

CHEMICAL CONSTITUTION AND AVAILABILITY OF IRON AND ALUMINUM PHOSPHATES I. STUDIES ON THE CONSTITUTIONS AND MANURIAL EFFECTS OF SCARCELY SOLUBLE PHOSPHATES

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CHEMICAL CONSTITUTION AND AVAILABILITY OF IRON AND ALUMINUM PHOSPHATES

I. STUDIES ON THE CONSTITUTIONS AND MANURIAL EFFECTS OF SCARCELY SOLUBLE PHOSPHATES

By

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It is of great necessity in Japan to give consideration to the scarcely soluble phosphates as well as the water-soluble phosphates. In our country, vast areas of arable fields are covered with volcanogenous ash loam of allitic nature, the reaction of these soils is somewhat acid, so the water-soluble phosphates applied as fertilizer to these soils are quickly fixed by alumina and iron oxide existing as soil colloids.

Moreover we were obliged to use poor quality phosphate rocks, rich in sesquioxides, as soluble phosphatic fertilizer, which are reduced to an insoluble form upon storing.

From this point of view, we made a special study on the chemical constitution and the manurial effect of iron, aluminium and other sesquioxide phosphates.

As we know, the chemical constitution of compounds of phosphoric acid and sesquioxides are very complicated, a number of formulae are postulated by many investigators, as shown in the literatures below.^{4,5,6,7}

Materials.

The samples used for our research were salts such as $\text{FeH}_6\text{P}_3\text{O}_{12}$, $\text{Fe}_2\text{H}_9\text{P}_5\text{O}_{20}$, $\text{FeH}_3\text{P}_2\text{O}_8$, $\text{Fe}_2\text{H}_3\text{P}_3\text{O}_{12}$, FePO_4 , $\text{AlH}_6\text{P}_3\text{O}_{12}$, $\text{Al}_2\text{H}_9\text{P}_5\text{O}_{20}$, $\text{AlH}_3\text{P}_2\text{O}_8$, $\text{Al}_2\text{H}_3\text{P}_3\text{O}_{12}$ and AlPO_4 which we prepared, according to the method shown in the cited literature, or the newly-devised synthesis method, because the chemicals on the market are not constant in their components.¹

Synthetic procedures:

Chemical analysis, X-ray analysis and measurement of hygroscopic qualities were also made.^{2,3}

Contribution from Laboratory of Soils and Fertilizers.

Table I.

$[\text{P}_2\text{O}_5]/[\text{R}_2\text{O}_3]$	Iron phosphates	Aluminum phosphates
4.00	$\text{H}_9\text{Fe}(\text{PO}_4)_4^6$	
3.00	$\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}^5$ $\text{Fe}_2(\text{H}_2\text{PO}_4)_{6,4,3}$	$\text{Al}_2(\text{H}_2\text{PO}_4)_{6,4,7}$
2.50	$\text{Fe}_2(\text{H}_2\text{PO}_4)_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}^5$	$\text{Al}_2(\text{H}_2\text{PO}_4)_4\text{HPO}_4 \cdot 2\text{H}_2\text{O}^5$
2.00	$\text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}^5$ $\text{FeH}_3(\text{PO}_4)_{2,4,5}$ $\text{Fe}_2(\text{H}_2\text{PO}_4)_2(\text{HPO}_4)_2^4$	$\text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5$ $\text{AlH}_3(\text{PO}_4)_{2,4,6}$ $\text{Al}_2(\text{H}_2\text{PO}_4)_2(\text{HPO}_4)_2^6$
1.75	$\text{Fe}_4(\text{HPO}_4)_5(\text{H}_2\text{PO}_4)_2^5$	$\text{Al}_4(\text{HPO}_4)_5(\text{H}_2\text{PO}_4)_2^5$
1.50	$2\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5^4$	$2\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$ $\text{Al}_2(\text{HPO}_4)_{3,6,7}$
1.425	$(\text{Fe}_2)_4(\text{PO}_4)_2(\text{PO}_4\text{H})_3^5$	
1.333	$\text{Fe}_6\text{H}_6\text{P}_8\text{O}_{32}^5$	
1.25	$(\text{Fe}_2)_4(\text{PO}_4)_4(\text{PO}_4\text{H})_6^5$	
1.167	$(\text{Fe}_2)_3(\text{PO}_4\text{H})_3(\text{PO}_4)_4 \cdot 12\frac{1}{2}\text{H}_2\text{O}^5$	
1.125	$(\text{Fe}_2)_4(\text{PO}_4)_6(\text{PO}_4\text{H})_3^5$	
1.00	$\text{FePO}_4^{4,5,6,7}$	$\text{AlPO}_4^{4,5,6,7}$

 $\text{FeH}_6\text{P}_3\text{O}_{12}$

This compound was prepared by a somewhat modified method according to Erlenmeyer and Heinrich.⁵ It is a brownish pink crystalline powder, which is very hygroscopic. After 24 hours exposure to air, it deliquesces remaining some solid. This salt shows the following chemical analysis.

