

STUDIES ON THE AVAILABILITY OF MIXED  
FERTILIZERS  
IV. THE MOVEMENT AND THE CHEMICAL REACTIONS  
OF FERTILIZER ELEMENTS IN SOILS.

By

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Regarding the factors which participate in the revelation of availability of fertilizers, FUJIWARA (1), one of the writers has remarked his opinion as follows:

1. Internal factor for nutritional availability
2. External factor for nutritional availability
  - a) crop conditions factor for nutritional availability
  - b) soil conditions factor for nutritional availability
  - c) climatic conditions factor for nutritional availability.

In other words, internal factors for nutritional availabilities include chemical and physical conditions like chemical constituent, which the fertilizer itself possesses, hardness and particle size, and external factors for nutritional availabilities include some conditions like soils, kinds of crops, weather conditions and cultivated method.

So I may safely say that people do not know the substance of availability till they make clear both internal and external factor. The writers have studied the availabilities on mixed fertilizers for long years and have been making clear the internal factors for nutritional availabilities. On the other hand, the availabilities are greatly regulated, as stated above, by such external factors as soils, crops and cultivated conditions. This study was done as a link in the chain of study trying to make clear the availabilities of mixed fertilizers from the external aspects, especially from the aspects of the dynamic behavior of fertilizer elements in soil-fertilizer system. In this report, phosphate, out of the fertilizer elements, was selected as the subject and its diffusion in soils, adsorption by soils and chemical reaction with soils were studied by use of  $^{32}\text{P}$  labeled granular mixed fertilizers.

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### Experimental materials

The fertilizers used in these experiments are three kinds of granular mixed fertilizers labeled with  $^{32}\text{P}$ . These are superphosphate system (L), monoammonium phosphate system ( $\text{H}_1$ ) and diammonium phosphate system ( $\text{H}_2$ ). The soils used are alluvial and volcanic ash soil. The chemical properties of fertilizers and soils used in this experiments are shown in table 1 and table 2.

Table 1. Properties of used fertilizers\*

Name of mixed fertilizers	Content of fertilizer elements (N : $\text{P}_2\text{O}_5$ : $\text{K}_2\text{O}$ ) (%)	Labeled form by $^{32}\text{P}$	Specific activity of $^{32}\text{P}$ ( $\mu\text{C/g-P}_2\text{O}_5$ )
Superphosphate system (L)	8 : 8 : 8	superphosphate	472
Ammonium phosphate system ( $\text{H}_1$ )	13 : 13 : 13	monoammonium phosphate	540
Ammonium phosphate system ( $\text{H}_2$ )	13 : 13 : 13	diammonium phosphate	929

\* the diameter of granule = 1~2<sup>mm</sup>

Table 2. Chemical properties of used soil

Name of soil	pH	Exchangeable acidity ( $y_1$ )	$\text{P}_2\text{O}_5$ absorption (mg)	1% Citric acid soluble $\text{P}_2\text{O}_5$	Cation exchange capacity (m.e)	Silica-alumina ratio
Minamikoizumi alluvial soil	5.89	1.65	954	0.043	28.0	5.79
Kawatabi volcanic ash soil	5.27	2.30	1678	0.011	37.5	1.96

### Experimentals

#### I. Diffusion in soils of $^{32}\text{P}$ labeled granular mixed fertilizers.

##### 1) Methods

The diffusion of granular mixed fertilizers was done with a one dimension limited system according to the method by MITSUI and KURIHARN (2), that is to say, 50 mg of air dried soil was filled equally in a small box (15×3×1.5 cm) made of hard polyethylene and distilled water was added to 90% of maximum water holding capacity. After that, 200 mg of granular mixed fertilizer with particle size arranged was put in the center of the box and kept at 28°C for forty-eight hours. Then the used fertilizers were diffused. After the diffusion, one part where the fertilizers were added that is to say that part of 1 cm's width was removed and the remaining part was cut into five sections of 1.4 cm's width. After each section was dried under

105~110°C in air bath, the radioactivity was measured with a G.M. counter. After that, each section was extracted by distilled water and radioactivity was measured regarding the parts extracted, and they were set as the value of the water soluble part, and in the case of the agar media, the same operation was done as in case of the soil media, and radioactivity of each section was measured.

