3.1 Materials and equipments

3.1.1 Materials

Ten surface soil samples from six locations in the states of Mysore, Kerala, Tamilnadu, Andhra Pradesh and Gujarat have been selected for these studies. Except for Gujarat, the remaining four states belong to the south zone of India, where the consumption of potassium is highest as compared to other zones. Hence the soils of this region were chosen. The soil samples under investigations are representatives of the major soil types of the respective regions viz., 1) Red soils, 2) Lateritic soils and 3) Black soils. The location, mechanical composition and other details of these soil samples are presented in table 3.1 on the next page.

3.1.2 Chemicals

All the chemicals used in these investigations were either of analytical grade or 'chemically pure' grade supplied by reputed firms.

3.1.3 Instruments

The instruments used during these investigations are 1) Bels flame photometer, 2) pH meter, model No. 820 of M/S Trombay Electronic Instruments Ltd., with glass-calomel electrode assembly, 3) Bausch and Lomb spectronic 20, photoelectric colorimeter, 4) "Cenco" moisture balance, 5) International Centrifuge etc.
Table 3.1 Location and mechanical composition of the soil samples under investigation

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>Soil group</th>
<th>CaCO₂</th>
<th>Mechanical composition; percent oven dry basis</th>
<th>Soil pH type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Coarse sand</td>
<td>Fine sand</td>
</tr>
<tr>
<td>No.</td>
<td></td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>1. Agricultural College Farm, Coimbatore</td>
<td>Ferruginous red</td>
<td>0.58</td>
<td>44.27</td>
<td>27.53</td>
</tr>
<tr>
<td>2. A cultivator's farm about one mile away from Agri. College Farm, Coimbatore</td>
<td>-do-</td>
<td>0.79</td>
<td>39.41</td>
<td>26.51</td>
</tr>
<tr>
<td>3. Farm of Agricultural Research Institute, Hyderabad</td>
<td>Deep black</td>
<td>3.06</td>
<td>1.47</td>
<td>14.88</td>
</tr>
<tr>
<td>4. A cultivator's farm about 2 miles away from A.R.I., Hyderabad</td>
<td>-do-</td>
<td>2.57</td>
<td>2.67</td>
<td>16.82</td>
</tr>
<tr>
<td>5. Plot No. 2, south block Lateritic farm of the A.R.S. Hebbal, Bangalore</td>
<td>Nil</td>
<td>31.47</td>
<td>32.78</td>
<td>8.13</td>
</tr>
<tr>
<td>6. A cultivator's farm about 1.5 miles from A.R.S. Hebbal, Bangalore</td>
<td>-do-</td>
<td>Nil</td>
<td>35.57</td>
<td>35.47</td>
</tr>
<tr>
<td>7. Farm under the control of Agricultural College, Coimbatore</td>
<td>Medium black</td>
<td>4.85</td>
<td>23.08</td>
<td>21.13</td>
</tr>
</tbody>
</table>

Contd...
<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Field No. 7 of the farm of Central Tobacco Research Institute, Rajahmundry</td>
<td>Deep</td>
<td>0.69</td>
<td>1.79</td>
<td>16.97</td>
<td>29.92</td>
<td>51.85</td>
<td>Clay</td>
<td>7.85</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Farm of the Agricultural College, Trivendrum</td>
<td>Lateritic</td>
<td>Nil</td>
<td>49.88</td>
<td>17.61</td>
<td>5.38</td>
<td>28.79</td>
<td>Sandy Clay loam</td>
<td>5.20</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Farm of Central Salt &amp; Marine Chemicals Research Institute, Bhavnagar</td>
<td>Medium</td>
<td>6.95</td>
<td>14.60</td>
<td>20.81</td>
<td>14.80</td>
<td>40.08</td>
<td>Clay loam</td>
<td>8.05</td>
<td></td>
</tr>
</tbody>
</table>

A.R.S. means Agricultural Research Station
FIGURE 3.1. MULTI PURPOSE WOODEN STAND

ASBESTOS SQUARES WITH HOLES OF DIFFERENT SIZE
3.1.4 Wooden stand for leaching operations

A special wooden stand has been designed for carrying out leaching of soils with equilibrating solutions, at constant liquid height. The details of this stand are shown in figure 3.1; It will be seen that with the help of the asbestos squares with holes of different diameters, glass columns up to 5 cm. diameter can be used in the same stand. Secondly, the height of liquid over soil layer can be adjusted at any desired level and the leachates can be collected in containers of different sizes and shapes. This stand can be conveniently used in hydrolic conductivity determinations as well.

3.2 Analytical methods

3.2.1 Soil moisture

It is determined with the help of 'Cenco' moisture balance. A few samples were treated in an oven to check the results of moisture balance. The agreement between the two was 98 to 99 per cent.

