\text{O}_8] + H^+ = HO. \text{Al Si}_3\text{O}_7 \] (II).

The chief requirement of hydroxilation reaction is that the statistical layer charge must decrease sufficiently to permit perpetuate rapid expansion of the inter-layer space.

(ii). Dealumination: Soil colloids usually have low hydroxyl contents in them, and for them alternative mechanism for mica layer charge decrease is:

\[ [\text{Al Si}_3\text{O}_8] = 3\text{SiO}_6 + \text{Al O}_2 \] (III).

(Tetrahedral) dealumination;

\[ \text{HO. Al Si}_3\text{O}_7 = \text{Si}_3\text{O}_6 + \text{Al OOH} \] (IV)

Dealumination in weathering will be in a acid solution and aluminum will appear as cation:

\[ \text{Al O}_2^- + 4H^+ = \text{Al}^{3+} + 2\text{H}_2\text{O} \] (V)

\[ \text{Al OOH} + 3H^+ = \text{Al}^{3+} + 2\text{H}_2\text{O} \]

(iii). Desilication: If the chemical weathering process removes silica from 2:1 layer silicates to form kaolinite and gibbsite, the phenomenon is referred as desilication.

Jackson et al. (1948) in 1948 reported that in soils reverse of weathering reactions described above also take place. According to this water, silica and influx of potassium reverts vermiculite.
to mines by "slow" exchange. As a result of drying of soils with
enough potassium on the exchange complex potassium fixation occurs,
ion, potassium enters between layers having a higher exchange
charge. Jackson et al (132) in 1952 reports that a mineral with
highest potassium fixation capacity was California Mg Hectorite
having b.e.c. 125 m.e/100. He described the chemical properties
of clay minerals as a function of weathering stage.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Illite</th>
<th>Intermediate</th>
<th>Vermiculite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium*</td>
<td>10.8</td>
<td>6.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Potassium (mole)</td>
<td>1.0</td>
<td>0.85</td>
<td>0.25</td>
</tr>
<tr>
<td>M.E. m.e./100</td>
<td>1.0</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>Layer charge (trioctahedral)</td>
<td>280.0</td>
<td>180.0</td>
<td>145</td>
</tr>
<tr>
<td>m.e./100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Layer charge (dioctahedral)</td>
<td>251.0</td>
<td>185</td>
<td>170</td>
</tr>
<tr>
<td>m.e./100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxyl equivalent (mole)</td>
<td>2.0</td>
<td>2.25</td>
<td>0.40</td>
</tr>
</tbody>
</table>

H. Effect of liming on the availability of potassium

The effect of liming on availability of potassium has
probably received more investigation than any other phase of
potassium availability studies. Mac Intire (174) in 1919 reported
that liming had liberated active soil potassium. It was thought
that soluble calcium salts could liberate available potassium
by simple replacement. He added one ton per acre of each CaO
and MgO to Cumberland loam and leached the soil. He found that
potassium in leachate had decreased over that from check plots
during a two year period. Subsequently MacIntire, Shaw and Young
(176) in 1930 observed from a 12 year lysimeter study at Tennessee
experimental station that economic additions of CaO, CaC, dolomite
and limestone decreased the availability of native supplies of potassium.

In India Vishwa Nath (304) in 1925 reported that availability of potassium was influenced by liming acid soils. Harris (109) in 1937 found that liming Sassafras, Norfolk and Chester soils resulted in an increased fixation of applied potassium but the native supply was made more available.

Jenny and Shade (136) in 1934 had reported rather conflicting findings to those of MacIntire and his associates (176). Addition of calcium carbonate to permutite, bentonite clay, Putnam clay and several natural and artificial soils, resulted in the release of large amounts of potassium. It was also noted that the presence of micro-organisms had reduced the amount of potassium in the leachings as compared to those from a sterile soil. This was particularly true in the presence of CaCO₃. The results obtained by MacIntire and his associates (176) in 1930 were at least partly attributed to the retention of liberated potassium by micro-organisms.

Peech and Bradfield (238) in 1934 independently observed similar kind of results to that of Jenny and Shade (136) in 1934. However, studies made by them were with electrodialysed clays of Miami and a bentonite. It was noted that calcium saturated clays did not facilitate the conversion of exchangeable potassium to non-exchangeable forms. It should be noted that exchangeable and insoluble CaCO₃ as was present in Jenny's experiments, was only calcium present.

Work of Volk (311) in 1934 indicated that out of his eleven widely distributed soils receiving three tons per acre of calcium hydroxide, eight had shown increased fixation over non-limed checks when wetted and dried ten times at 70°C.
Mann and Barnes (182) in 1940 reported that on high leaching Wobam soils had liberated potassium during 50 years of wheat and barley cropping and further observed that on some soils, addition of small amounts of lime, NaNO₃ and (NH₄)₂SO₄ decreased the quantity of potassium leached. Exchangeability of potassium had decreased under low potassium saturation of the exchange complex. This effect is dependent on the nature of the complementary cation.

Abel and Magistad (1) in 1935, York and Roger (338) in 1947 and Hoover et al (123) in 1949 stated that liming had liberated potassium from their soils.

Ayres (15) in 1949 reported that Hawaiian Ca-saturated soils had released 2.5 times as much potassium as did H-saturated soils.