2) Derivation of theoretical equation

Regarding the diffusion of ion in soils, the application of Fick's law by some reserchers (3, 4, 5) has been tried. In case of the diffusion in the transitive state, Fick's law can be expressed as the following fundamental equation of the diffusion.

$$\frac{\partial \theta}{\partial t} = D \frac{\partial^2 \theta}{\partial x^2} \tag{1}$$

where  $\theta$  is concentration (c p m),  $t$  is time (seconds),  $x$  is distance (cm) and  $D$  is diffusivity ( $\text{cm}^2 \cdot \text{sec}^{-1}$ )

Solving the equation (1) under the boundary condition:

$x=0, \theta=\theta_1$ , and initial condition:  $t=0, x=\infty, \theta=0$ , we obtain the equation as follows (6)

$$\theta = \theta_1 [1 - \text{erf} (y) ] \tag{2}$$

only  $\text{erf} (y) = \frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy$  is error function and this value can be obtained from

the table of number if the  $y$  is fixed, and as  $y = \frac{x}{2\sqrt{Dt}}$ , we can easily obtain diffusivity  $D$  from it.

3) Results and considerations

The diffusion of granular mixed fertilizers was showed in figure 1~3. The diffusion in the soil media showed low values in the following order  $H_2 > H_1 > L$ , in

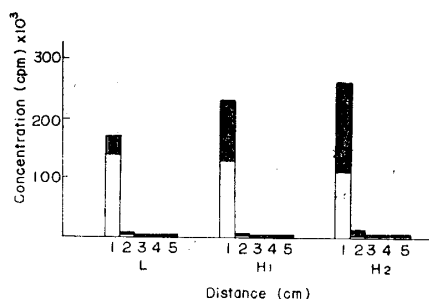


Fig. 1 The diffusion of various mixed fertilizers in alluvial soil.

(L): mixed fertilizers in superphosphate system, (H<sub>1</sub>): mixed fertilizers in monoammonium phosphate system, (H<sub>2</sub>): mixed fertilizers in diammonium phosphate system.

1) ■ = water-soluble division

2) Distance was indicated with number of soil section (1, 2, 3, 4 and 5)

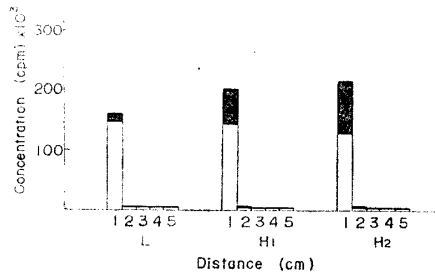


Fig 2. The diffusion of various mixed fertilizers in volcanic ash soil.

(L): mixed fertilizers in superphosphate system, (H<sub>1</sub>): mixed fertilizers in monoammonium phosphate system, (H<sub>2</sub>): mixed fertilizers in diammonium phosphate system.

- 1) = water-soluble division
- 2) Distance was indicated with number of soil section (1, 2, 3, 4 and 5)

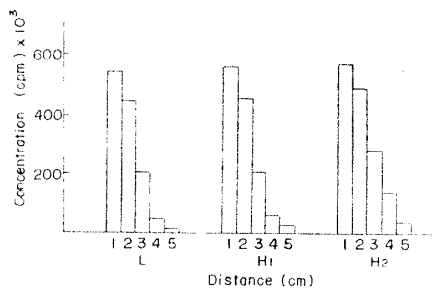


Fig 3. The diffusion of various mixed fertilizers in agar media.

(L): mixed fertilizers in superphosphate system, (H<sub>1</sub>): mixed fertilizers in monoammonium phosphate system, (H<sub>2</sub>): mixed fertilizers in diammonium phosphate system.

- 1) Distance was indicated with number of agar section (1, 2, 3, 4 and 5)

both total and water soluble part. That is to say the ammonium phosphate system shows a high rate of soil diffusion, and in its diffused and fixed part the water soluble form was recognized to occupy high rate, while the diffusion in the agar media made little difference. But the value of H<sub>2</sub> seemed somewhat high.

The fact that the differences, though few, appeared in the agar media where the adsorption, fixation and insolubility of ion are not under consideration, may show that it is mostly caused by the solubility of the phosphatic salts. From the above-mentioned results, remarkable differences between the diffusion in the soil media and that in the agar media were seen. Supposing the diffusion in the agar media to be unmixed and to be positive diffusion, the diffusion in the soil media, where the adsorption and fixation of ion was happened, will justifiably be supposed to be apparent diffusion.