	P_2O_5	Fe_2O_3	H_2O^+	$[\text{P}_2\text{O}_5]/[\text{Fe}_2\text{O}_3]$	$[\text{H}_2\text{O}]/[\text{Fe}_2\text{O}_3]$
Analysis	61.12	23.26	15.61	2.95	5.95
$\text{FeH}_6\text{P}_3\text{O}_{12}$ theory	61.38	23.05	15.56	3.00	6.00

This analysis agrees with $\text{Fe}_2\text{O}_3(\text{P}_2\text{O}_5)_3 \cdot 6\text{H}_2\text{O}$ or $\text{FeH}_6\text{P}_3\text{O}_{12}$.^{12,13} The X-ray pattern was hindered by hygroscopicity and showed a somewhat diffused ring.

 $\text{Fe}_2\text{H}_9\text{P}_5\text{O}_{20}$

In making this compound, 30% phosphoric acid was saturated with commercial FeFO_4 , and the supernatant solution was separated, then evaporated in a steam bath.

Fine pink crystals were formed during the evaporation. After being washed thoroughly with ether, the crystals were analysed with the following result.

	P_2O_5	Fe_2O_3	H_2O^+	$[\text{P}_2\text{O}_5]/[\text{Fe}_2\text{O}_3]$	$[\text{H}_2\text{O}]/[\text{Fe}_2\text{O}_3]$
Analysis	58.33	26.07	14.60	2.51	4.96
$\text{Fe}_2\text{H}_9\text{P}_5\text{O}_{20}$ theory	58.71	26.40	14.89	2.50	5.00

Deliquescent.

X-ray pattern shows many clear rings.

$FeH_3P_2O_8$

This is so called Winkler's salt.⁸

The filtrate from $Fe_2H_9P_5O_{21}$ crystal above, was stored in the desiccator for about one year. During this time many pinkish gray crystalline powders were formed on wall of the flask, the composition of which was as follows;

	P_2O_5	Fe_2O_3	H_2O^+	$[P_2O_5]/[Fe_2O_3]$	$[H_2O]/[Fe_2O_3]$
Analysis	47.79	26.91	25.27	1.99	8.31
$FeH_3P_2O_8 \cdot 5/2H_2O$ theory	48.30	27.21	24.49	2.00	8.00

Nonhygroscopic, X-ray analysis showed crystalline nature.

$Fe_2H_3P_3O_{12}$

This salt is synthesised by newly devised method; 70 g of ammonium dihydrogen phosphate dissolved in 50 ml of distilled water is added to 80 g of ferric sulphate in 300 ml of water containing 10 g concentrated sulphuric acid.

The mixture is neutralized with ammonia and boiled. Yellow precipitates are produced.

	P_2O_5	Fe_2O_3	H_2O^+	$[P_2O_5]/[Fe_2O_3]$	$[H_2O]/[Fe_2O_3]$
Analysis	46.61	37.66	15.73	1.40	3.70
$Fe_2H_3P_3O_{12} \cdot 2H_2O$ theory	48.89	36.65	14.96	1.50	3.50

The chemical composition is similar to $(Fe_2O_3)_2 \cdot (P_2O_5)_3 \cdot (H_2O)_7$ or $Fe_2H_3P_3O_{12} \cdot 2H_2O$. Nonhygroscopic. The X-ray pattern presents many clear rings and shows highly crystalline nature.

$FePO_4$

Concentrated water solution of $FeH_6P_3O_{12}$ was boiled, until yellow powders were precipitated.

	P_2O_5	Fe_2O_3	H_2O^+	$[P_2O_5]/[Fe_2O_3]$	$[H_2O]/[Fe_2O_3]$
Analysis	33.03	34.70	32.27	1.07	8.24
$FePO_4 \cdot 4H_2O$ theory	31.85	35.81	32.33	1.00	8.02

Nonhygroscopic. X-ray pattern shows one faint, diffused wide ring, which indicates that this salt is nearly amorphous.