Lawton and Pierre (162) in 1946 had kept limed soils in moist incubation and then they were leached. They found that there was decrease in potassium release due to liming. Evan and Attoe (79) in 1948 described that acid soils under oat cropping had decreased in release of potassium on liming. Fine et al (82) in 1941 had reported that liming had decreased release of fixed potassium during freezing and thawing treatments. Iowa and Wisconsin (128) acid soils were shown to decrease in release of potassium by liming.

Fech and Bradfield (238) in 1934 had shown that potassium in feldspars and micas was more soluble under acid than under neutral conditions. McClelland (192) in 1952 while working with silt particles of soil forming minerals had found that potassium was released faster under acid than under neutral weathering condition.

Pratt et al (247a) in 1956 divided acid soils into two
categories. The first category of acid soils is due to Paver and Marshall (231) in 1934 who considered acid soils as Al-H-clays. Yarusov (337) in 1948 considered that the chief exchangeable ion in acid soils was Al$^{+++}$. Russel (266) in 1950 proposed that acid soils were largely Al-soils. He advocated that soils saturated with H$^+$ ions on the exchange complex (H$^+$ is dominating ion on the complex) liberate potassium from the mineral as a result of liming. In cases of acid soils on which dominating ion is Al$^{+++}$ in place of H$^+$, liming decreases the potassium release. Pratt (247) cited three important types of soils forming three series showing decreasing of potassium release by cations in a definite order.

First type of soils were that of Ohio soils. From them release of potassium by cations was in the order of Ca$>$H$>$NH$_4$$>$Al.

Second type of soils were represented by California soils in which the order in releasing potassium was H$>$Ca$>$NH$_4$$>$Al.

The third type of soils were those of New York soils. The decreasing order for release of potassium was Na$>$H$>$NH$_4$$>$Mg$>$Ca$>$Ba.

Bower and Pierre (38) in 1944 studied potassium uptake by various crops when grown on a potassium deficient high limed soil. They found that sorghum and corn gave large responses to potassic fertilizers; flex, oats and soybeans gave only slight responses; sweet clovers gave no response and buckwheat gave negative responses.

Although much work has been done on the effect of liming relative to availability of potassium, the amount of conflicting data obtained makes additional work necessary before this effect
can be definitely ascertained.

5. Mobilization of Fixed Potassium:

De Turk et al (66) in 1943 observed that under certain conditions depending on the soil type potassium may be fixed in soils in a non-exchangeable form to a limited extent, which however is recoverable in course of time of a few weeks and completely after a long time.

Walsh and Cullinan (318) in 1945 reported that fixation caused by alternate wetting and drying treatment was not permanent but mobile. This fixation was however large enough to cause severe potassium deficiency symptoms in the first crop of mustard in pots while the growth of a second crop revealed a release of potassium from the fixed condition.

Ayres et al (17) in 1947 reported that Hawaiian soils under napier grass released 3,400 to 4,200 lb. K₂O per acre in 4½ years from non-exchangeable forms with little corresponding decrease in the level of exchangeable potassium. Attoo (10) in 1948 shows oats crop recovered almost all non-exchangeable potassium fixed by adding potassic fertilizer. This seems to be the opinion of many other workers although Kolodny and Robbins (155) in 1940 declare that the fixed potassium is only slightly available to plants. Hoover, Jones and Cholston (123) in 1949 have stated that the fixed potassium obtained by alternate wetting and drying treatment was more readily available from soils which were more weathered or contained 2:1 clay mineral types or limed to pH 6.6 to 7.2 as compared to others less weathered or containing 1:1 clay mineral types or pH 5.7 to 6.6. This reveals that the potassium of the secondary minerals is more readily available than the potassium of the primary minerals;
and as the primary minerals are not ordinarily expected to be present in the clay fraction, fixation of potassium takes place more in the clay than in any other mechanical fractions. The potassium of silicates like feldspars is relatively less available.

Sen, Deb and Bose (279) in 1949 stated that part of both citric acid soluble potassium and that actually adsorbed by rice crop from the red and lateritic soils of India came from the non-exchangeable form and was determined by the nature of the fertilizers or manures added.

York and Roger (339) in 1947, Ayres (15) in 1949 and Merwin (198) in 1951 stated that potassium might be released in faster rates by calcium saturated soils then the hydrogen saturated ones.

Russe, E.W. (267) in 1954 stated that the Rothamsted clay loam at pH 7.00 was not able to supply enough potassium to give even a moderate potato crop, although its clay contained a high proportion of illite whereas Woburn sandy loam at pH 5.5-6.0 containing degraded illite gave sufficient potassium supply for a moderate crop. Soils at Rothamsted and Woburn had received the same dressings of nitrogen and phosphate.

Chamber (52) in 1953 studied release of potassium by wheat crop from the various plots on Broadbalk. He found that from the plots which had only received ammonium sulphate and superphosphate wheat crop removed potassium to the extent 1.5 tons/ha during 78 years as compared with about 3.5 tons/ha from plots which had potassium fertilizer in addition to nitrogen and phosphate. The exchangeable potassium in the top soil receiving no potassium, fell by an amount no greater than about 200 Kg/ha. He further showed that from the plot receiving potassium...
fertilizer nearly 7.5 tons per ha. of potassium during 108 years, 3.5 tons were removed by the crop so that soil gained about 4 tons per ha. of potassium and the exchangeable potassium in the top soil increased only by 300 Kg/ha.

Lueb et al (170) in 1956 reported that moisture plays an important role in release of fixed potassium. He found that air drying and remoistening at certain staging soils release but on rigorous air drying and then moistening exchangeable K goes to non-exchangeable K. Potassium supplying power must be determined on moist soils.

