CHAPTER V

Summary and Conclusion

(A). Fixation

Numerous investigators have shown that exchangeable potassium held by inorganic base exchange material of soil may become non-
exchangeable. This change is commonly known as potassium fixation. Since some of the cash crops need luxurious amounts of potassium for their growth, a farmer needs exact information regarding the fate of potassic fertilizer that he adds to the soil. Although several theories have been advanced to explain the mechanism by which this occurs but none of these seem to explain the fixation phenomenon involved adequately. It was thought that by measuring the potassium fixation capacities of various clays and by studying the composition of the clays and their properties before and after potassium fixation and also by studying the potassium release from the fixed state might give some clue concerning the mechanism of the potassium fixation.

It has been shown by various investigators that inorganic fixation may occur in the clays or soils in the moist and drying conditions. Exchange complex must be saturated with potassium before potassium fixation can occur. Alternate wetting and drying of a potassium saturated exchange complex causes maximum potassium fixation in them. In this investigation potassium fixation consisted of giving alternate wetting and drying treatment to the potassium saturated exchange complex which was once washed with benzene before drying. At the end of each treatment base exchange material was dried at 105°C for 12 hours.

Thirteen soils covering ten localities in five States of the Indian Union representing all types of soils occurring in
India and five minerals of purity were selected for this study.

Previous investigators have shown that the exchange material decrease in base exchange capacity, increase in potassium content, and the lattice plates contract as a result of potassium fixation.

A few factors which influence this fixation were studied. The present investigation studied larger range of factors which were responsible for influencing potassium fixation and also took into consideration properties which were changed as a result of potassium fixation in them.

Potassium fixation under the influence of the following factors were studied:

1). Nature and type of clay mineral
2). pH
3). Rate of fixation and defixation.
4). Concentration of the salt solution and the saturation of the complex.
5). Wet and drying conditions.
6). Nature of the associating cations.
7). Relative humidity.
8). Base exchange capacity.
9). Drying in the presence of the dehydrating organic liquids.
10). Liming.
11). Contact of the organic liquids.
12). Large cations and organic radicals, etc. etc.

All the above factors except the eleventh factor (Contact of organic liquids) showed positive influence.

K-saturated clay did not fix potassium when shaken for 48 hours in presence of organic dehydrating liquid, showing that K-ion does not travel towards lattice in presence of non-polar
solvents.

It was noted that potassium was fixed in the clay minerals and soil fractions depending on their type and condition. The order of potassium fixation is as follows:

Vermiculite > Illite > Montmorillonite > Muscovite > Biotite

Drying and dehydration caused greater amount of potassium fixation. pH higher than neutral point shows higher fixation whereas pH lower than 4.5 shows no fixation of potassium. Potassium fixation increases with increase in concentration. Whole soil and its fractions fixed potassium. Particles of less than 2 u fixed potassium more than the particles of greater sizes. Calcium and sodium cations increased the fixation under certain conditions. Other cations also directed their influences according to their directive forces. The presence of NH₃ and Mg on the complex did not induce large fixation. Attempts were made to find out if any cation or radical would inhibit K-fixation completely. To achieve this, cations and radicals of large radii were selected and it was noted that an appreciable fixation had taken place in each case. In the presence of diethylamine and Ca, potassium was oriented in preference to both cations to enter itself to the region of base exchange chance and thus got itself fixed. The same observation was made when the complex was saturated with organic radical before the potassium fixation treatment was given to it.

Since potassium fixation is related to soils it was thought to find out whether the clay can fix potassium under high relative humidity. It was noted that there was appreciable fixation when clays were dried at room temperature at 87 per cent relative humidity.
An experiment was arranged to study the influence of cations other than potassium, on the potassium fixation in clays. It was noted that the order in which potassium fixation was effected due to the presence of associating cation is as follows:

\[ K^+ > Na^+ > Ca^{++} > H^+ > Mg^{++} > NH_4^+ \] in montmorillonite and

\[ K^+ > Ca^{++} > H^+ > Na^+ > NH_4^+ > Mg^{++} \] in illite clay.

Base exchange capacity of the clay was decreased as a result of potassium fixation.

Five properties of clays related to base exchange reactions and hydration were changed as a result of fixation:

1. **Total content of crystal potassium increased.**
   *K-fixer***

2. **Base exchange capacity decreased equivalent to potassium fixed.** Hence a law of equivalence between K-fixed and the base exchange capacity was established for 2:1 type clay minerals. Though attapulgite and halloysite minerals have b.e.c. very near to illite clay but they do not fix potassium. Hence K-fixation property is of the 2:1 type minerals.