In order to make clear the differences between the positive diffusion and the

apparent diffusion or the differences of diffusivity among the used media, a theoretical formula participating in the diffusion was applied. Regarding the theoretical formula, when D was kept constant, the distribution of theoretical concentration which was obtained from the equation (2) and that obtained from the experimental data, show nearly approximate value in distance (X) was small values (see Fig. 4), and so under the conditions in this experiment, we thought that the application of this theoretical formula was possible.

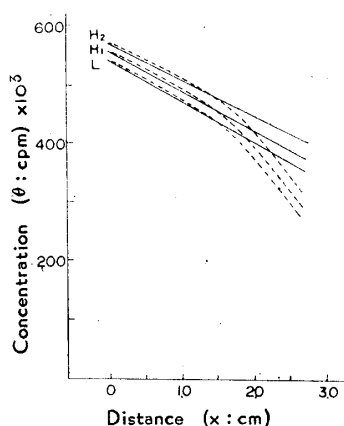


Fig 4. The distribution of theoretical concentration of diffusion in the agar media. (L): mixed fertilizers in superphosphate system, (H<sub>1</sub>): mixed fertilizers in monoammonium phosphate system, (H<sub>2</sub>): mixed fertilizers in diammonium phosphate system.

(note) D: Constant  
 —: the theoretical value  
 ----: the value of actual measurement

Regarding the diffusion of ions in the soils, still another new theoretical formula was led by PORTER (4) or OLSEN (5).

We examined the diffusion of ions in solution as one stage and showed that they can be indicated as error functions when D is constant.

In case of diffusion in the agar media, the distribution of theoretical concentration, when D was made constant, is shown in fig. 4, and the value of diffusivity which was computed is shown in table 3. From the table 3, it was recognized

Table 3. The diffusivity of various mixed fertilizers

Used fertilizers	Agar media (cm <sup>2</sup> sec <sup>-1</sup> )	Alluvial soil (cm <sup>2</sup> sec <sup>-1</sup> )	Volcanic ash soil (cm <sup>2</sup> sec <sup>-1</sup> )
L	0.829 × 10 <sup>-4</sup> (1.000)	1.972 × 10 <sup>-6</sup> (0.024)	1.933 × 10 <sup>-6</sup> (0.023)
H <sub>1</sub>	0.936 × 10 <sup>-4</sup> (1.000)	2.538 × 10 <sup>-6</sup> (0.027)	2.321 × 10 <sup>-6</sup> (0.025)
H <sub>2</sub>	1.132 × 10 <sup>-4</sup> (1.000)	2.691 × 10 <sup>-6</sup> (0.024)	2.648 × 10 <sup>-6</sup> (0.023)

(annotation) 1. Diffusivity was indicated with the average value of five.  
 2. The value of ( ) was indicated with index when the agar media was fixed 1.0.

that the diffusivity of granular mixed fertilizer in soils showed clear differences in figures in compliance with the forms of phosphate, and the superphosphate system showed a lower value than that of the ammonium phosphate system.

Computing the index number in soil media under the fixation of diffusivity in agar media, the differences of its value by the phosphate forms or the soil forms was scarcely perceived. This may be due to the fact that the value of diffusivity, which showed  $10^{-2}$  order in the soil media, is remarkably lower in comparison with that in the agar media and the difference of diffusivity by the phosphate forms in soil media is remarkably lower in comparison with that in the agar media. In observing, however, the diffusion extending for a long time, it is guessed that same changes will perhaps occur according to the soil-forms and the diffusion in volcanic ash soil which has a big phosphate fixation capacity became remarkably lower.

So the same phenomena can happen also in the phosphate form. But in this case, it is possible that the difference which is due to the phosphate-forms depends much upon the ratio in which the water soluble form in the diffusion fixed parts rather than the size of diffusivity. As the result of this experiment, in the fertilizers of the ammonium phosphate system water soluble forms occupied a greater ratio than that of the superphosphate system. It can be guessed that the fertilizers of the ammonium phosphate system, as OKUDA (7) et al described, is often high in availability of place. The obtained value of diffusivity was fairly higher than that obtained by other researchers (2, 3, 8). This might be due to the fact that the used concentration was high and that the diffusion time was long and that the water capacity was great.