6. Inorganic Fixation:

Two distinct kinds of inorganic fixation have been reported by several workers, one brought by drying, particularly alternate wetting and drying, and the other taking place even in continuously moist condition.

(1). Moist condition fixation:

Volk (307) in 1938, Hauser (110) in 1941, Raney and Hoover (252) in 1947, Attoo (10) in 1948, Stanford (287) in 1948 and many other workers have studied the fixation under moist conditions and moist storage. Raney and Hoover (252) recorded that 23% of the 2160 p.p.m. of the potassium applied to the montmorillonite soils became fixed during one month moist storage. With kaolonite soils moist fixation was much smaller. Illinois soils were also found to fix potassium in small amounts in moist conditions. It was also observed that potassium fixation in moist conditions was very low and slow.

Stanford (287) in 1948 stated that certain calcareous soils containing micaceous minerals rapidly fix potassium under moist conditions. In acid soils fixation was slow. In acid
illitic soils Fe and Al ions are present in the lattice and they restrict the entrance of potassium and hence little or no fixation occurs in moist conditions. Removal of Al ions by precipitation increased the amount of fixed potassium under these conditions. Rapid fixation of potassium in calcareous soils was explained by the fact that they contained Ca, Mg and Na ions in positions potentially capable of fixing of potassium. On adding potassium ions these ions are easily replaced and when the concentration of potassium in soluble and exchangeable forms exceeds 0.40 m.e./100 gm. soil, the fixation is attained in 48 hours. Addition of lime and phosphorus fertilizer increases potassium fixation in illite clay under moist conditions when pH is near and above neutral point; and considerable amount is fixed when the mineral is dried.

Montmorillonite fixes much potassium under similar conditions. At pH 4 to 5 montmorillonite fixes practically no potassium under moist conditions but it fixes large quantities on drying.

Marel (185) in 1955 while working on Dutch soils reported that potassium fertilization reduces fixation in such soils by wet process. This was particularly noted in soils having high fixation capacity and which were fertilized with large amounts of potassium. He declared that by fertilization 26% potassium can be increased on the exchange complex in the exchangeable form.

(ii). Fixation under Drying Conditions:

Raney and Hoover (252) in 1947 showed that montmorillonite soils fixed 12 to 57% potassium out of 2160 p.p.m. of the applied potassium on subsequent drying. They also noted that kaolinite soils released fixed potassium on air drying. Light soils gave good response to fixation under these conditions. Several workers
have shown that the potassium fixation is reduced by preventing the tendency of the soil to dry out and the greatest fixation occurs in those layers in the soil profile that are subject to alternate wetting and drying. Truog and Jones (298 and 299) in 1938 attributed this type of fixation to the strong attraction offered by adsorbed potassium which prevent a re-expansion of the crystal lattice and hence re-entrance of water. Hendrick and Dyal (118) in 1950 and De Castro (64) in 1950 have shown that potassium fixation is accompanied by a loss of water of hydration and reduction in surface area of the clay. Kaolinites are not known to take part in inorganic fixation.

Stanford (287) in 1948 agreed with the explanation given by Truog and Jones (298,299) in 1938 and he considers this kind of inorganic fixation due to drying, occurring with montmorillonite type of clay minerals and is of a small value compared to the fixation taking place under humid condition by exchange reactions with illite and other micaceous minerals. Seatz and Winter (277) in 1944 also confirm that soils containing micaceous minerals possess the greatest potassium fixing capacity.

Ayres (13) in 1941, Hauser (110) in 1941 and Martin (189) in 1946 report that the concentration of potassium solution, critical moisture content and high temperature favour fixation of potassium. Pathak et al (226) in 1949 reported on the fixation of potassium by manured and unmanured soils at different depths and also by their clay fractions.

Volk (308) in 1942 compared the potash fixing powers of pure clay minerals and of some soils. He concluded that the clay fraction of a soil had the highest fixing power. He cited the following figures of potassium fixing capacity for various minerals:
(a) Powdered kaolinite 440 p.p.m., (b) Muscovite 0 to 1700 p.p.m., (c) Bentonite 8850 p.p.m.

These figures depend on the nature of the cation in the exchangeable complexes and in the fixed position which explain differences in the order of fixation for different clay minerals obtained by different workers.

Jacob (134) in 1940 ascribes the very high fixing power in tropical soils to montmorillonite. According to Hauser (110) in 1941 mica minerals were most strongly potassium fixing agent.

According to Levine and Joffe (165,166) in 1947, Page and Fever (223) in 1940, Stanford (287) in 1948, Truog and Jones (298) in 1938, Wear and White (323) in 1951, Wiklander (327) in 1950 and Marahad (24) in 1948 that potassium is definitely fixed in non-exchangeable forms by montmorillonite, hydrous mica, vermiculite and there is practically no fixation by kaolinite. Drying appears necessary for the fixation to occur in montmorillonite but not in hydrous mica. Both groups of clay minerals often occur together in soils. Moisture conditions of soils in the field are extremely variable, and it is difficult to predict the behaviour of the field soils with regard to the fixation of added potash. They also state that a necessary condition for fixation is the co-existence of a moderate or high level of readily exchangeable potassium. The various forms of soil potassium comprise an equilibrium system, so that potassium tends to be fixed when the exchange level is above the equilibrium value and to be released when it is below this value.