3.2.2 Lime reserve of the soil

The carbonates of the soil are decomposed by dilute hydrochloric acid and the volume of the liberated carbon dioxide is measured. The carbonate content of the soil, expressed as calcium carbonate, is calculated from the data of the volume of carbon dioxide liberated, ambient temperature and atmospheric pressure duly corrected for temperature and vapour pressure variation. At the outset, it may be mentioned that the entire determination is carried out in an air conditioned room. The water over which carbon dioxide is collected is first saturated with it by passing carbon dioxide
Figure 3.2 Apparatus for the estimation of lime reserves of soil.
The apparatus used for this determination is shown in figure 3.2. Appropriate quantity of soil is taken in flask 'A' which has two air-tight female joints 'B' and 'C'. The soil is then moistened with 10 ml of water. Ten ml of hydrochloric acid of appropriate strength, depending upon the carbonate content of the soil, is placed in the bulb 'D' with a male joint to fit in the female joint 'B'. The flask is then connected to a calibrated tube 'E' which is surrounded by water contained in another tube 'F' as shown in the diagram. The closed system is brought to atmospheric pressure by equalising the water levels in the tubes 'E' and 'F' by means of a stop cock 'G'. The acid in the bulb 'D' is introduced in the flask 'A' by turning the bulb upwards as shown in the diagram. The flask 'A' is then shaken intermittently for 15 minutes. The entire system is then left undisturbed for about half an hour so that it attains the ambient temperature. Thereafter the system is brought to atmospheric pressure by equalising the water levels in tubes E and F. The volume of the liberated carbon dioxide is read off the calibrated tube 'F'. The lime reserve is then calculated from the data.

3.2.3 Mechanical analysis of soil

It is carried out by the International pipette method as described by Piper (104). A motor dispersion unit is used for the dispersion of the soil, the dispersion agent used being normal sodium hydroxide solution.
3:2.4 Dispersion coefficient of soil

It is found by determining, by the International pipette method, the percentage of conventional clay (less than 2 microns) of the soil sample which has been soaked in water for twentyfour hours (referred to as dispersion factor) and expressing it as a percent of the total clay content of the same soil sample obtainable on its complete dispersion by means of a dispersing agent. If, after keeping the soil in contact with water for 24 hours, the soil water mixture is shaken for 1-2 hours, as in mechanical analysis, then the dispersion coefficient so obtained is termed as normal dispersion coefficient. On the other hand, if the soil-water mixture is not shaken, the dispersion coefficient is termed autodispersion coefficient (105). In both the above cases, the soil:water ratio is taken as 1:50; the same as in the determination of mechanical composition of the soil.

3:2.5 Soil reaction

This determination is made on 1 : 2.5 soil water mixture, which is shaken for half an hour and then its pH is determined by means of a pH meter. The water used is first equilibrated with atmospheric carbon dioxide by aerating it for 1 to 2 hours.

3:2.6 Hydraulic conductivity of soils

Air dry soil, passing through 1 mm sieve, is uniformly packed in a glass percolation tube of suitable size. Uniformity of packing is achieved by subjecting the soil column to a succession of 20 sharp taps from a height of 2.5 centimeters. The height of the soil column is always less than 2/3 of the
The diameter of the glass tube. The rate of percolation of water through the soil column is then measured over a period of six hours. During this period the hydraulic head over the soil column is kept constant. The hydraulic conductivity is then calculated.

3:2.7 Cation exchange capacity (C.E.C.) and exchangeable cations of soil

A) Leaching of soils in glass column: For both the above determinations, the treatment of soil with neutral normal ammonium acetate or normal sodium chloride, and the washing etc., has been carried out by column operation. Appropriate quantity of soil is first thoroughly mixed with four times its weight of deactivated quartz sand. This mixture is then uniformly filled in a glass column of suitable size. Six such columns are arranged in the special stand described under 3:1.4. The solution with which the soil is to be leached, is filled in a litre conical flask as shown in figure 3.1. The process of leaching is started by blowing air which starts the syphon. Once started, the solution in the column is automatically replenished and the level of liquid in the column remains constant.

B) Determination of cation exchange capacity: The soil columns prepared as above are first leached with 60 per cent alcohol to remove soluble salts. The complete removal of soluble salts is judged by the negative chloride test in the leachate. Then the soil column is leached with neutral normal ammonium acetate solution adjusted to pH 7.0. The rate
of flow through the soil column is so adjusted that the contact time is not less than four hours. The leachate is collected and used for the estimation of exchangeable sodium and potassium in the case of calcareous soils ($\text{CaCO}_3 > 0.75$ per cent) and also for the estimation of calcium and magnesium in the case of non-calcicous soils.

The occluded and last traces of free ammonium acetate are removed by washing with 60 per cent alcohol as described above. The completeness of washing is tested by first adding a few ml of ammonium chloride solution to the soil column before commencing the washing and then testing the washings for chloride ion. Negative chloride test indicates complete removal of free or occluded ammonium ions. The soil in the column is then transferred without loss to a litre capacity round bottomed flask. After the complete transfer of soil, the water level in the round bottom flask is so adjusted that the soil is completely under water. 20 ml of 20 per cent sodium hydroxide solution is then added and the slurry immediately subjected to steam distillation. The liberated ammonia is absorbed in 20 ml of 4 per cent boric acid solution and finally estimated by titration of this boric acid solution against standard hydrochloric acid, using methyl-red—bromocresolgreen mixed indicator. The cation exchange capacity is calculated from the amount of ammonia liberated.