$AlH_6P_3O_{12}$

This acid salt was synthesized according to a somewhat modified Erlenmeyer's⁵ method. It is a very hygroscopic needle crystal, which easily deliquesces in air.

	P_2O_5	Al_2O_3	H_2O^+	$[P_2O_5]/[Al_2O_3]$	$[H_2O]/[Al_2O_3]$
Analysis	67.32	15.86	16.82	3.05	6.00
$AlH_6P_3O_{12}$ theory	66.93	16.03	16.99	3.00	6.00

It was confirmed that the crystal is accord with $Al_2O_3 \cdot (P_2O_5)_3 \cdot (H_2O)$ namely $AlH_6P_3O_{12}$.

$Al_2H_9P_5O_{20}$

White crystals were obtained by the evaporation of a saturated solution of commercial $AlPO_4$ in 30% phosphoric acid. These were filtered and washed with ether, the crystal was analysed, with results shown below.

	P_2O_5	Al_2O_3	H_2O^+	$[P_2O_5]/[Al_2O_3]$	$[H_2O]/[Al_2O_3]$
Analysis	49.49	14.15	36.36	2.51	14.53
$Al_2H_9P_5O_{20} \cdot 10H_2O$ theory	49.42	14.20	36.38	2.50	14.50

It is a white deliquescent crystal, X-ray analysis shows that this salt is highly crystalline. Analytic results agree with $(Al_2O_3)_2 \cdot (P_2O_5)_5 \cdot (H_2O)_{20}$ or $Al_2H_9P_5O_{20} \cdot 10H_2O$.

 $AlH_3P_2O_8$

At first it was intended to synthesize this salt according to the method used for $FeH_3P_2O_8$ but this method failed. Then $AlPO_4$ was added to a hot concentrated solution of phosphoric acid in a steam bath, until the ratio of Al_2O_3 and P_2O_5 attained the proportions of $AlH_3P_2O_8$. Therefore the constitution of this salt is not as certain as the other salts cited above.

	P_2O_5	Al_2O_3	H_2O^+	$[P_2O_5]/[Al_2O_3]$	$[H_2O]/[Al_2O_3]$
Analysis	41.67	15.22	43.11	1.98	16.03
$AlH_3P_2O_8 \cdot 6\frac{1}{2}H_2O$ theory	42.12	15.12	42.76	2.00	16.00

The analysis agrees with that of $Al_2O_3 \cdot (P_2O_5)_2 \cdot (H_2O)$ or $AlH_3P_2O_8 \cdot 6\frac{1}{2}H_2O$.

 $Al_2H_3P_3O_{12}$

This salt was prepared by Millot's method slightly modified.¹⁰ The result was a white crystalline nonhygroscopic powder.

	P_2O_5	Al_2O_3	H_2O^+	$[P_2O_5]/[Al_2O_3]$	$[H_2O]/[Al_2O_3]$
Analysis	48.01	23.54	28.45	1.46	6.84
$Al_2H_3P_3O_{12} \cdot 11H_2O$ theory	48.30	23.11	28.59	1.50	7.00

This results indicates that this salt is $(P_2O_5)_2 \cdot (Al_2O_3)_3 \cdot (H_2O)_{14}$ or $Al_2H_3P_3O_{12} \cdot 11H_2O$.

X-ray patterns showed many clear rings, indicating that this powder is highly crystalline in nature.

 $AlPO_4$:

A concentrated water solution of $AlH_6P_3O_{12}$, namely 1:20, was boiled. White powders were precipitated.

	P_2O_5	Al_2O_3	H_2O^+	$[P_2O_5]/[Al_2O_3]$	$[H_2O]/[Al_2O_3]$
Analysis	41.24	28.83	29.93	1.03	5.88
$AlPO_4 \cdot 3H_2O$ theory	40.33	28.96	30.71	1.00	6.00

X-ray examination showed the patterns of this powder, to be two diffused rings, one wide and one narrow. This powder is not crystalline, almost amorphous but possesses some embryonic structure of crystal lattice.

This salt was synthesized after the hydrolysis method, X-ray analysis confirmed that the white colloidal precipitate resulting from mutual precipitation of soluble phosphates and aluminum salts, coincided in its structure with this white powder.

As a result of X-ray analysis of these salts, it was assured that the acid salts were crystalline, while the neutral salt were nearly amorphous. The neutral salts of iron, namely FePO_4 , are more amorphous than those of aluminum, namely AlPO_4 .