## II. Adsorption and its fractionation by soils of $^{32}\text{P}$ labeled granular mixed fertilizers.

### 1) Method

The functional determination of phosphate which was absorbed in soils was done under the method by CHANG and JACKSON (9, 10). That is to say, the used soil of 2 mg was put in the Erlenmeyer's flask of 100 cc, and after that 5 cc of distilled water and 25 mg of the used fertilizers were added gradually, they were incubated separately for 24 hours and for a week under  $28^{\circ}\text{C}$ . After the incubation, the phosphate was immediately fractionated by form and the radioactivity of each form was measured with a G.M. counter.

### 2) Results and consideration

The distribution of each form of the phosphate which was absorbed in the soil were shown in table 4~5. From these tables, the initial adsorption capacity of volcanic ash soil was larger than that of alluvial soil, and the superphosphate system showed a higher value than that of the ammonium phosphate system. From table 4, regarding the rate of the composition of phosphate to the first adsorption capacity,  $\text{NH}_4\text{F}$  extract that is to say Al-compound, which occupied 50~70%, was large in every system, and NaOH extract that is Fe-compound was next to the

former.

**Table 4.** Distributions of phosphate absorbed by soils. (in case of 24 hours later)

Used soil	Name of the used fertilizers	Amount of initial adsorption	1N-NH <sub>4</sub> Cl extract (%)	0.5N-NH <sub>4</sub> F extract (%)	0.1N-NaOH extract (%)	0.5N-H <sub>2</sub> SO <sub>4</sub> extract (%)	Residues (%)
Alluvial soil	L	125.1	1.0	51.7	32.0	12.6	2.7
	H <sub>1</sub>	111.8	3.2	52.5	27.6	14.6	2.1
	H <sub>2</sub>	104.1	5.7	50.9	27.4	14.3	1.7
Volcanic ash soil	L	157.4	0	57.9	28.4	11.0	3.0
	H <sub>1</sub>	140.9	1.2	67.4	18.5	10.4	2.5
	H <sub>2</sub>	143.4	1.7	67.0	18.7	10.7	1.9

(annotation) L=Mixed fertilizers in superphosphate system  
 H<sub>1</sub>=Mixed fertilizers in monoammonium phosphate system  
 H<sub>2</sub>=Mixed fertilizers in diammonium phosphate system

**Table 5.** Distributions of phosphate absorbed by soils. (in case of a week later)

Used soil	Name of the used fertilizers	Amount of initial adsorption	1N-NH <sub>4</sub> Cl extract (%)	0.5N-NH <sub>4</sub> F extract (%)	0.1N-NaOH extract (%)	0.5N-H <sub>2</sub> SO <sub>4</sub> extract (%)	Residues (%)
Alluvial soil	L	194.0	0.9	38.3	43.4	11.7	5.7
	H <sub>1</sub>	169.7	1.6	44.9	38.9	10.4	4.2
	H <sub>2</sub>	163.6	3.2	46.3	34.0	12.5	4.0
Volcanic ash soil	L	258.8	0.5	44.6	41.9	9.0	4.0
	H <sub>1</sub>	189.1	1.2	55.8	31.2	8.3	3.5
	H <sub>2</sub>	171.7	1.0	59.7	26.0	10.6	2.7

(annotation) L=Mixed fertilizers in superphosphate system  
 H<sub>1</sub>=Mixed fertilizers in monoammonium phosphate system  
 H<sub>2</sub>=Mixed fertilizers in diammonium phosphate system

But the differences according to the used fertilizers were not clear except in the case of the NaOH extract, and regarding the soil form, NaOH extract in alluvial soil and NH<sub>4</sub>F extract in volcanic ash soil showed a little higher value. This value will be influenced by the quantity of Al or Fe which are contained in the soil and by their activity. From table 5, the pattern in the distribution of each form of the adsorbed phosphate in case of the incubating for a week showed a pretty change in comparison with the case of 24 hours. That is to say the NH<sub>4</sub>F extract decreased, but on the contrary the rate of NaOH extract has been gradually increasing. This increment has been perceived in the fertilizers of the superphosphate system.