3. **Absorption of cations over the exchange complex depends on the total charge present over it.** After K-fixation specific charges are neutralised by K-ions by becoming non-exchangable and hence the property of cation absorption after K-fixation should be lowered. Experiments were arranged to study this effect and it was found that absorption ratios between Na and Ca and K and Ca were lowered as a result of K-fixation.

4. **Loss on ignition before and after fixation were found to be different.** Atterberg's constants and ethylene glycol retention values were lowered, showing disturbances in the hydration of the material.
(5). Contracted and expanded condition of lattice space after K-fixation:

According to Jackson et al (130) and Bailey (20), contracted lattice condition was obtained after K-fixation. They also observed that the lattice space of the same clay in which potassium was fixed could be brought to expanded condition by washing the clay with N/2 CaCl₂ solution. The present study found that a major portion of fixed-K₂O remained in fixed condition during washing with 0.5 N CaCl₂ or after expanded condition.

(8). Release of K₂O:

Clays release potassium from their fixed state under the physical factors and the chemical influences. The physical factors which release potassium are, air and oven drying, moist storage, freezing and thawing and leaching with rain water etc.

The chemical influences which cause release of K₂O are, the effects of cations, leaching and extraction with dilute acid solutions and salt solutions and by acid digestion.

Release of potassium depends on the type of clay mineral, for example, illite liberates potassium from its fixed state more than from any other mineral. In the process of leaching and extraction cations play an important role in releasing potassium from the fixed state. In the present investigation the order of effectiveness of cations in liberating potassium from the fixed state is as follows:

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

Feldite liberates potassium in large quantities under the influence of magnesium chloride solution. This agrees with the findings of Parshad (28).
All fractions of the soil release potassium and the order of release is the same as found under potassium fixation by the fractions. Clay fraction contributes about 60-70 per cent of the total release (vide Table 57).

It was noted under the present investigation that the properties of clays altered after the potassium fixation were reigned to the original level when potassium was released from them. Hence potassium fixation and release of potassium from the 2:1 type of expanding clays are inverse processes. This agrees with the previous observations of Feitelson (256).

The digestion of clays with boiling acids particularly N HNO₃ give an order of the soils indicating potassium supplying power. The order of potassium supplying power is:

Black cotton soil > Soils of Delhi > Karmal
Sirsa > Srinagar > Lateritic of Bihar and Miras
Calcareous of Pusa > Acid soil of Palampur.

Values expressed in m.e./100 K₂O released by digestion with boiling N HNO₃ indicate K-supplying power of a soil. Hence the values for 13 soils were determined and soil samples were tabulated in the ascending order of K-supplying power (vide Table 56,57).

(C). Conversion:

Base exchange reactions involving movement of K-ion to and from lattice space.

The two reactions known as potassium fixation and defixation (depotassification) are reversible. Non-potassium bearing minerals increase in K₂O content after neutralising specific charges on tetrahedral layer by potassium fixation treatment. Each mineral seems to have limited power to fix potassium. The following limits of K-fixation were observed in the three clays.

1). Montmorillonite ---- 1.42 per cent K₂O
II). Illite ---- 0.52 per cent K₂O

III). Vermiculite ---- 4.23 " "

Various extract / like MgCl₂, NaNO₃, and Ca(NO₃)₂ were employed to define potassium from potassium bearing minerals. It was observed that base exchange capacity and hydration of clay increased as a result of deflation. Even under deflation a limit has been found. The limits of conversion by deflation were:

i). Muscovite to Illite ---- 30 per cent
ii). Illite to Montmorillonite-30 "
iii). Biotite to Vermiculite 49 "

Mineralogy

Since by fixation a decrease per cent in base exchange capacity is constant for every individual mineral so it was felt that this constant would be a good identification value in estimation of soil mineralogical composition. From the data on b.e.c., K₂O content, and potassium fixation capacity and the calculated per cent decrease in b.e.c. led to the conclusion that soils of Karnal, Delhi and Sirsa were rich illite mineral whereas the remaining ten soils contained both illite and montmorillonite but the latter was the dominant clay mineral in them.

The following twelve observations were noted in the study of mechanism of K-fixation in silicates:

1). Each clay mineral exhibited a standard per cent decrease in b.e.c. Montmorillonite = 24 to 27 per cent; Illite = 30 to 35 per cent and Vermiculite = 65 per cent.