The hygroscopicity is stronger in the acid salt of both of aluminum and iron phosphates groups. Aluminum salts have much more hygroscopicity than the iron salts of the same form.

Manurial effect

A number of investigations on the manurial effect of aluminum and iron phosphates was made by researchers.^{15, 16, 17, 18, 19, 20, 21, 22, 23} The conclusions are various and not uniform. The reason for the differences of opinion is in the nature of salt tested, for example, the difference between newly precipitated or commercial compounds. In general the manurial effect of iron and aluminum phosphates depends upon the type of plants upon which it is used. Gramineous crops have less ability to absorb these phosphates than leguminous or cruciferous plants which have strong powers of absorption. In addition, the properties of soil, particularly water content, mechanical composition, reaction, degrees of base saturation, content of humic matter and availability of soil phosphate, affect the manurial effect of scarcely soluble phosphates.

The chemical and physiological reaction of commonly used fertilizers, particularly the nitrification of nitrogenous fertilizer, could also materially affect the manurial value. The effect of the addition of lime upon the utilization of the scarcely soluble phosphates shows various results and no conclusions can be drawn regarding its effectiveness.

From above mentioned factors, it can be seen that the manurial effect of aluminum and iron phosphates are controlled mainly by external growing factors.

We determined the manurial effect of above mentioned salts in tests on paddy rice, upland rice and barley by precise cultivation tests. As cultivating vessels 1/2017 are (1/2000 Tan) Wagner pots were used, each with 12kg of top soil of Kwanto-loam (Tanashi volcanogenous ash loam). To these were added 1gm each of N, P_2O_5 and K_2O as sulphate of ammonia, synthesized phosphates and potassium sulphate.

The cropping results are as follows :

Table II.

	Paddy-rice plant						Barley				Upland-rice plant					
	No. of ears	Weight of ear (gm)	Weight of straw (gm)	Ear weight against 100 of $\text{CaH}_4\text{P}_2\text{O}_8$ section	No. of ears	Weight of ear (gm)	Weight of straw (gm)	Ear weight against 100 of $\text{CaH}_4\text{P}_2\text{O}_8$ section	No. of ears	Weight of ear (gm)	Weight of straw (gm)	Ear weight against 100 of $\text{CaH}_4\text{P}_2\text{O}_8$ section	No. of ears	Weight of ear (gm)	Weight of straw (gm)	Ear weight against 100 of $\text{CaH}_4\text{P}_2\text{O}_8$ section
non- P_2O_5	9.0	6.20	10.40	19.3	4.5	0.35	1.70	0.9	9.0	8.05	11.40	40.7	9.0	8.05	11.40	40.7
$\text{CaH}_4\text{P}_2\text{O}_8$	35.0	32.20	41.55	100.0	31.0	38.95	24.50	100.0	21.0	19.80	36.05	100.0	21.0	19.80	36.05	100.0
$\text{FeH}_6\text{P}_3\text{O}_{12}$	35.0	32.10	40.00	99.7	24.5	23.00	20.10	59.1	19.5	19.40	37.10	98.0	19.5	19.40	37.10	98.0
$\text{Fe}_2\text{H}_9\text{P}_5\text{O}_{20}$	34.5	32.30	40.20	100.4	19.5	14.85	13.40	38.1	19.0	18.90	35.40	98.5	19.0	18.90	35.40	98.5
$\text{FeH}_3\text{P}_2\text{O}_8$	35.0	31.75	39.10	98.6	9.5	8.35	10.40	21.2	14.5	15.65	31.35	79.0	14.5	15.65	31.35	79.0
$\text{Fe}_2\text{H}_3\text{P}_3\text{O}_{12}$	29.5	29.95	35.37	93.1	9.0	4.10	9.65	10.5	14.0	14.80	27.30	74.7	14.0	14.80	27.30	74.7
FePO_4	31.0	27.50	35.15	85.4	8.5	2.65	6.55	6.8	3.0	13.45	24.30	67.9	3.0	13.45	24.30	67.9
$\text{AlH}_6\text{P}_3\text{O}_{12}$	34.0	31.80	41.52	98.7	26.5	26.95	23.60	69.2	19.0	18.25	33.25	92.2	19.0	18.25	33.25	92.2
$\text{Al}_2\text{H}_9\text{P}_5\text{O}_{20}$	34.0	30.30	39.98	94.2	27.0	26.00	22.05	66.7	19.5	19.20	35.80	97.0	19.5	19.20	35.80	97.0
$\text{AlH}_3\text{P}_2\text{O}_8$	35.5	29.60	38.90	91.9	28.0	22.70	22.30	58.3	17.5	15.60	29.65	78.8	17.5	15.60	29.65	78.8
$\text{Al}_2\text{H}_3\text{P}_3\text{O}_{12}$	33.0	28.50	35.75	88.6	15.0	8.45	11.00	21.7	17.5	15.35	29.05	77.5	17.5	15.35	29.05	77.5
AlPC_4	25.5	22.80	28.90	70.8	7.5	5.50	8.85	14.1	14.0	12.50	18.60	63.1	14.0	12.50	18.60	63.1