Together with the lapse of time, as mentioned in the preceding sentence, there occurred some changes in case of the distribution of each form of adsorbed phosphate, and from this, it became clear that the phosphate applied is initially absorbed as Al compound and next as Fe compound. SAEKI (11), YUAN (12) and some other researchers have stated that most of the phosphate applied was fixed as chemical compounds of Al and Fe, and MACHOLD (13) also has perceived that, after he had done the fractional determination of phosphate adsorbed in soil, the Al and Fe compounds are especially numerous. JACKSON (14, 15) et al, after investigating the solubility products of aluminium phosphate and iron phosphate, has stated that the aluminium phosphate is easily created in the system where both compounds were mixed under the same pH, furthermore they have stated that in the phosphate once created, iron phosphate was hard to dissolve and stable. Thus Fe gradually replaced the Al phosphate. From our experimental results, regarding the increment of the rate, which Fe compounds occupies, increased together with the lapse of time, we can easily understand it by the explanations by JACKSON and some researchers.

And in comparison with that of ammonium phosphate system, the fertilizers of the superphosphate system rather inclined to show a high value of NaOH extract. As WILLIAM(16) and some other researchers describes about this, if the Fe compound controls the intensity of the phosphate fixation, the fertilizers of the superphosphate system can be said to contain the factor which intensifies the phosphate fixation capacity.

This can be guessed from the fact that the part of residues that is to say the phosphate form of occluded type was much more evident in the fertilizers of the superphosphate system. From this it can be guessed that there are some differences between the superphosphate system and the ammonium phosphate system in point of the capacity which is adsorbed and fixed by soil and in point of mechanism of phosphate fixation. This may be safely guessed to be the important factor which regulate the difficulty or easiness in absorption and its utilization of phosphorus by plants.

### III. *The chemical reaction of various phosphates to soils.*

#### 1) *Method*

From the used soil the clay which is the nucleus of the soil, was separated by sedimentation method and Ca-clay, the diameter of which is below  $2\mu$ , was obtained. But from the nature of this experiment, these clay is not tried removal of aluminium or removal of iron. The obtained clay made the clay mineral of montmorillonite type the subject not only in alluvial soil but also in volcanic ash soil.

About volcanic ash soil which contains montmorillonite, MASUI (17) et al has described in detail. The standard bentonite for comparison was refined by the same method as above mentioned. 200mg of clay was put in a triangle flask of 100 cc, and after IM phosphate solution was added to this, this was reactioned



separately for a week and for four weeks under 28°C.

The used phosphate solution consists of kinds of different from that is to say monocalcium phosphate (MCP), monoammonium phosphate (MAP) and diammonium phosphate (DAP) (each reagent used was guaranteed) after the reaction, crystallized phosphates were analyzed and identified by Geiger Flex X-ray diffraction.

2) *Results and considerations*

The identified salts by x-ray diffraction were shown in table 6~7. From table 6, fair differences were perceived in the identified salts according to the forms of phosphate. That is to say, silicate chemical compound which contains Fe and Al and basic phosphate which contains Al in DAP form, and basic phosphate, which contains Al, Fe and  $\text{AlPO}_4$  in MAP form, and basic phosphate which contains Al,  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  in MCP form were confirmed respectively. According to the differences of the identified salts, it was made out that the reaction of the phosphate fixation is promoted most in the MCP form and in slow in order of MAP form and DAP form. That is still made clear from the fact that, though none salts were confirmed in the DAP form in Bentonite-clay,  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  in MCP form and basic phosphate in MAP form were identified. Examining the degrees of reaction of the fixation of phosphate about each clay, it was inclined to progress in volcanic ash soil rather than in alluvial soil. As the above mentioned result, the crystallization of phosphate was most progressed in MCP form, and it was made clear that it was remarkable especially in volcanic soil. In case of the reaction of a week later, the creation of basic phosphate was perceived and at the same time it is guessed that phosphate minerals such as variscite or strengite are created in large qualities.