C) Determination of exchangeable cations of soil: In calcareous soils ($\text{CaCO}_3$ more than 0.75 per cent), exchangeable calcium and magnesium have been determined by leaching the
soil with normal sodium chloride solution as described by Piper (104); and determining calcium and magnesium in the leachate by versanate method. The determination of exchangeable sodium and potassium in calcareous soils and exchangeable calcium, magnesium, sodium and potassium in non-calcareous soil have been done by first leaching the soils with neutral normal ammonium acetate and then treating the leachate as follows. The ammonium acetate leachate is carefully evaporated to dryness in a silica dish. The dried residue is moistened with a little concentrated nitric acid (A.R.), and again dried. It is then incinerated in a muffle furnace at a temperature between 450°C - 500°C. To this incinerated residue, about 2 ml of concentrated hydrochloric acid is added and the mixture evaporated to dryness over water bath. This hydrochloric acid treatment is repeated twice whereby the silica is rendered insoluble. The final dry residue is taken up in 25 to 30 ml of 0.1 normal hydrochloric acid and transferred without loss to a volumetric flask. The solution is then just neutralised with ammonia solution, using methyl red as indicator (pH between 6-7) whereby ferric, aluminium and titanium ions are precipitated as hydroxides or phosphates, if the leachate contains phosphate ion. The solution is then made up to the mark, shaken and filtered in another clear dry flask without prior moistening of filter paper. The clear solution containing calcium, magnesium, potassium and sodium ions derived from the soil, is analysed for these elements, the calcium and magnesium, by versanate method and potassium and sodium, by flamephotometry.
3:2.8 Determination of potassium and sodium by flame photometry

The reference graph for potassium was prepared for the range 0.01 to 0.1 per cent potassium chloride and that of sodium was for the range 0.001 to 0.01 per cent sodium chloride. The variation in the values due to a unit deviation in the galvanometer scale reading (experimental error) is not more than 3.33 per cent as against the usual 2.5 per cent in an ideal straight line graph.

3:2.9 Estimation of calcium and magnesium in presence of phosphate ion

First, calcium is estimated gravimetrically by precipitating it as calcium oxalate, as per procedure prescribed in A.O.A.C's official methods (106). Magnesium is then estimated in the filtrate from the calcium estimation, by the usual magnesium ammonium phosphate gravimetric procedure.

3:2.10 Estimation of phosphate

Phosphate is estimated by first precipitating it as ammonium phosphomolybdate, dissolving this precipitate in excess standard sodium hydroxide solution and back titrating the excess alkali by standard acid as per details given by Vogel (107).

3:2.11 Determination of mineral constituents of plant material

The determination of magnesium, potassium and phosphorus in seeds as well as in the residual dry matter was carried out by ashing the material. The procedure for ashing and subsequent analysis was as per the methods prescribed by Piper (loc cit.).
3:2.12 Determination of crude fat in groundnut seeds

The crude fat is determined by extracting an aliquot quantity of the groundnut seed powder, with petrolatum ether (B.P. 40°-60°C), in a soxhlet extractor. This ether extract is evaporated to dryness in an oven at 100°-105° C. The residue is crude fat.

3:3 K - Mg exchange equilibrium

The exchange characteristics of the soils under investigation, with reference to the ion pair K - Mg, especially in the sulphate form, have been studied in the following way.

1) Adsorption isotherms are obtained by equilibrating the soils with mixed solutions of potassium sulphate and magnesium sulphate and then plotting the equivalent fraction of potassium in equilibrating solution (E.S.) against the corresponding fraction on the soil exchange complex.

2) The validity of the ion-exchange equations developed by Kerr (108), Krishnamoorthy and Overstreet (109,110,111), Vanselow (112) and Gapon (113) with respect to the data obtained, has been tested.

3:3.1 Adsorption isotherms

In order to investigate the effect of concentration on the exchange equilibrium, four ionic strengths were chosen, viz., 1.75, 1.00, 0.5 and 0.1. The choice of these ionic strengths was based on the assumption that the range of concentration of soil solution, during the life cycle of a field crop receiving moderate to heavy doses of manures and fertilizers
is approximately 0.1-1.5. In this thesis the concentration of ions in solutions is expressed in milliequivalents per litre (me/l) and that of ions on soil exchange complex, as milliequivalents per 100 g. of air dry soil. Now ionic strength \( I \), of a solution is defined as

\[
I = \frac{1}{2} \sum_{i} m_i z_i^2
\]

where, \( m_i \), is the molal concentration and \( z_i \), the valency of ion \( i \); and the summation is carried out for all ions. Further, except for very concentrated solutions, molalities, \( m_i \), can be replaced by concentration \( C_i \); Expressing \( C_i \) in milliequivalents per litre, ionic strength can be expressed as

\[
I = \frac{1}{2000} \sum_{i} C_i z_i
\]

The effect of relative concentration of potassium and magnesium i.e. K:Mg ratio in the equilibrating solutions, on the exchange equilibrium, has been studied by choosing three K:Mg equivalent ratios viz 1:1, 1:4 and 4:1 in the solutions of each of the four ionic strengths. The choice of these ratios is based on the consideration that the K:Mg equivalent ratio in potassium schoenite is 1:1. The other two ratios, 4:1 and 1:4 are selected to represent the maximum range in which this ratio is likely to vary under field conditions. Thus, for the present investigation, twelve mixed solutions of potassium sulphate and magnesium sulphate, representing four ionic strengths and three K:Mg ratios, have been prepared. The exact composition of the solution is worked out by making use of the relation between potassium concentration \( C_K \), ionic strength \( I \) and \( C_K : C_Mg \) ratio, which works out to be as below:
where the ionic concentrations $CMg$ and $CMg$ are expressed in milliequilivalents per litre. The composition and other details regarding the mixed solutions of potassium sulphate and magnesium sulphate are presented in tables 3.2 and 3.3. The solutions mentioned in table 3.2 have been used for studies on soils at serial Nos 1 to 6 and those of table 3.3 have been used for studies on soils at serial Nos 7 to 10 of table 3.1.