For the rice plant, $\text{FeH}_6\text{P}_3\text{O}_{12}$ was found superior to soluble $\text{CaH}_4\text{P}_2\text{O}_8$. Also the other iron salt groups are better than the same type of aluminum salt groups. During the early stage of plant growth, aluminum salts appeared more effective than iron salts, but in the mid-summer plants fertilized with iron salts caught up with those on which aluminum salts were used.

In general, the effectiveness increases as the value of $[\text{P}_2\text{O}_5]/[\text{R}_2\text{O}_3]$ increases.

In contrast to the above the barley plants fertilized with iron salts fell behind those fertilized with aluminum salts. At the time of harvest plants on which iron salt groups were used, were very poor compared with those grown on the aluminum salt groups. Aluminum salt groups were far inferior to soluble calcium phosphate.

The result for the cultivation experiment on upland-rice, was midway between barley and paddy rice.

(1) These results reveal, generally speaking that the manurial effect increases as the value of $[\text{P}_2\text{O}_5]/[\text{R}_2\text{O}_3]$ increases, in the case of acid salts. (2) Manurial effect of iron salts group is less effective for barley. Upland rice indicates intermediate phenomenon. (3) Moreover, manurial effect of both iron and aluminum salts groups is very high for paddy rice, but in general low for barley, except in the case of one or two acid salts such as $\text{AlH}_6\text{P}_3\text{O}_{12}$, $\text{Al}_2\text{H}_9\text{P}_5\text{O}_{20}$ and $\text{FeH}_6\text{P}_3\text{O}_{12}$. (4) The inhibitional action of the soluble aluminum and iron ion was never found.

It appears that the fluctuation of the manurial effect of scarcely soluble phosphates depends upon the conditions of cultivation namely the amount of water available in paddy or upland field conditions.

Experimental I

Various experiments were made in order to clarify the causes for the phenomena. At first habitual methods of research were used to determine the manurial effect of these salts.

As a whole, the phosphates of sesquioxides are easily soluble in Petermann's solution, namely alkaline ammonium citrate, without regard to the ratio of $[\text{P}_2\text{O}_5]/[\text{R}_2\text{O}_3]$.

Solubilities in water and 2% citric acid solution are affected by the ratio of $[\text{P}_2\text{O}_5]/[\text{R}_2\text{O}_3]$, aluminum salts groups are more easily soluble than iron salts, but the solubilities in both solutions are not proportional to the manurial effect. So we were obliged to find another simple determination method for manurial effect.

Then seedling method by Neubauer, was adopted. As a cultivation

Table III.

	Total P ₂ O ₅ (T.P.)	P ₂ O ₅ Soluble in water (H.P.)	P ₂ O ₅ Soluble in Petermann's Solution (P.P.)	P ₂ O ₅ Soluble in 2% citric acid(C.P.)	H.P./T.P.	P.P./T.P.	C.P./T.P.
AlH ₆ P ₃ O ₁₂	63.72	66.72	66.72	66.72	100.0	100.0	100.0
Al ₂ H ₉ P ₅ O ₂₀	45.91	24.72	45.80	30.89	53.8	99.8	67.3
AlH ₃ P ₂ O ₈	41.67	6.02	40.89	18.11	14.5	98.3	43.5
Al ₂ H ₃ P ₃ O ₁₂	36.40	0.61	35.98	10.93	1.7	98.8	30.0
AlPO ₄	41.47	0.16	41.02	1.35	0.4	98.9	3.3
FeH ₄ P ₃ O ₁₂	57.69	20.14	57.65	41.58	34.9	99.9	72.1
Fe ₂ H ₉ P ₅ O ₂₀	53.74	6.36	53.08	30.49	11.8	98.8	56.7
FeH ₃ P ₂ O ₈	47.79	2.76	47.50	10.20	5.8	99.4	21.3
Fe ₂ H ₃ P ₃ O ₁₂	39.05	0.35	38.89	7.71	0.9	99.6	19.7
FePO ₄	33.03	0.12	32.68	0.88	0.4	98.9	2.7

media, white quartz sand washed with concentrated hydrochloric acid, was used, other treatment is the same as Neubauer's method.

