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著者	FUJIWARA Akio
journal or publication title	Tohoku journal of agricultural research
volume	1
number	2
page range	229-232
year	1951-03-15
URL	http://hdl.handle.net/10097/29039

AGING OF SCARCELY SOLUBLE PHOSPHATES DURING LONG PERIODS AND ITS INFLUENCE ON AVAILABILITY

IV. STUDIES ON THE CONSTITUTION AND MANURIAL EFFECT OF SCARCELY SOLUBLE PHOSPHATE

By

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(*Received January 1. 1950*)

It was made clear in the last report that the fact that $FePO_4$ is amorphous and $Ca_3P_2O_8$ is crystalline, while $AlPO_4$ is of imtermediary nature, has various bearings on manurial effect. We further investigated how the manurial effect of these phosphates will change when stored for long periods. $FePO_4$ and $AlPO_4$, synthesised according to the method reported in former report, were adequately hydrated and preserved in an air tight, dark thermostat. The $FePO_4$ was examined after one year and the $AlPO_4$ after two years storage, it was found that both precipitates had generally changed their external appearance, became somewhat crystalline.

The chemical analysis showed no appreciable change in the chemical composition of the salts, as follows.

Table 1.

		P_2O_5	Fe_2O_3	Al_2O_3	H_2O
at the beginning	$FePO_4$ hydrated	30.04	34.01		35.95
	$FePO_4$ dehydrated	46.48	52.63		0.89
	$AlPO_4$ hydrated	35.01		25.36	39.63
	$AlPO_4$ dehydrated	57.26		41.48	1.25
at the end	$FePO_4$ hydrated	30.36	34.39		35.25
	$FePO_4$ dehydrated	46.46	52.62		0.92
	$AlPO_4$ hydrated	35.35		35.51	39.13
	$AlPO_4$ dehydrated	57.34		41.29	1.37

X-ray analysis showed that amorphous $FePO_4$ adequately hydrated, crystallizes during storage over a long period of time. The amorphous

$FePO_4$ is yellowish in color, the crystallized salt appears as a greyish-pink bristly crystalline powder. Some moisture seems to be required in the process of crystallization. So that, if preserved after dehydration by drying, for the same length of time, it does not crystallize. Judging from these phenomena, the existence of micelle water in it, seems to have a close relation with aging, which may influence manurial effect and solubility, as will be shown later.

It was also shown by X-ray analysis that $AlPO_4$ also crystallizes when preserved in a hydrated state.

The cultivation test for paddy-rice and barley was achieved using this crystallized salt and dehydrated original amorphous salt. As shown in Table 2, the manurial effect of crystallized salts is far inferior to amorphous salt, especially in upland field conditons, growth of barley plants fertilized by crystallized salts was very poor.

Table 2.

	Total weight (gm)	No. of ears	Weight of ear (gm)	Weight of straw (gm)	Ear weight against 100 of $CaH_4P_2O_8$ section
Paddy-rice					
Non-P_2O_5	16.60	9.0	6.20	10.40	19.3
$CaH_4P_2O_8$	73.75	35.0	32.20	41.55	100.0
$FePO_4$ hydrated (crystalline)	60.95	31.0	28.15	32.80	87.4
$FePO_4$ dehydrated (amorphous)	64.50	32.0	29.70	34.80	92.2
$AlPO_4$ hydrated (crystalline)	51.30	26.0	22.90	27.40	71.1
$AlPO_4$ dehydrated (amorphous)	53.20	26.5	23.60	29.60	73.3
Barley					
Non-P_2O_5	2.05	4.5	0.35	1.70	0.9
$CaH_4P_2O_8$	63.45	31.0	38.95	24.50	100.0
$FePO_4$ hydrated (crystalline)	4.85	9.0	1.05	3.80	2.7
$FePO_4$ dehydrated (amorphous)	8.90	9.0	2.05	6.40	6.4
$AlPO_4$ hydrated (crystalline)	13.20	10.0	4.25	8.95	10.9
$AlPO_4$ dehydrated (amorphous)	15.35	10.5	6.00	9.35	15.4

The solubility of crystallized salt in dilute suspension by the same method as in report I, was determined and compared with that of original $AlPO_4$ and $FePO_4$, as shown in Fig. 1.