3:3.2 Technique of equilibration

Appropriate quantity of soil is thoroughly mixed with four times its weight of deactivated quartz coarse sand and this mixture is packed in glass columns as per procedure described under 3:2.7 A. In the case of equilibration with solutions of ionic strengths of 1.75, 1.00 and 0.5, the quantity of soil taken is 10 g for all soil samples except soil No 9 of which 25 g was taken and mixed with 50 g deactivated sand. But in the case of solutions of ionic strength of 0.1 the quantity of soil taken was 5 g for soil Nos 3, 4, 7, 8 and 10; 10 g for soil Nos 1, 2, 5 and 6 and 25 g for soil No. 9.

This soil sand mixture is then leached with appropriate quantities of K-Mg mixed solutions mentioned in tables 3.2 and 3.3 in such a way that the leaching was continuous and the time of contact was not less than four hours, till an equilibrium
Table 3.2 Mixed solutions of potassium sulphate and magnesium sulphate used for equilibration of soils 1 to 6 mentioned in table 3.1

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>CK me/L</th>
<th>CMg me/L</th>
<th>CK+CMg me/L</th>
<th>CK+K₂SO₄</th>
<th>f⁺ MgSO₄</th>
<th>Ionic strength</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>495</td>
<td>501</td>
<td>996</td>
<td>0.50</td>
<td>0.3250</td>
<td>0.0987</td>
<td>1.75</td>
</tr>
<tr>
<td>2</td>
<td>181</td>
<td>737</td>
<td>918</td>
<td>0.20</td>
<td>0.3458</td>
<td>0.0829</td>
<td>-do-</td>
</tr>
<tr>
<td>3</td>
<td>886</td>
<td>224</td>
<td>1110</td>
<td>0.80</td>
<td>0.3149</td>
<td>0.1497</td>
<td>-do-</td>
</tr>
<tr>
<td>4</td>
<td>142</td>
<td>150</td>
<td>292</td>
<td>0.49</td>
<td>0.4648</td>
<td>0.2039</td>
<td>≈ 0.50</td>
</tr>
<tr>
<td>5</td>
<td>56</td>
<td>218</td>
<td>274</td>
<td>0.29</td>
<td>0.6319</td>
<td>0.1466</td>
<td>-do-</td>
</tr>
<tr>
<td>6</td>
<td>247</td>
<td>64</td>
<td>311</td>
<td>0.79</td>
<td>0.3966</td>
<td>0.4017</td>
<td>-do-</td>
</tr>
<tr>
<td>7</td>
<td>302</td>
<td>291</td>
<td>593</td>
<td>0.51</td>
<td>0.3919</td>
<td>0.1241</td>
<td>≈ 1.00</td>
</tr>
<tr>
<td>8</td>
<td>121</td>
<td>444</td>
<td>565</td>
<td>0.21</td>
<td>0.5441</td>
<td>0.1061</td>
<td>-do-</td>
</tr>
<tr>
<td>9</td>
<td>504</td>
<td>124</td>
<td>628</td>
<td>0.80</td>
<td>0.3143</td>
<td>0.3002</td>
<td>-do-</td>
</tr>
<tr>
<td>10</td>
<td>27</td>
<td>31</td>
<td>58</td>
<td>0.46</td>
<td>0.6745</td>
<td>0.5042</td>
<td>≈ 0.10</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>44</td>
<td>54</td>
<td>0.19</td>
<td>0.7905</td>
<td>0.4697</td>
<td>-do-</td>
</tr>
<tr>
<td>12</td>
<td>54</td>
<td>13</td>
<td>67</td>
<td>0.80</td>
<td>0.5923</td>
<td>0.5951</td>
<td>-do-</td>
</tr>
</tbody>
</table>

* Calculated according to the equation of Glueckauf.
Table 3.3. Mixed solutions of potassium sulphate and magnesium sulphate used for equilibration of soils 7 to 10 mentioned in table 3.1