The results were as follows ;

Table IV.

	P ₂ O ₅ mg Amount absorbed by rice seedling	Rate of absorption %
CaHPO ₄	5.5	22.0
C ₁₃ P ₂ O ₈	3.5	14.0
FeH ₄ P ₃ O ₁₂	4.0	16.0
Fe ₂ H ₃ P ₃ O ₁₂	2.3	9.2
FePO ₄	1.1	4.4
AlH ₆ P ₃ O ₁₂	7.0	28.0
Al ₂ H ₃ P ₃ O ₁₂	4.4	17.6
AlPO ₄	1.5	6.0

The salt was used in the proportion of 25 mg P₂O₅ to each pot.

The rate of P₂O₅ absorbed by seedling is fairly similar to manurial effect estimated by pot cultivation test. By this method we can easily estimate the general trend of the manurial effect.

Experimental II

Then experiments to determine the basic nature¹⁴ of the release of phosphate ion from scarcely soluble phosphates were made, at first degree of solution or hydrolyse of phosphate in the water, was examined.

The sample of salt, each containing 10 mg of P₂O₅, was weighed in a

250 ml Telex flask, 100 ml distilled water or water containing various amount of hydrochloric acid or sodium hydroxide was added to obtain the desired PH.

The flask was stoppered and shaken for 3 hours, left stand for 12 hours, and then again shaken for an hour. The suspension was filtered and carefully analysed and the solubilities of P_2O_5 were plotted against the final hydrogen iron concentration. The results are shown below (figure 1 and 2) :

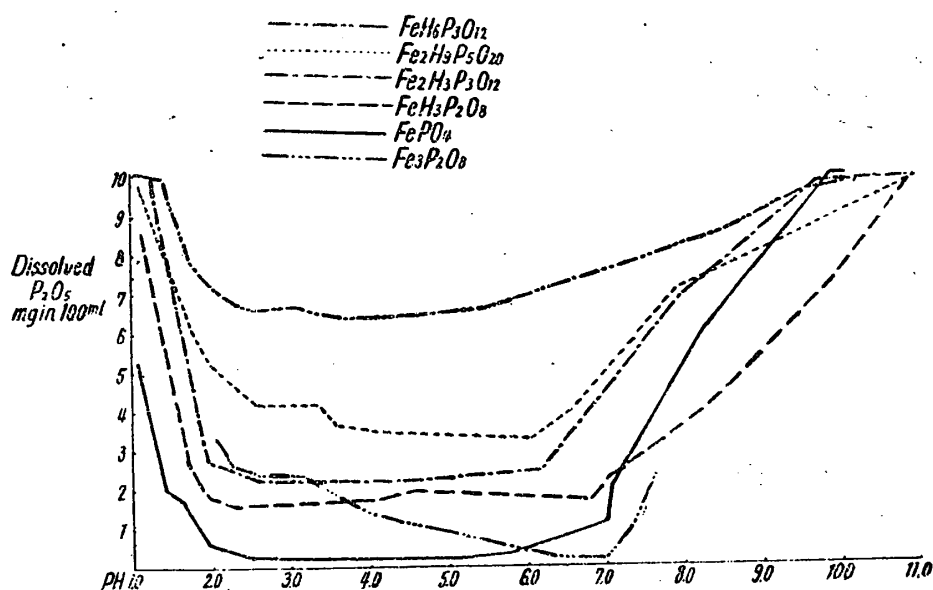
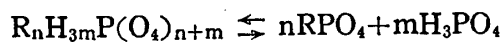


Fig. 1.

When these salts are suspended in water, acid salts are fairly well dissolved, isolating a part of phosphate ion, and the precipitates becomes richer in R_2O_3 than the original salts. Next, the precipitates are hydrolysed isolating phosphate ion again. When the final hydrogen ion concentration was greater and the reaction was acid, both cation and phosphate ion went into the solution. While, if the reaction of the final solution turned less acid to some degree, the cation disappeared and phosphate-ion in the solution diminished but did not disappear. The pH value at the disappearance of cation differs in the aluminum and iron groups, at pH 2.4 for aluminium, at pH 1.6 for the iron group. In the alkaline side, from a definite pH the phosphate ion again increases in solution by hydrolysis. Aluminium ion goes into solution as aluminate, but iron ion does not.