2). Potassium fixation is limited to a certain value in all the three clays. Montmorillonite = 1.42 per cent; Illite = 0.52 per cent and Vermiculite 4.20 per cent.

3). Potassium release from native state from micas are
also limited. Muscovite - 30 per cent; Illite - 30 per cent and
Riotite - 40 per cent.

4). Potassium fixation takes place even in presence of
big cations and organic radical on the complex.

5). Competitive cation absorption ratios decreased as a
result of potassium fixation.

6). Clays become dehydrated after K₂O fixation.

7). Clays become hydrated after K₂O release from them.

8). Clays change in certain properties as a result of
K-fixation.

9). About 1 to 3 per cent fixed-K₂O is released by shaking
with distilled water.

10). Base exchange capacity does not reduce to zero.

11). Composition of clays remains constant after K-fixation.

12). Properties of clays which chance as a result of
potassium fixation are remained after K₂O release.

Explanation of observations in the light of current
theories for K-fixation.

All these observations are explained on Henin's theory of
K-fixation by floe of colloids and on basis of the entrapment of
K-ions in the "voids" of the lattice layers in the tetrahedra
forming co-ordination complex compounds.

It is proposed that there might be certain type of charges
on the exchange complex directing K-ions to enter the "entrapment"
in the "voids". As a result of potassium fixation these charges
are neutralised and hence there is a reduction in base exchange
capacity after K-fixation. On reversing the reaction, namely,
defixation of potassium sets free these specific charges and they
show base exchange properties and the lost base exchange capacity is regained.

To form a coordination complex compound, "void" of the tetrahedral position loses equivalent amount of water from the crystal structure and hence there is dehydration of crystal after potassium fixation.

The limits of potassium fixation by each clay are explained by limiting K-fixation to only a few spaces in the lattice layer of tetrahedron. The same assumptions explain also why K-fixation is greater in illite as compared to montmorillonite. The spaces in lattice layer having Si - Al in the silica sheets might have these few specific charges attracting K-ions for fixation. These views are supported by certain well established facts:-

(1). Total charges on illite and montmorillonite tetrahedral layers are 96 and 18 to 47 respectively; (ii). Distances between the seat of K-fixation in the "void" in tetrahedral and octahedral positions and centre of K-ion are 2.19 Å and 4.99 Å respectively. (iii). Total amount of lattice potassium after fixation (including previously occupied K₂O in the crystal structure) both in illite and montmorillonite was found to increase with the amount of specific charges available by substitution in the tetrahedral position.

After K-fixation ratios of competing cations were reduced, that is, the absorption ratios were shifted towards the absorption of cations of larger hydrated ionic radius and of ionic ratio \( \frac{r_c}{r_a} \) value ranging from 0.73 to 1.00. Thus showing that there were less charges acting at closer range after K-fixation.

It was observed that on exchange complex previously washed with a solution of 0.25 N with respect to CaCl₂ and KCl, fixed greater per cent of exchangeable K₂O on drying than when it was
entirely saturated with potassium. Similar results were obtained with diethyamine in place of Ca. Thus it is clear that potassium was absorbed in preference to Ca and \((C_2H_5)_2NH_2\) by the charges capable of effecting K-fixation.

Hence potassium fixation capacity seems to depend largely upon the number of charges arising from Si - Al sheets of the tetrahedral layer. This view is explainable as to why total base exchange capacity of clays cannot be negated with the fixed potassium - a much discussed problem but unexplained so far.

**Specificity of K to fix**

To study this aspect of the problem values of different cations relating to ionic sizes, ratio of cation and anion reaction and ionic potential (valency/radius) were studied. It was argued that only those cations will take part in fixation which 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 and this brings in question of ionic sizes very near to the "void". After studying values of ionic sizes, ratio of cation and anion, ionic potential and co-ordination number, it became clear that cations having following values would fix in silicates.

1). Ratio of cation and anion radii \(\frac{R_+}{R_-}\) = 0.73 to 1.00

2). Ionic potential = 0.71

3). Co-ordination number = 6

All these factors give specificity to K-ion. The present study agrees with the above facts.

**Contracted and expanded conditions of lattice:**

The present investigation has shown that drawing together of the lattice plate condition is not necessary for K-fixation, because K-fixation had occurred even when lattice plates were kept apart with camelin. Secondly, by moving contracted lattice
plate to an expanded condition did not release fixed potassium to an appreciable amount.

**Role of Ca-ion**

The present study found Ca⁺⁺ inducing both fixation and defixation.