According to Wear and White (323) in 1951 potassium fixation in the expanding 2:1 lattice type of clay minerals is currently regarded as the entrapment of potassium ions between some lattice sheets which do not readily re-expand due to the
presence of critical sized potassium ions and lack of hydration.

DeTurk, Wood and Bray (66) in 1943 state that in the non-expanding or slightly expanding hydrous mica lattices, fixation of potassium is probably a restoration of interlayer potassium that had been previously removed by weathering processes or similar leaching stress. They refuted the statement of Cheminade (54) of unavailability of fixed potassium and they declared that it is not wholly wasteful as it retards less by leaching and some of the fixed potassium was available when the exchangeable level became reduced again.

The existence of montmorillonite, mica, hydrous mica, vermiculite, intermediate hydrous mica and kaolinite minerals have been claimed in soils by workers mentioned above. Barshad (23) in 1952 found sweeney soil clay to contain hydrobiotite which is an inter-stratified mineral compound of alternate layers of vermiculite and hydrous mica.

Joffe and Levine (141) in 1940 showed that this fixation of potassium was peculiar to this element as other cations like Na, Ca, Mg etc., do not appear to be fixed in this way.

7. Organic Fixation

In 1943 Hurwitz and Batchelor (127) found micro-biological fixation of potassium in unleached form of soil on adding plant material to neutral silt loam. This kind of fixation can occur in many soils when they are manured with organic matter under moist condition. The potassium fixing bacteria takes up potassium from the added organic and inorganic matter including the silicate material. In 1949, Aleksandrov (4) reported that bacillus siliceous had the ability to decompose alumina and silicates and fix potassium in their body to begin with and after their death, their bodies decompose and render potassium available. Pchelkin (233) in 1946 showed that chernozeme soils treated with H₂O₂ reduced the potassium fixation.
8. Organic Versus Inorganic Fixation

Martin et al (189) in 1946 reported that potassium fixation in arid soils was mostly inorganic because bacterial population do not thrive well in them. Joffe and Levine (139) in 1947 showed that organic matter reduced inorganic fixation. They explain it on the basis that potassium salts of organic acids are weak and can ionise less thereby reducing the effective concentration of the potassium ion in solution, which can be converted into exchangeable and from there into the fixed condition. Possibly the organic matter blocks the attraction spots in the mineral lattice responsible for potassium fixation. Martin et al (189) in 1946 stated that the reduction of fixation by organic matter may be due to its action to prevent the shrinkage of the crystal lattice which was found responsible for some types of inorganic fixation.

9. Theories and Mechanism of Potassium Fixation

In the past decade the process by which exchangeable potassium became non-exchangeable, i.e., not extractable by neutral salts, hereafter referred to as "potassium fixation" has been a subject of considerable interest and investigation.

Earlier Concept:
(1) Muscovite formation theory

Volk (309) in 1933 showed that alternate wetting and drying of soils facilitated potassium fixation. It was then found that the fine clay fraction was capable of effecting more potassium fixation than any other soil separate. X-ray studies of a Hagerstown silt loam to which 5,000 lb./acre of potassium chloride had been applied over a period of 50 years led him to postulate that potassium reacts with the silicate to form difficultly soluble
The theory of muscovite formation in soils does not explain many of the experimental facts, namely, potassium fixation under moist conditions, fixation by primary and secondary minerals, release of non-exchangeable potassium from the mineral separates of the soil, change in properties of the soil separates, changes in the ratios of the competitive cations on the complex etc. etc.

(ii) Colloid-electrokinetic Theory:

According to Gorbunov (99) in 1936 silica gels fix potassium by the occlusion process depending on the electrokinetic conditions of the soil or soil separates. Chaminade and Drouineu (54) in 1936 thought that potassium fixation is caused by the migration of the potassium ion from the surface of a colloid to the interior of the crystal which is coated by the colloid. Since soil colloids are considered crystalline so this theory fails to represent the phenomenon fully.

(iii) Conversion of one form of Mineral to another:

Gholston and Hoover (93) in 1949 showed that chief minerals in the soil separates containing non-exchangeable potassium are feldspar, muscovite, biotite and the hydrous mica. These are the silicates in which potassium enters to compensate the loss of positive charge resulting from the part replacement of Si\(^4\) by Al\(^3\) in the silicate tetrahedra. Pauling (229) in 1930 and Grunner (107) in 1939 while working on micas and glauconite showed that potassium of these minerals could be replaced to certain extent by other cations. Barshad (24) in 1948 reported that by leaching biotite with magnesium chloride it could be converted into vermiculite. He was able to bring about a reverse change. Thus it is clear that the reactions are possible for the entry
of potassium into fixed positions in certain minerals and its release by prolonged leaching with suitable reagents. Thus according to this theory the conditions of fixation appear to be capable of being reversed. Volk (307) in 1938 explains this fixation to different processes and he does not think that it is due to any single soil mineral.

(iv) Base Exchange Capacity Theory:

Volk (307) in 1938 found that free alumina was in most cases closely correlated with the ability to fix potassium. On the treatment with hydrochloric acid which removed considerable quantities of alumina and silica resulted in a decreased potassium fixation capacity. Subsequent addition of colloidal alumina gave slight increased fixation. He proposed the possibility of replacement of one-fourth of the silicon atoms in the surface occurring in the tetrahedral layers of the crystal lattice of phyllite by aluminium atoms. The two positive charges arising from the substitution of two aluminium for two silicon atoms could then be satisfied with two potassium atoms.