So the figures indicate that $AlPO_4$ and $FePO_4$ curves are fundamental, and curve of other acid salts is one with the phosphate ion, added namely ;



The concentration of phosphate ion is the lowest at pH 3~5 in case of iron salts, and at pH 4~6 in case of aluminium salts. For example RPO_4 hydrolyses as follows;

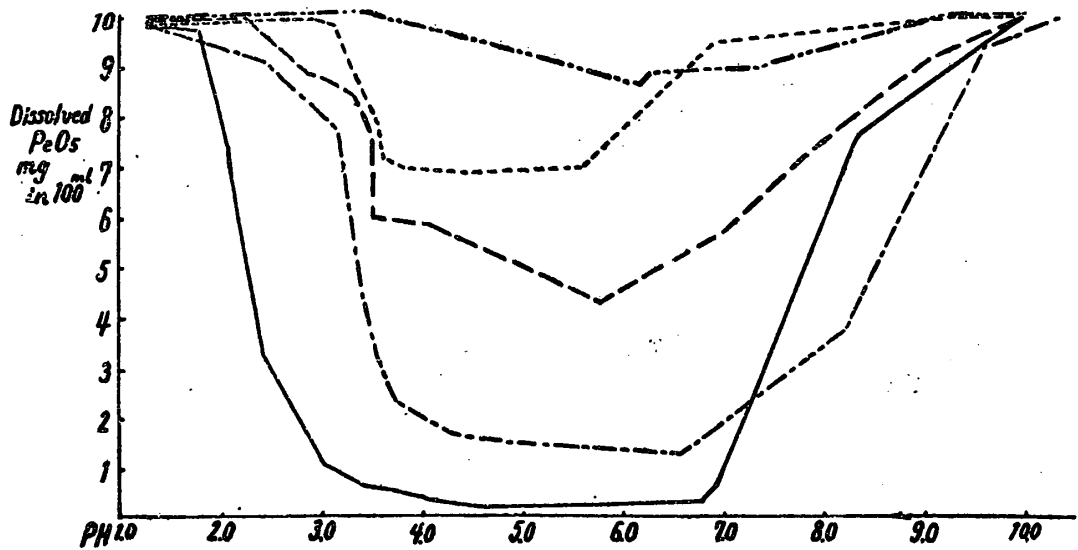
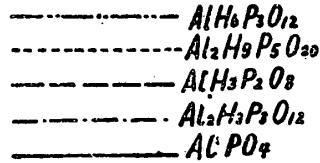
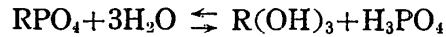


Fig. 2.

$R(OH)_3$ is scarcely soluble or almost insoluble, while H_3PO_4 is weak acid and will, to some degree, dissociate and release hydrogen ions, so that the solution turns fairly acidic.

When an alkaline substance was added and exhausted the hydrogen ion, the reaction tends to move to right side of the formula, and release soluble phosphate ions as a result. On the contrary, when the acidic matter was added, then by the law of mass action, the reaction turns to left side and diminishes the solubility of phosphate ion.

As to $Fe_3P_2O_8$, the experiment was carefully controlled to prevent oxidation by filling the remaining space of the flask with gaseous hydrogen. In the alkaline side $Fe_3P_2O_8$ reacts quite similarly to $FePO_4$, but in the acid side $Fe_3P_2O_8$ easily goes into solution and releases phosphate ions and ferrous iron ions. $Fe_3P_2O_8$ reacts in the acid side as if it was the phosphate of alkaline earth, such as $Ca_3P_2O_8$ or $Mg_3P_2O_8$.

Apart from the above mentioned low solubility range, regardless of acidic and alkaline side, phosphate ion is easily released. In the acid side the solution of total salt goes on, and alkaline side the hydrolysis is working. In the water lodged paddy condition, high temperature, a large amount of water and alkaline reaction of surface water are present which accelerates the hydrolysis. Therefore research concerning factors on hydrolysis was carried out :

Table V. Effect of Temperature.