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>CK me/L</th>
<th>CMg me/L</th>
<th>CK+CMg me/L</th>
<th>CK/CK+CMg</th>
<th>f+ K₂SO₄*</th>
<th>f+ MgSO₄*</th>
<th>Ionic strength</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>490</td>
<td>507</td>
<td>997</td>
<td>0.49</td>
<td>0.3243</td>
<td>0.0980</td>
<td>≈ 1.75</td>
<td>7.00</td>
</tr>
<tr>
<td>2</td>
<td>164</td>
<td>765</td>
<td>929</td>
<td>0.21</td>
<td>0.3430</td>
<td>0.0817</td>
<td>do-</td>
<td>6.55</td>
</tr>
<tr>
<td>3</td>
<td>860</td>
<td>232</td>
<td>1092</td>
<td>0.79</td>
<td>0.2903</td>
<td>0.1185</td>
<td>do-</td>
<td>7.00</td>
</tr>
<tr>
<td>4</td>
<td>141</td>
<td>146</td>
<td>287</td>
<td>0.49</td>
<td>0.4646</td>
<td>0.2545</td>
<td>≈ 0.50</td>
<td>6.40</td>
</tr>
<tr>
<td>5</td>
<td>51</td>
<td>216</td>
<td>267</td>
<td>0.19</td>
<td>0.5619</td>
<td>0.1472</td>
<td>do-</td>
<td>6.05</td>
</tr>
<tr>
<td>6</td>
<td>242</td>
<td>66</td>
<td>308</td>
<td>0.79</td>
<td>0.4178</td>
<td>0.3990</td>
<td>do-</td>
<td>6.85</td>
</tr>
<tr>
<td>7</td>
<td>275</td>
<td>287</td>
<td>562</td>
<td>0.49</td>
<td>0.3866</td>
<td>0.1292</td>
<td>≈ 1.00</td>
<td>6.65</td>
</tr>
<tr>
<td>8</td>
<td>101</td>
<td>428</td>
<td>529</td>
<td>0.19</td>
<td>0.4433</td>
<td>0.1080</td>
<td>do-</td>
<td>6.35</td>
</tr>
<tr>
<td>9</td>
<td>490</td>
<td>128</td>
<td>618</td>
<td>0.79</td>
<td>0.3539</td>
<td>0.2995</td>
<td>do-</td>
<td>6.95</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>33</td>
<td>63</td>
<td>0.48</td>
<td>0.6658</td>
<td>0.5010</td>
<td>≈ 0.10</td>
<td>6.45</td>
</tr>
<tr>
<td>11</td>
<td>11</td>
<td>49</td>
<td>60</td>
<td>0.22</td>
<td>0.7791</td>
<td>0.4587</td>
<td>do-</td>
<td>6.40</td>
</tr>
<tr>
<td>12</td>
<td>47</td>
<td>13</td>
<td>60</td>
<td>0.78</td>
<td>0.6105</td>
<td>0.5961</td>
<td>do-</td>
<td>6.50</td>
</tr>
</tbody>
</table>

* Calculated according to the equation of Glueckauf
between the solid phase and solution phase is established as evidenced by the absence of any difference in the composition of the eluant and the effluent solution. It is observed that the quantities of mixed solutions found sufficient for equilibration are, 250 ml, 500 ml, and 1 litre for solutions of ionic strengths of 1.75, 1.00 and 0.5 respectively. In the case of solutions of ionic strength of 0.1 the quantities required for different soils were 2.5 litres for soil Nos 3,4,8 and 10; 2.0 litres for soil Nos 2,3 and 7; and 1.25 litres for soil Nos 5,6 and 9.

With the above mentioned quantities of soil and the solutions used for equilibration, it turns out that in every case, for each milliequivalent of exchange capacity, atleast 50 milliequivalents of total cations (K + Mg) in solution have been employed for equilibration process.

After equilibration, the last traces of free and occluded salts are removed by washing the soil in the column by 60 per cent alcohol till the washings are free from sulphate ion. The exchangeable potassium and magnesium at equilibrium, are then determined by the usual ammonium acetate method described under 3:2.7 C. Equivalent fraction of potassium on soil exchange complex is then plotted against the equivalent fraction of potassium in the corresponding equilibrating solution to get the required adsorption isotherms. Separation factor $\sqrt{\frac{K}{Mg}}$ has also been worked out.

3:3.3 Quantitative evaluation of the ion exchange phenomenon

According to the theory of Donnan equilibrium, the
mutual relations of ions K, Mg and SO\textsubscript{4} in the ion-exchange phenomenon occurring in soils, equilibrated with mixed solutions of potassium sulphate and magnesium sulphate, can be expressed as follows:

\[
\frac{f''K \cdot m''K}{f'K \cdot m'K} = \frac{f''Mg \cdot m''Mg}{{\left( f''SO_4 \cdot m''SO_4 \right)}^{\frac{3}{2}}} = \frac{f'\text{SO}_4 \cdot m'\text{SO}_4}{{\left( f'\text{SO}_4 \cdot m'\text{SO}_4 \right)}^{\frac{3}{2}}}
\]

where \( f \) is activity coefficient and \( m \) is molal concentration and superscripts ' and " represent the solid and the solution phases respectively. Multiplying equation 3.10 by a common factor \( \frac{f''\text{SO}_4}{{f'\text{SO}_4}} \) it turns into

\[
\frac{f''K \cdot (f''\text{SO}_4)^{\frac{3}{2}} \cdot m''K}{f'K \cdot (f'\text{SO}_4)^{\frac{3}{2}} \cdot m'K} = \frac{f''\text{Mg} \cdot f''\text{SO}_4 \cdot m''\text{Mg}}{f'\text{Mg} \cdot f'\text{SO}_4 \cdot m'\text{Mg}} = \frac{m'\text{SO}_4}{{m''\text{SO}_4}}
\]

Rearranging equation 3.11 and replacing superscripts ' and " by subscripts I and II for the solid and the solution phases respectively one gets

\[
\frac{fK \cdot (f\text{SO}_4)^{\frac{3}{2}} \cdot mK}{(f\text{Mg} \cdot f\text{SO}_4)^{\frac{3}{2}} \cdot (m\text{Mg})^{\frac{3}{2}}} \quad \equiv \quad \frac{fK \cdot (f\text{SO}_4)^{\frac{3}{2}} \cdot mK}{{(f\text{Mg} \cdot f\text{SO}_4)^{\frac{3}{2}} \cdot (m\text{Mg})^{\frac{3}{2}}}} \quad \equiv \quad 3.12
\]

Now the mean activity coefficient \( f^+ \) of an electrolyte in solution is defined by
\[ f^+ = (f^+, f^-)^{\frac{1}{3}} \] for 1:1 or 2:2 or 3:3 electrolytes like NaCl, MgSO₄, AlPO₄ etc., and
\[ f^+ = (f^+, f^-)^{\frac{1}{3}} \] for 1:2 electrolyte like K₂SO₄.