The solubility of the phosphate ion of crystallized salts is far less than in the amorphous salt. Under alkaline conditions solubility diminished little, but when in an acid media the solubility, especially $FePO_4$, dropped

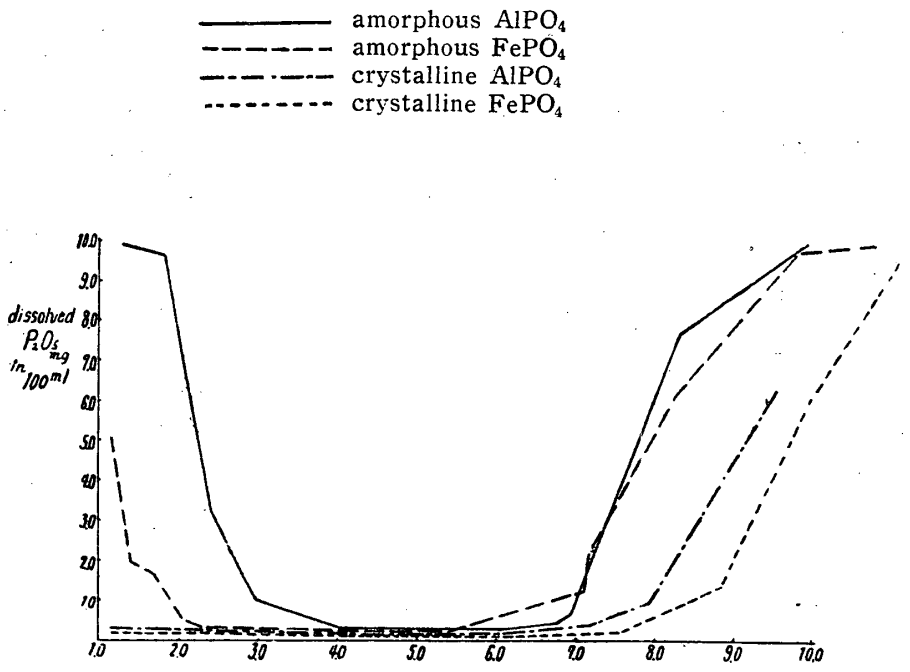

Fig. 1

severely.

In a cultivation test on upland soil fertilized by crystallized salts, it was found barley was poorly supplied with minerals, which showed that the slightly acid condition of soils makes the phosphate much less soluble.

In these salts, the fall of availability and solubility seems to be due to the fact that, during storage, the internal moleculecoordination undergoes a change,[1,2,3,4] the colloidal amorphous parts age and the constitution, especially that on the surface, changes from an unstable to a stable state and crystallizes. Many researches were made by colloid scientists as to the crystallization or aging of the colloid of vanadium pentoxide and other colloids.[1,2] We observe that the same process could occur in the salt as in newly supplied phosphate. Soil phosphoric acid is, in most cases, found in a large quantity in those parts of colloidal substances which have smallest diameter.[5,6] Its availability to plants is low in the volcanic ash soils in Japan which are rich in R_2O_3 and slightly acid in reaction.[7,8] Perhaps this soil phosphoric acid may have something of a crystalline nature in spite of its name "Colloidal". In other words, it appears that due chiefly to the phenomenon of aging or crystallization the phosphoric acid while acting effectively in such soils as mentioned above when newly fertilized, shows a sudden fall of availability as time passes. This can also be proved by the fact that even $FePO_4$ has a considerably higher availability if it can be kept in the same state as when it is newly precipitated.

Year after year, $FePO_4$, $AlPO_4$ and $Ca_3F_2O_8$ was synthesised by the same method, and preserved it in an airtight dark room. The salts were preserved for three years, the solubility was determined each spring and autumn, and cultivation tests, were made each year on paddy rice and upland barley. Numerical values obtained from these experiments are omitted. From these numerous results obtained from cultivation tests, which although differ remarkably from one year to another, being influenced yearly by varying weather conditions, nevertheless show that; on the whole, the fall in availability through preservation is greatest in $FePO_4$, smallest in $Ca_3P_2O_8$ and moderate in $AlPO_4$, more over, the range of variation of availability is greatest in $FePO_4$, followed by $AlPO_4$ and $Ca_3P_2O_8$ in this order. Correlation of field and laboratory tests show that fall in manurial effect through preservation is directly proportional to the degree of crystallization of the salt.

References

1. Duclaux; 1929, Les Colloides.
2. K. Sato; 1943, J. Chem. Soc. Jap., 64, 197. (in Japanese)
3. Buzagh; 1936, Kolloidik.
4. Freundlich; 1932, Kapillar Chemie II., 101.
5. Robinson, Holmes; 1924, U. S. Dept. Agr. Bull., 1311.
6. Novak, Smolik, Gedroiz; 1929, Adsrobierende Boden Komplex.
7. S. Ai; 1934, J. Soc. Sci. Soil Manure, 8, 195. (in Japanese)
8. S. Kasugai; 1934, J. Agr. Chem. Soc. Jap., 10, 31, 193. (in Japanese)