An investigation of the fixation capacity showed that bentonite having a high base exchange capacity effected the most fixation. Truog and Jones (298) in 1938 followed up Volk's work of investigation of the fixation capacities of various clays showing that they were roughly parallel to the base exchange capacities. The clays on which these workers had investigated had base exchange capacity ranging from 4.3 to 130.1 m.e./100 gm. soil. Their work showed that fixation capacities of these clays were running parallel to the base exchange capacities of same clays. Thus it was concluded that base exchange material was responsible for effecting potassium fixation. To get definite proof of this they attempted to show relationship between the
decrease in base exchange capacity and the fixation capacities of the clay. Joffee and Kolodny (143) in 1939 showed that there was a decrease in base exchange capacity as a result of potassium fixation but the decrease was not necessarily equivalent to the fixation capacity. Later work of Joffee and Levine (141) in 1940 with soils of Chester, Montalto and Gloucester led to the conclusion that "except perhaps in the case of Montalto there is not a faintest hint of the equivalence between fixation and decrease in the exchange capacity". This work is open to criticism because the exchange capacities as well as fixation capacities were so low that experimental error could invalidate the results obtained.

Joffee and Levine (139, 140) in 1947 reported the amount of potassium fixed actually increased with the amount of potassium adsorbed into exchange complex and that potassium from a fertilizer must first be absorbed on the complex before it can be fixed. This explains the role of cations already adsorbed into exchangeable positions in the exchange complex before it can be fixed. Thus if the exchange complex has Ca, Na, Mg etc., cations on it they must be replaced by potassium before any fixation can be effected. NH₄ and H cations are difficult to be replaced by potassium.

(v). Iron, Aluminium, Calcium, Phosphate Complex Theory

Joffee and Kolodny (144) in 1937 showed that phosphate complexes of iron, aluminium, calcium and magnesium were capable of fixing potassium. This probability was further studied by Wood and DeTurk (333) in 1940. They found that when potassium phosphate was used as a manure to Toledo and Dixon soils, an excessive amount remained non-extractable with boiling N HNO₃ for ten minutes over that when added potassium chloride. The water extractable potassium was also lower in the case of phosphate addition than in that of the chloride application.

(vi). Ionic size and drawing together sheet plates
Page and Baver (223) in 1939 proposed a mechanism for potassium fixation based on ionic size and drawing together during drying of individual sheet plates comprising the crystal lattice. It is shown that fixation of Ca, Ba, Fb, NH$_4$, etc., by Miami and bentonite colloids correlate very well with the closeness of the dehydrated ionic sizes into the size of the "holes" in the exposed oxygen tetrahedral of the plates in the crystal lattice of the clay. The potassium ions with a diameter 2.66 Å most closely approaches 2.8 Å diameter of these openings. It was postulated that the drawing together of the plates during drying forced potassium or other allied ion into these openings. Potassium, because of its close placement at the seat of charge and its inaccessibility, is displaced with greatest difficulty and consequently is fixed in the greatest quantity. This theory appears to be very logical explanation for potassium fixation. There are several points, however, which are open to criticism. Among them are:

Firstly, after potassium fixation treatment the plates of the crystal lattice are assumed to remain together upon addition of water. This condition is attributed to the inability of the fixed potassium to re-hydrate itself without regard to the possibility of re-hydration of the exchangeable potassium. Secondly, addition of a solution of 0.75 N with respect to (C$_2$H$_5$)$_2$NH$_2$ and 0.25 N with respect to K$^+$ to a clay was assumed to effect a 75% (C$_2$H$_5$)$_2$NH$_2$ and 25% K distribution on that clay. This was arbitrary as it was not based on any experimental facts. Thirdly, no explanation was given as to why a potassium could not be forced into each space in the surface occurring oxygen tetrahedral. If this were possible, the resulting clay would contain, in the case of montmorillonite, approximately 21.6% potassium. At a maximum fixation capacity, however, this clay contains only 1.2 per cent. Fourthly, the (C$_2$H$_5$)$_2$NH$_2$ ion applied with potassium in the same ratio as above
was assumed to prevent sufficient drawing together of the lattice plates for entrapment. Fifthly, this theory does not explain why Ba with a diameter 2.62 Å comparable with that of potassium does not show this fixation in illites, while hydrogen with an infinitely small diameter shows it.

(vii). Henin's Theory:

According to Henin (119) in 1950 crystalline structures take up potassium in non-exchangeable forms and are converted to a stable form of mineral, namely, montmorillonite and vermiculite into mica, halloysite into metahalloysite and montmorillonite into chlorite. His mechanism offers explanation for fixation of cations between the sheets of montmorillonite and on the surface of each type of clay mineral through precipitation of hydroxide.

He also suggests other possibilities, namely, the migration of the cations into structure. This explanation may apply to mica and montmorillonite. He also considers that cations might become entrapped in a floc of colloidal complex.

(viii). Theory of competing of complexes for Co-ordination

Compound formation (751) 

Ionic potential (Valency) plays an important role in the explanation of fixation of cations in crystalline structures of silicates. On this property depends the capacity of the cations to form hydrates and complexes. The values of ionic radius and ionic potentials according to Emeléus and Anderson (77) in 1938 are tabulated herewith.
The above table shows how cations of potassium and barium are very much separated by their ionic potentials which when it is greater, greater is also the capacity for hydrate formation etc. The ability to enter fixed positions in 12 co-ordination in those alumino-silicate lattices is determined by the competitive capacity of alumino silicate oxygen structures to compete with the hydration complex for the cation. Therefore, if the cation has higher ionic potential and found highly hydrated in aqueous solution, the less will be the capacity of the alumino-silicate oxygen structure to take away cation from hydration complex. This theory explains how potassium and barium ions are far separated having ionic potentials equal to 0.71 and 1.4 respectively with Ba requiring a stronger force to pull it from its water hull.