Replacing the mean activity coefficient \( f^+ \) in place of \( f^+ \) and \( f^- \) in the solution phase, equation 3.12 can be expressed as shown in equation 3.13

\[
\begin{bmatrix}
  fK \cdot (fSO_4)^{\frac{2}{3}} \cdot mK \\
  fMg \cdot fSO_4^{\frac{2}{3}} \cdot (mMg)^{\frac{1}{3}}
\end{bmatrix}
\begin{bmatrix}
  f^+ \cdot K_2SO_4 \cdot mK \\
  f^+ \cdot MgSO_4 \cdot (mMg)^{\frac{1}{3}}
\end{bmatrix}
\]

\[ \text{I} \quad \text{II} \]

The anion exchange capacity of soils is very small and therefore the term \( fSO_4 \) can be omitted from the left hand side of the equation 3.13 which will turn into:

\[
\begin{bmatrix}
  fK \cdot mK \\
  (fMg)^{\frac{2}{3}} \cdot (mMg)^{\frac{1}{3}}
\end{bmatrix}
\begin{bmatrix}
  f^+ \cdot K_2SO_4 \cdot mK \\
  f^+ \cdot MgSO_4 \cdot (mMg)^{\frac{1}{3}}
\end{bmatrix}
\]

\[ \text{I} \quad \text{II} \]

The mean activity coefficient of potassium sulphate and magnesium sulphate in their mixed solutions have been calculated using the equation developed by Glauechauf (114) for mixed solution of only two electrolytes with the common anion \( Y \),

\[
\log f^+ X_1Y = \log f^+ X_1Y - \frac{X_2}{4I} \cdot \left[ k_1 \log f^+ X_1Y \right. \\
\left. - k_2 \log f^+ X_2Y - \frac{k_3}{1+(1)^{\frac{1}{3}}} \right] \quad 3.15
\]

where \( X_1Y \) & \( X_2Y \) are the two electrolytes with the common anion \( Y \), and where \( k_1, k_2 \) and \( k_3 \) are constants having the values...
\[ k_1 = x_2 (2x_2 - x_1 + y) \]
\[ k_2 = x_1 (x_2 + y)^2 (x_1 + y)^{-1} \]
\[ k_3 = 0.5 x_1 x_2 y (x_1 - x_2)^2 (x_1 + y)^{-1} \]

and \( x \) and \( y \) are the ionic charges on \( X \) and \( Y \), and \( [X] \) is the molar concentration of \( X \) and

\[ \log f^+ X_1 Y = \text{mean activity coefficient of } X_1 Y \text{ in mixed solution containing } X_2 Y \]

On the other hand, the activity coefficients of ions on the solid phase are not known with certainty and even their approximate evaluation is cumbersome. Therefore various workers viz., Kerr, Vanselow, Krishnamoorthy & Overstreet and Gapon have suggested different hypothesis for this quotient of activity coefficients, to evaluate the laws of ionic distribution in such a system. Recently Hutcheon (174) has worked out the activity coefficients of ions on clays. He has reported that at the same equivalent fraction, the activity coefficient of potassium on clay is more than that of calcium. Since calcium and magnesium have been treated as a single ion species by several workers (38, 46, 175, 176), it can be inferred that at the same equivalent fraction, the activity coefficient of potassium on clay will be more than that of magnesium.

Kerr (108) propounded that the quotient of activity coefficients of ions on the solid phase is a constant; i.e., activities of ions are proportional to their molalities. With this assumption equation 3.14 will turn into
In the present work the ionic concentration \( C_{iK} \) or \( C_{iMg} \) on the solid phase - soil - are expressed as milliequivalents (me) per 100 g soil and those in solution phase are expressed as milliequivalent per litre (me/L). It can be shown that

\[
C_i = 1000 z_i \bar{m}_i
\]

where \( C_i \) is the concentration of ion \( i \) in me/L and \( \bar{m}_i \) is molality of ion \( i \). Replacing molality \( m \) by concentration \( C \) in equation 3.16, one gets

\[
\begin{bmatrix}
\frac{mK}{(mMg)^{\frac{1}{2}}}
\end{bmatrix}
= k
\begin{bmatrix}
\frac{f^{\frac{1}{2}} K_2SO_4}{f^{\frac{1}{2}} MgSO_4} \cdot \frac{mK}{(mMg)^{\frac{1}{2}}}
\end{bmatrix}
\]

II

Another assumption similar to the above is that the activities of ions on the solid phase are proportional to their equivalent fraction. With this assumption and replacing concentration for molality, equation 3.14 will turn into

\[
\begin{bmatrix}
\frac{CK}{(CMg)^{\frac{1}{2}}}
\end{bmatrix}
= k
\begin{bmatrix}
\frac{f^{\frac{1}{2}} K_2SO_4}{f^{\frac{1}{2}} MgSO_4} \cdot \frac{CK}{(CMg)^{\frac{1}{2}}}
\end{bmatrix}
\]

II

In soils with pH above 7, equilibrated with mixed solutions, it can be assumed that the entire cation exchange capacity is occupied by the two cations of the mixed solution. Hence equation 3.18 will turn into
It will be seen that equation 3.17 and 3.19 are similar except that the numerical value of the constant \( k \) will be altered.

