Phosphate Solubility in Relation to Cations and pH: Magnesium

ALFRED T. PERKINS

The effect of pH and cation on phosphate solubility and availability is of great importance. Many publications have appeared on this general subject dealing with it either directly or indirectly. The effect of magnesium on phosphate solubility and availability has been studied for many years and recently the role of magnesium has been studied intensely. A recent issue of *Soil Science* has been devoted entirely to magnesium and soils.

The present paper includes data showing the effect of some cations commonly found in soils on phosphate solubility in the presence of kaolin. The work was outlined to give information on the role magnesium plays in phosphate solubility with the purpose of helping evaluate the use of dolomitic limestone in place of calcitic limestone on acid soils deficient in phosphate, and on the role that magnesium might play in rendering the phosphate of rock phosphate available. Among the many publications dealing with phosphate solubility may be listed that of Gaarder who showed that phosphate in the presence of iron or aluminum is almost completely insoluble at an acidity of pH 3.0, but that as the solutions become more basic the solubility of the phosphate increases. This and similar data have led to the general statement on precipitation of phosphate that iron and aluminum are active below pH 5.5, that calcium is dominant at pH 6.5, and that magnesium enters the picture at pH 7.5.

**METHODS**

Phosphate solubility and precipitation was determined by placing 0.0075 gram of orthophosphoric acid in a 90-ml centrifuge tube with 5 grams of kaolin, ground to pass a 100-mesh screen, and the indicated amounts of calcium, magnesium, and ferric chloride. The pH of the suspension was adjusted by hydrochloric acid or sodium hydroxide and about 25 ml of water. The mixture was shaken over night in an end-over shaker running at 6 RPM m a constant-temperature room at 25° C. After shaking, the tubes were centrifuged to remove solid materials which might affect the pH determinations and phosphate analysis. The amount of phosphate precipitated or fixed was determined by difference and reported along with pH values in Tables I, 2, 3, and 4.

The pH measurements were made with a glass electrode and the phosphate in solution was determined by the coeruleomolybdate method of Deninges as improved by Atkins (1). A Coleman spectrophotometer was used in the phosphate measurements.

**DISCUSSION OF RESULTS**

**EFFECT OF CATIONIC CONCENTRATION**

The results obtained are presented in Tables 1, 2, 3, and 4. Reference to the tables shows that, within the limits of the cation phosphate ratios studied, regardless of pH, an increase in cation phosphate ratio increases the percentage of phosphate precipitated. This increased precipitation holds for calcium, magnesium, and iron and for mixtures of these cations. The only noteworthy exception reported is where we compare phosphate equivalencies of one-third calcium plus one-third iron with the corresponding two-thirds and three-thirds equivalencies of these same mixed cations, as shown in Table 4 between pH values 3.0 and 6.0. Other exceptions are irregular, minor in nature, and approximately within experimental error.

**EFFECT OF pH**

The effect of reaction and single cations on phosphate solubility is shown in Tables 1, 2, and 3. Calcium, except when added in minimum amounts equivalent to one-third of the phosphate, shows a general increase in phosphate fixation from pH 2.5 through pH 9.5. The phosphate precipitation curve with equivalencies of one-third calcium is different than the curves for greater concentrations of calcium.

The effect of magnesium on phosphate fixation is somewhat different than that of calcium. Magnesium acts much like calcium from pH 2.5 to pH 4.5, with fixation increasing as the pH rises. However, from this pH reaction to pH 9.5 phosphate precipitation gradually decreases in the presence of magnesium, while in the case of calcium there is a constant increase. From these data it would appear that phosphate precipitation by magnesium at pH values in the agricultural range is of little consequence.

Iron (ferric) acts much like magnesium in precipitating phosphate, the maximum precipitation occurring at reactions of pH 2.5 and steadily decreases.

**TABLE 1.---Effect of calcium on phosphate solubility.**

<table>
<thead>
<tr>
<th>Calcium equivalency of phosphate</th>
<th>Percentage phosphate precipitated at pH of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>1/3 &amp;noline;CaH2(PO4)2</td>
<td>0</td>
</tr>
<tr>
<td>2/3 = CaHPO4</td>
<td>0</td>
</tr>
<tr>
<td>3/3 = Ca3(PO4)2 + Ca</td>
<td>26</td>
</tr>
<tr>
<td>4/3 = Ca3(PO4)2 + 2Ca</td>
<td>32</td>
</tr>
<tr>
<td>6/3 = Ca3(PO4)2 + 3Ca</td>
<td>33</td>
</tr>
</tbody>
</table>

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1 Contribution No. 343 Department of Chemistry, Kansas Agricultural Experiment Station, Manhattan, Kan.
2 Soil Chemist and Professor of Chemistry.
4 Figures in parenthesis refer to "Literature Cited", p. 187.

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