The radius ratio measures the co-ordination number of the cations in ionic crystals (293), because the number of the anions that can be accommodated tightly around the cation is obviously determined by their relative sizes. A cation can co-ordinate six anions when this ratio is between 0.41 and 0.73 and eight when the ratio is between 0.73 and 1.0. When this ratio is 1.0
the metallic bond with the capacity to hold 12 partners arises under adequate circumstances. In micaceous structures a cation can co-ordinate six from each of the two adjacent alumina layers. A cation that can co-ordinate all the 12 and can fit into the space between them, that would form a compact structure from which once formed it would be hard to replace cation by ordinary exchange reaction. The radius ratios for the cation and anion shows that potassium can form 12 co-ordinate structure while Ba Cannot.

Since potassium fixation in clay minerals is an exchange reaction therefore in addition to the mass action law, the phenomenon of potassium fixation will depend, firstly, on competitive capacity, secondly, on co-ordination number of the cation with oxygen, thirdly, on size of the cation and the fit it makes in the vacant space and fourthly, the number and the positions of the oxygen atoms available for co-ordination from the two adjacent silica layers in different clay minerals. All of these conditions are fully satisfied in illite and micaceous minerals in respect to potassium or ammonium but not to Ba. If the Hoffmann's structure of montmorillonite is accepted then the conditions in the montmorillonite must be the same as that in illite. But Page and Baver (223) had found high fixation of Ba in the montmorillonite, and hence the bond attaching this cation must be stronger here than in the illites or micas so as to offer a force greater than that between Ba and its water hull, while the number of co-ordinated oxygen atoms must also be less than twelve which is not the case with the Hoffmann's structure. Thus the facts appear to support Edelman's (73) structure wherein the bonds are Si-OH type and not simply blocked Al-tetrahedra. The strength of the bond is determined by the fact that fixed potassium by drying
montmorillonite could not be extracted with N/2 hydrochloric acid while that of micas occurring under moist conditions could be extracted. The position of the potassium can be compared with feldspars rather than with the micas. For the determination of the relative or specific cation fixation capacity for Ba, Pb, Ca and NH₄, neutral salt solution for leaching but with low fixing capacity should be used so as to avoid erroneous conclusions. Joffee and Levine (141) in 1940 used NH₄ salts for leaching montmorillonite and since NH₄ has high fixation capacity itself, so Ba fixation was marked in montmorillonite. Page and Baver (223) in 1939 used acid leaching reagent and had shown fixation of Ba.

For the fixation capacity of H-ion there are two views. One of the views considers the H-ion effects on the presence of polyvalent Al³⁺ and Fe³⁺ which were produced by the destruction of some of the complexes during the process of introducing H-ion into complex. Second view attributes direct effects to the H-ion. Since H-ion has exceedingly small radius, there is a deficit of positive valency and remain close to the Al-ion after it has substituted Si⁴⁺ in the layer and framework of silicates. It will then be near and compact as possible compared to the unsubstituted tetrahedra. Therefore, it is difficult for bigger cations to replace this H-ion so entangled by exchange reactions. That is how if H or NH₄ ions which can themselves go into the fixed condition are present in the exchangeable, it is difficult even for potassium to compete and replace Ca, Mg, Ba and Na etc. Therefore effect of liming on potassium fixation and its release reported by a number of workers is produced by replacing the tough H by Ca in the exchangeable position and subsequent replacement of Ca by potassium resulting in an alteration in the fixed
potassium.

No theory as yet adequately explains the mechanism by which potassium becomes fixed. It is not clear whether the drawing together of the plates of the crystal lattice is a cause or a result of potassium fixation. It is not known whether the fixed potassium would remain as such should the lattice plates draw apart. No theory has explained why the entire exchange capacity of clays cannot be negatived by fixed potassium, or why potassium fixation expressed as a percentage of the original exchange capacity of the material is not the same for clays.

Works of Raney and Hoover (252), Barshad (22, 24), Wiklander (327, 328) and many others showed that the site of potassium fixation lies in the type of clay minerals. According to them mica, hydrous mica, montmorillonite, and vermiculite minerals of 2:1 type are responsible for potassium fixation under field conditions. Potassium bearing clay minerals are weathered in the tropical soils as a result of leaching and lose potassium and become "degraded" form of hydrous mica.

10. Replacing powers of Different Cations from Exchange Complex: Russel (266)

Any cation except hydrogen can neutralise negative charges present on the clay particles and therefore these charges are accessible to a fairly large cations. Organic radicals and large cations (75, 95 and 115) can neutralise charges between montmorillonite layers and may force them apart as far as 48 A. This accessibility of the charged spots is a special characteristic of clay minerals. The base exchange equilibria in clays are reached very quickly.

Different cations are absorbed on clays with different intensities. For example, if Ca-saturated clays are shaken with
dilute salt solutions of different bases, but all of constant normality, it is found that some cations are more powerful replacers of calcium from the clay surface than others. Thus it was observed that Li⁺ and Na⁺ ions are poorer replacers of base from a clay than K⁺ or NH₄⁺ ions. Rubidium or caesium are better replacers than NH₄⁺ and K⁺. Place of Ca and Mg is the same as for Rb and Cs but they are poorer placers of base than Sr or Ba. H⁺ ion from strong acids, trivalent lanthanum and tetra-valent thorium are still stronger displacers of bases than the divalent cations.