Vanselow (112) postulated that the ionic activities on the adsorbed phase are proportional to their molar fraction. Applying this assumption to equation 3.14, one gets

\[
\left[ \frac{\text{CK}}{\left[ \text{CMg} \cdot (\text{CK} + \text{CMg}) \right]^\frac{1}{2}} \right] = k \left[ \frac{f^\pm \text{K}_2\text{SO}_4}{f^\pm \text{MgSO}_4} \cdot \frac{\text{CK}}{(\text{CMg})^\frac{1}{2}} \right] \quad \cdots 3.19
\]

Replacing molalities by concentration, expressed in milliequivalents one gets

\[
\left[ \frac{m\text{K}}{\left[ m\text{Mg} \cdot (m\text{K} + m\text{Mg}) \right]^\frac{1}{2}} \right] = k \left[ \frac{f^\pm \text{K}_2\text{SO}_4}{f^\pm \text{MgSO}_4} \cdot \frac{m\text{K}}{(m\text{Mg})^\frac{1}{2}} \right] \quad \cdots 3.20
\]

Yet another assumption made by Krishnamoorthy, Davis and Overstreet (109) takes into account a fact that two monovalent ions can occupy any two available exchange sites while a single bivalent ion has to occupy two adjacent sites. Based on the restrictions arising out of this fact and making some assumptions regarding the pattern of exchange sites, they
developed an equation which when applied to the heterovalent exchange K-Mg, can be represented as

\[
\frac{\text{CK}}{[\text{CMg} \cdot (\text{CK} + 0.75\text{CMg})]}^{\frac{1}{2}} = k \left[ \frac{\frac{f_+}{f_{\text{K}^2}} \text{K}_2\text{SO}_4 \cdot \frac{\text{CK}}{\text{f}_+ \text{MgSO}_4 \cdot (\text{CMg})^{\frac{1}{2}}} \right] \quad (3.22)
\]

All the above equations viz., Kerr, Vanselow and Krishnamoorthy & Overstreet, are derived from the consideration of Donnan equilibrium. The phenomenon of ion exchange in soils has been studied by analysing the conditions in the vicinity of a soil particle. It is well known that a soil particle (colloid) carries a negative charge which is assumed to result in the formation of an electrical double layer when the soil colloidal particle is in equilibrium with soil solution. For the quantitative evaluation of the heterovalent ion exchange, based on the Stern picture of the double layer, Gapon (113) developed an equation, which after introducing activities in the solution phase, can be expressed as

\[
\frac{\text{mK}}{\text{mMg}} = k \left[ \frac{\frac{f_+}{f_{\text{K}^2}} \text{K}_2\text{SO}_4 \cdot \frac{\text{mK}}{\text{f}_+ \text{MgSO}_4 \cdot (\text{mMg})^{\frac{1}{2}}} \right] \quad (3.23)
\]

for the exchange involving ions K and Mg. Replacing molalities by concentrations, expressed as milliequivalents, equation 3.23 turns into
It will thus be seen that due to the complex nature of the soil–cation exchange phenomenon, various workers have put forward different hypothesis and consequently developed different equations to quantitatively evaluate the phenomenon of ion-exchange by soils. It is understandable that because of the many assumptions, there can be large variations in the values of equilibrium constants. Still however, the relative suitability of any one of these equations can be much useful in the interpretation of the observed data.

3:3.4 Method for testing the validity of various ion-exchange equations and comparing their relative suitability for the observed data

The validity of the ion exchange equations of Kerr, Vanselow, Krishnamoorthy & Overstreet and Gapon is tested by calculating the respective equilibrium constants $k_{kerr}$, $k_{van}$, $k_{kgo}$ and $k_{gapon}$.

Since the concentration of the equilibrating solution has a considerable influence on the exchange phenomenon, it is but natural that the values of these constants will be different for ion exchange involving solutions of different ionic strengths. Therefore while comparing the relative suitability of the above mentioned equations values of constants arising out of treatment with solutions of equal ionic strengths only have been considered.
The relative suitability of these equations has then been judged by comparing the coefficient of variation in the values of equilibrium constants. Coefficient of variation (115) is defined as

\[
C.V. = \frac{\sum X^2 - (\sum X \cdot \bar{X})}{N-1} \cdot \frac{100}{\bar{X}} \cdot 3.25
\]

where \( X \) is the observed value, \( N \) is the total number of values and \( \bar{X} \) is the arithmetic mean of all the \( N \) values. The equation in which the values of the equilibrium constant show least coefficient of variation can be considered as the most suitable one, which can interpret the observed data on a quantitative basis.