**Table 6.** Identified salts by X-ray diffraction (in case of a week later)

The form of the used clay	The form of added phosphate	Identified compounds
Alluvial soil	MCP	$\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$ , basic Al.Phos. hydrate
	MAP	Basic Al. phos. hydrate
	DAP	Basic Al. silicate, $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$
Volcanic ash soil	MCP	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$
	MAP	Basic Fe. phos. hydrate, $\text{AlPO}_4$
	DAP	Basic Al. phos. hydrate, basic Fe silicate
Bentonite	MCP	Basic Al.phos. hydrate, $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$
	MAP	Basic Al. phos. hydrate
	DAP	none

(annotation) MCP=Monocalcium phosphate  
 MAP=Monoammonium phosphate  
 DAP=Diammonium phosphate

**Table 7.** Identified salts by X-ray diffraction (in case of four weeks later)

The form of the used clay	The form of added phosphate	Identified compounds
Alluvial soil	MCP	$\text{CaHPO}_4, \text{FePO}_4 \cdot 2\text{H}_2\text{O}, \text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ Basic Al. phos. hydrate
	MAP	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}, \text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
	DAP	Basic Fe phos. hydrate, $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$
Volcanic ash soil	MCP	$\text{CaHPO}_4, \text{AlPO}_4 \cdot 2\text{H}_2\text{O}, \text{AlPO}_4, \text{FePO}_4, 3\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$
	MAP	$\text{CaHPO}_4, \text{AlPO}_4, \text{FePO}_4 \cdot 2\text{H}_2\text{O}$ , Basic Fe phos. hydrate
	DAP	$\text{AlPO}_4, \text{FePO}_4 \cdot 2\text{H}_2\text{O}$
Bentonite	MCP	$\text{CaHPO}_4, \text{AlPO}_4, \text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ , Basic Al phos. hydrate
	MAP	$\text{CaHPO}_4, \text{AlPO}_4$
	DAP	none

(annotation) MCP=Monocalcium phosphate  
 MAP=Monoammonium phosphate  
 DAP=Diammonium phosphate

Presumably these may exist in amorphous form (13). From table 7, in case of the reaction of four weeks later, it was guessed that the rate of phosphate are fairly progressing in comparison with the case of that of a week later. That is to say, the typical salts as phosphate mineral such as  $\text{AlPO}_4$ ,  $\text{FePO}_4$  and  $\text{CaHPO}_4$  in each part of phosphate forms could be confirmed, and according to the differences of identified salts, the speed of crystallization was slow in order of  $\text{MCP} > \text{MAP} > \text{DAP}$ , and its tendency did not as in case of the reaction of a week later. From the obtained result, the fixation of DAP form was difficult and so the degree of crystallization as phosphate mineral was little. Judging from this, it can be guessed that the rate of effectiveness of phosphate of DAP form to plants were fairly high, on the contrary low in MCP form. It can also be guessed that such differences are greatly due to the chemical properties such as the solubility, the kinds of combined cation and maintaining pH of added phosphate. From table 7,  $\text{CaHPO}_4$  was identified in all parts. That the clay acted on this as a catalyst and became a stable form, can be supposed in the MCP form. But in this case, it may be still be proper to consider that, from the viewpoint that the creation of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  form was not perceived at all and that  $\text{CaHPO}_4$  was created even in the part of MAP form, the added phosphate had directly reacted on the calcium ion in Ca-Clay and as the result,  $\text{CaHPO}_4$  was created. From the reaction of various phosphates to clay mineral it has been confirmed that, by such researchers as HASEMAN (18, 19), JACKSON (20), WADA (21), and BEATON (22) the creations by reaction finally crystallize as such phosphate minerals as variscite, strengite, minyulite and taranakite like, and the creation of various phosphate minerals from the reaction of various phosphate

fertilizers to soil have been recognized recently by LINDSAY (23) and some other researchers. In case of this experiment, though the used clay-minerals was montmorillonite type, from the creations by reaction, minyulite, taranakite like phosphate minerals were not perceived. But as the early-creations by reaction, basic phosphate could be clearly confirmed. The possibility of being formed for this form as the creation by reaction had already been indicated by SWENSON (24).

### Summary

The factors, which may participate in the availabilities of mixed fertilizers, were examined from the standpoint of the movements of fertilizers elements in soils. The obtained result can be summerized as follows: In the case of the ammonium phosphate form, in comparison with that of the superphosphate form, 1) the water soluble form occupied a greater part on the diffused and fixed parts in the soils, 2) Fe compounds occupied fewer part in the distribution by each form of phosphate adsorbed in soils, 3) phosphate minerals like variscite, strengite were not easily created in the chemical reaction to the clay-mineral.

From the above mentioned result, it can be guessed that the ammonium phosphate form has a higher rate of effectiveness of phosphate to the plants than that of the superphosphate form.

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