Replacing power of different cations:

m.e. of Mg, Ca or Ba displaced from 100 gm. soil (Chernozem) by certain ions added as chlorides. Table is taken from Gedrois (92).

<table>
<thead>
<tr>
<th>Chlorides added</th>
<th>Mg</th>
<th>Ca</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. of chlorides</td>
<td>0.1N</td>
<td>0.01N</td>
<td>0.1N</td>
</tr>
<tr>
<td>Li</td>
<td>7.5</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>9.1</td>
<td>1.8</td>
<td>13.4</td>
</tr>
<tr>
<td>K</td>
<td>13.5</td>
<td>5.0</td>
<td>20.4</td>
</tr>
<tr>
<td>Rb</td>
<td>15.5</td>
<td>5.7</td>
<td>20.4</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>12.9</td>
<td>5.7</td>
<td>20.4</td>
</tr>
<tr>
<td>Mg</td>
<td>15.4</td>
<td>5.3</td>
<td>20.4</td>
</tr>
<tr>
<td>Ca</td>
<td>20.4</td>
<td>35.2</td>
<td></td>
</tr>
</tbody>
</table>

The difference of replacing powers between monovalent or alkali cations and divalent alkaline earth cations depends on their concentration in solution. The more dilute the solution containing the cations, the more powerful are the alkaline earths relative to the alkali cations as displacers of exchangeable cations. Therefore it can be said that an increase in ionic concentration in the solution will increase replacing powers of
alkali bases relative to the divalent alkali earths.

Schofield's ratio law (266) states: "When cations in a dilute solution are in equilibrium with a larger number of exchangeable ions, a change in the concentration of the solution will not disturb the equilibrium if the concentrations of all monovalent ions are changed in one ratio, those of all the divalent ions in the square of that ratio, and those of all the trivalent in the cube of that ratio".

Summary of the base holding mechanism in soil as given by Pussel (266) on page 117:

Soils can hold bases through the mechanisms cited below:

"1. Permanent negative charges on the clay and other minerals due to isomorphous replacement. These minerals need not occur in the particle size range of the clay fractions, though for most soils they do. Soil containing vermiculite and other sponge-like minerals can have these minerals occurring in the silt or fine sand fraction.

2. Negative charges developed by hydrogen ions dissociating from hydroxyls attached to silicon atoms at the broken edges of the clay mineral. This reaction can be written:

\[ \text{Si} - \text{OH} + \text{H}_2\text{O} \rightarrow \text{Si} - \text{O}^- \cdot \text{H}_3\text{O}^+ \]

It only occurs under neutral or alkaline conditions and the more the alkaline conditions the greater is the negative charge developed".

(B). Potassium Fixation in Indian Soils and its availability to the crop

Vishwa Nath (304) in 1925 is reported to have studied availability of potassium as influenced by liming of acid soils of India. Nandy (214) in 1946 studied both potassium fixation and its release while liming acid soils of Bengal. He reported
that potassium fixation or its release by liming occurred only between pH 6 and 7.00. Pathak, et al (226,227) in 1949 and Pathak (228) in 1954 studied potassium by manured and unmanured soils at different depths and in different fractions both before and after destruction of organic matter. They confirm that micaceous soils have high fixation capacity and organic matter reduced this amount. Because they find high values for silt also, it is felt that perhaps it is possible to presume that primary micas are taking part in this phenomenon. They observed that the unmanured wheat soil had the maximum potassium fixing capacity in the surface soil only while the manured soil had it in the 2nd ft. layer. Vidyanathan's report (304) in 1936, reads that potash has not been given fair trials in India in past experiments Titabar Farm in Assam significantly increased yield of paddy as a result of manuring soils with potassic fertilizers that year and soil after this crop gave better response to the second crop.

Sethi, Ramiah and Abraham (281) made a very important statement which runs as:-

"Since none of the experiments in any part has indicated any effect, beneficial or harmful by the application of potassium, it has not been left out of discussion. It is also surprising that potassium has also shown no interaction with nitrogen or phosphorus in any form or with their combination".

Stewart (296) in 1947 stated in his report to the Government of India that there were references here and there on positive responses of potash manuring and increases in yield. He cites the cases of wheat responses at Nagpur, Saugor, Sabhnaid and Powerkhara in Madhya Pradesh and Patna in Bihar. Responses to potassic manuring in 15 groundnut trials at Akola in Madhya Pradesh were also recorded.
Malye (181) in 1952 reports that good effects of potassic manuring was observed on cotton in Ahmednagar in Bombay State.

Rama Moorthy, Desai and Raychaudhuri (251) published a review on potassium fixation in soils with reference to India, in which they report that potash availabilities in Indian soils are related to geological origin. According to them soils from Gangetic alluvium to bordering the Vindhyan system have generally low potassium availability or high potassium fixation capacity while soils of the crystalline gneiss or coastal alluvium bordering cretaceous or the Gondwana systems had high availability or low fixation capacity.

Kochhapa (154) and Jonee P. De (146) in 1951 reported that coconut and ten crops responded very well to the application of potash. They recommended that phosphate could be omitted from fertilizers containing nitrogen and potassium to get the best results.