3:3.4 Effect of associated anion on the potassium-magnesium exchange equilibrium

With a view to investigate this aspect, three soils - one from each type viz., red, black and lateritic, have been equilibrated with mixed solutions of potassium chloride and magnesium chloride. Solutions of only one ionic strength viz., 0.5 have been used. The other experimental details e.g. the \( K: Mg \) ratio of the solutions, technique of equilibration, analytical procedure etc., are exactly the same as those of the experiments in which mixed solutions of potassium sulphate and magnesium sulphate were used.
Effect of adsorbed potassium and magnesium on physical properties of soil

3.4.1 Soil reaction

The exchange complex of the soils equilibrated with different mixed solutions of potassium and magnesium sulphates, take up, by adsorption, the ions K and Mg in different proportions. The effect of various K and Mg saturations of the soil exchange complex, upon the soil reaction has been studied by measuring the pH of the equilibrated soils. For this study, as well as for the studies on the hydraulic conductivity and dispersion coefficient, the technique of column operation for equilibrating the soil is unsuitable because of the admixture of the sand. Therefore equilibration was carried out by thoroughly mixing an aliquot portion of soil with the equilibrating solution in the ratio (wt/vol) of 1 : 2.5 or more, centrifuging the slurry and then decanting off the supernatant liquid. This process is repeated at least fifteen times. As in column operation, for every milliequivalent of the exchange capacity of the soil, at least 50 milliequivalents of cations (K + Mg) are applied for equilibration. For the removal of free and occluded salts, the soil is repeatedly washed with 60% percent alcohol, till the centrifugated wash liquor is free of sulphate ion. The soil is then air dried. An aliquot portion of this treated soil is taken for pH determination by method 3.2.5
3.4.2 Effect of adsorbed potassium and magnesium on the hydraulic conductivity of soils

The hydraulic conductivity of soil indicates the openness of its structure. The influence of the adsorbed K and Mg on this property of the soil is evaluated by determining the hydraulic conductivity of soils equilibrated with various mixed solutions of potassium sulphate and magnesium sulphate and comparing the results with those of untreated soil. For this study as well as studies on the influence of adsorbed K and Mg on soil reaction and dispersibility, soils equilibrated with mixed solutions No 1, 4, 7 and 10 only are considered; because these solutions contain K and Mg in the same ratio as that of potassium schoenite and therefore their influence can be considered as the influence of potassium schoenite. The hydraulic conductivity is determined by the method described under 3.2.6.

3.4.3 Influence of adsorbed K and Mg on soil dispersion

The effect of adsorbed potassium and magnesium on the dispersibility of the soil has been studied by determining the autodispersion coefficient of the treated soils and comparing it with autodispersion coefficient of untreated soils. The soils treated with equilibrating solutions Nos 1, 4, 7 and 10 have been chosen for this study because the soils in equilibrium with these solutions will reflect the equilibrium conditions that are likely to result by the use of potassium schoenite.
Influence of other fertilizers when used along with potassium schoenite

Potassic fertilizers are seldom applied alone; they are always applied along with nitrogenous and/or phosphatic fertilizers. All the relevant potassium salts viz. chloride sulphate, phosphate, carbonate etc are water soluble. Therefore when any single potassium salt e.g. chloride, sulphate, nitrate is used as a source of fertilizer potassium, its interaction with other commonly used fertilizers is not likely to result in the formation of any insoluble or sparingly soluble compound, thus inactivating any fertilizer nutrient element. However when potassium schoenite is used as a source of fertilizer potassium, the magnesium constituent of potassium schoenite is likely to form sparingly soluble magnesium compounds like magnesium ammonium phosphate, magnesium hydrogen phosphate etc., depending on the pH of the soil solution. With a view to investigate this aspect a few laboratory experiments have been carried out, as detailed below:

A mixture of calculated quantities of potassium schoenite, ammonium sulphate and diammonium phosphate or superphosphate are added to 500 ml of water, stirred thoroughly and its pH adjusted to a desired value. This slurry is kept overnight and thereafter the solid and the solution phases are separated by filtration. Both, the solid and the solution phases are analysed for their cation and anion contents.

Fertilizer trials with potassium schoenite

The objective of these trials is to find out.
schoenite can replace potassium sulphate and/or potassium chloride in the fertilizer schedule of field crops.

3.6.1 Field fertilizer trials on groundnut

A field trial on groundnut, variety A.H.32 has been conducted on the farm of the Central Salt and Marine Chemicals Research Institute, Bhavnagar. Three levels of K₂O viz., 10 kg, 20 kg and 30 kg K₂O per acre have been tried and potassium is applied as KCl, K₂SO₄ and potassium schoenite. The details about the lay out are given in chapter 4. The experiments have been conducted during the monsoon of three consecutive years 1966, 1967 and 1968 and the crop was grown as a rainfed crop because of irrigation facilities were not available. As pointed out in chapter 2, magnesium influences the uptake of phosphates, while the uptake of magnesium itself is not materially affected. With a view to investigate this aspect, composite samples of groundnut seeds and the fodder (comprising of the whole dry plant except seeds) have been collected and analysed for their magnesium and phosphate content. The seeds have also been analysed for their fat content. The data has been statistically analysed.

3.6.2 Fertilizer trials conducted in cooperation with other agencies

Potassium schoenite was sent to a few agricultural research stations with a request to conduct fertilizer trials on the crops of their region. The necessary details regarding the composition of schoenite, objective and layout of the experiment etc., were also supplied. The results of these trials are also reported in chapter 4.