Temperature	FePO ₄		AlPO ₄	
	pH	P ₂ O ₅ dissolved mg/100 ml.	pH	P ₂ O ₅ dissolved mg/100 ml.
1. 0°C	5.66	0.10	5.96	0.13
2. 10°C	5.58	0.10	5.70	0.14
3. 20°C	5.58	0.12	5.64	0.17
4. 30°C	5.54	0.19	5.64	0.18
5. 40°C	5.50	0.28	5.50	0.26
6. 50°C	5.41	0.55	4.72	0.50
7. 60°C	5.90	0.98	4.52	0.80
8. 80°C	4.16	1.14	4.42	1.11
9. 90°C	4.07	1.22	4.37	1.14
10. 100°C	3.97	1.37	4.10	1.28

This hydrolysis goes on to a remarkable extent in cases where alkaline solution, high temperature and large quantity of water are present, because these phosphates consist of moderately weak anion and amphoteric cation.

Discussion

As shown above, the manurial effect of aluminum and iron phosphates is very different according to the external condition. Generally speaking the manurial effect of iron salts is higher for paddy-rice and in aluminum salts are higher for barley, though the effect of both iron and aluminum salts are high for paddy rice crop, but low in general regarding barley crop except for one or two acid salts. In summer, top-soil of water lodged paddy field profile, consists of two principal layers. The surface layer of top-soil is brownish red colored by the presence of ferric iron.

This surface layer is oxidised, by the supply of oxygen in the irrigation water and oxygen generated by photosynthesis of autotrophic microplants, mainly algae, situated on the uppermost surface of paddy soil. Reaction of paddy surface water is apt to incline to alkaline reaction by the exhaus-

tion of soluble carbon dioxide by the photosynthesis of algae. So the surface layer is rich in oxygen and can be called an oxidation layer, where ferric iron, nitrate, sulphate and manganic mangan are stable and perhaps iron phosphate is present as FePO_4 .

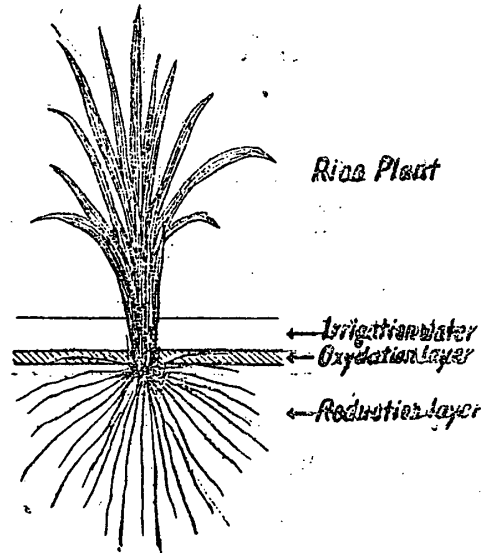


Fig. 3.

While the underlying layer is in reduced condition, oxygen is consumed by the decomposition of organic matter, so the colour is greyish blue by the presence of ferrous iron. In this reduction layer, ferrous iron, ammonia, sulphide and manganous mangan are stable and iron phosphate is in the form of $\text{Fe}_3\text{P}_2\text{O}_8$.

The release of phosphate ion by hydrolysis in this layer is the same in the oxidation layer which forms the surface of paddy field soil in summer.

Therefore the scarcely soluble phosphates, particularly iron salts, become high in manurial effect, by the promotion of hydrolysis resulting from high temperature, alkaline reaction of surface water, and large quantity of water.

In the reduction layer, which forms the subsurface of the paddy field, ferric phosphate is reduced to ferrous phosphate which is apt to be absorbed by the rice plant root.

The root secretes some carbonic acid or organic acid to acidify surrounding medium, this slight change in reaction to the acid side causes solution of $\text{Fe}_3\text{P}_2\text{O}_8$ and releases phosphate ion, Iron phosphates prove to have high manurial effect for summer crops, but low for winter crops.

In case of barley, however, the soil condition being drier and therefore adverse, sesquioxide phosphates, particularly iron salts have low manurial

effect.

This is as reported before, because ferric salt in paddy field is converted into ferrous salt and increase its manurial effect in summer, but in winter when water is removed, is oxidized into ferric salt and its efficacy lowered. It may be concluded that in this country, paddy soil is rich in ferrous phosphates, while upland field soil abounds in ferric phosphates.

Aluminum phosphate is not reduced in paddy condition. So the manurial value for paddy rice is slightly inferior to iron salt, but owing to the water lodged condition, hydrolysis goes on and increases its effect. In winter, the soil condition being adverse, the degree of hydrolysis is lowered but aluminum salts are not reduced and have an effect superior to iron salts, for barley crops.

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