Mukerji (208) in 1952 reported that certain soils in Bihar responded very well to potassic manuring for wheat and oat crops grown at Jallalgarh and Isalampur respectively and gave an increase in yield by 2 to 3 maunds per acre.

Private communication of T.C.M. relating to fertilizer agronomical trials on paddy to Chemistry Division (341) -- 1953-54, reveals that Bihar, Madras and Rajasthan soils gave good responses to application of potassic fertilizer when combined with nitrogen and phosphate fertilizers.

Kibe and his co-workers (150) in 1953 reported that black cotton soils released potash by the application of sodium chloride.

Sen (278) in 1954 stated that potash was needed by sugar-cane crop throughout its growth for better out-turn while N and P were required for early stage.
Desai (341) (unpublished) at the Indian Agricultural Research Institute, New Delhi, tabulated the uptake of potassium by different crops.

<table>
<thead>
<tr>
<th>Crop</th>
<th>Yield (Lb/acre)</th>
<th>K2O taken up (lb/acre)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat</td>
<td>2,400</td>
<td>60</td>
</tr>
<tr>
<td>Rice</td>
<td>2,000</td>
<td>60</td>
</tr>
<tr>
<td>Jawar</td>
<td>1,600</td>
<td>130</td>
</tr>
<tr>
<td>Faupra</td>
<td>1,000</td>
<td>59</td>
</tr>
<tr>
<td>Maize</td>
<td>1,800</td>
<td>35</td>
</tr>
<tr>
<td>Barley</td>
<td>1,000</td>
<td>31</td>
</tr>
<tr>
<td>Gram</td>
<td>700</td>
<td>44</td>
</tr>
<tr>
<td>Sugar-cane</td>
<td>60,000</td>
<td>180</td>
</tr>
<tr>
<td>Groundnut</td>
<td>1,700</td>
<td>40</td>
</tr>
<tr>
<td>Rape and Mustard</td>
<td>600</td>
<td>25</td>
</tr>
<tr>
<td>Linseed</td>
<td>900</td>
<td>29</td>
</tr>
<tr>
<td>Castor</td>
<td>2,000</td>
<td>56</td>
</tr>
<tr>
<td>Cotton</td>
<td>400</td>
<td>40</td>
</tr>
<tr>
<td>Jute</td>
<td>1,400</td>
<td>60</td>
</tr>
<tr>
<td>Tea</td>
<td>800</td>
<td>25</td>
</tr>
<tr>
<td>Coffee</td>
<td>800</td>
<td>30</td>
</tr>
<tr>
<td>Tobacco</td>
<td>1,300</td>
<td>81</td>
</tr>
</tbody>
</table>

(C). Manuring Policies adopted by developed Countries after ascertaining Potassium supplying powers of their Soils.

Agriculture Departments of U.K., U.S.A., Russia and other European countries (245) from their fertilizer agronomical trials arrived at the conclusion that for obtaining a good yield of crop the soil must be supplied with a balanced manuring with respect to N, P and K supply.

For example Agriculture Department of Switzerland (245)
reported that their 1/3 of the soils needed potash, more than 1/6 needed replacement of potassium withdrawn by crops and at least 2/5 have greater or lesser reserve stock of easily assimilable potassium.

Finnland, Denmark, Norway, Sweden have given suitable ratios of N,P,K, which are maintained in their commercial fertilizers so as to balance manuring in their respective soils. The ratios maintained by these countries are:

<table>
<thead>
<tr>
<th>Country</th>
<th>N</th>
<th>P2O5</th>
<th>K2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Finnland</td>
<td>1</td>
<td>3.07</td>
<td>1.65</td>
</tr>
<tr>
<td>Denmark</td>
<td>1</td>
<td>1.17</td>
<td>1.84</td>
</tr>
<tr>
<td>Norway</td>
<td>1</td>
<td>1.06</td>
<td>1.02</td>
</tr>
<tr>
<td>Sweden</td>
<td>1</td>
<td>1.56</td>
<td>1.34</td>
</tr>
</tbody>
</table>

From the review it is clear that the study of potassium fixation in soils and clay minerals is important as it has a great bearing on soil fertility.

Hence the present investigation was planned out to collect exact information on fixation and release of potassium in Indian soils, soil colloids and clay minerals.

(D) Scope of the Investigation:

The present investigation aims at to study the problem of potassium fixation and its release using representative soils, primary minerals and clay minerals.

(i) Distribution of potassium in soils and their mechanical fractions. Composition of soils and soil fractions were determined.

(ii) Distribution of potassium in minerals. Composition of minerals was also determined.
(2) Physical and Chemical methods to effect potassium fixation in silicates.

(3) Quantitative aspect of potassium fixation both in moist and drying condition.

(4) Determination of factors which are largely responsible for this phenomenon.

(5) To make note of the properties of silicates which are changed as a result of potassium fixation.

(6) Physical and Chemical methods to release potassium.

(7) Conversion of one type of clay mineral to another.

(8) Application, if any, of potassium fixation and its release in the study of clay mineralogy.

(9) To answer a pertinent question:-
"Does potassium come out of the lattice cavity when the lattice sheets are expanded".

(10) To find facts to support further the explanations advocated by present theories on the subject.
SOIL SAMPLES WERE COLLECTED
SHOWING PLACES FROM WHERE
MAP OF INDIA
FERTILISATION FIXATION

POTASSIUM FIXATION
KAOLINE
VERMICULITE
MUSCOVITE
BOULTITE
BENTONITE
SOIL SAMPLES