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EFFECTS OF HEATING AND DEHYDRATION ON  
THE CONSTITUTION AND AVAILABILITY  
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III. STUDIES ON THE CONSTITUTIONS  
AND MANURIAL EFFECTS OF  
SCARCELY SOLUBLE PHOSPHATES

By

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We have heretofore often observed that the availability of phosphates, can be promoted by heating in one case, while in another it is lowered.<sup>7,8,9,10,11,12</sup> Already Marais<sup>12</sup> recognized the promotion of manurial effect, by heating, of crystalline phosphatic minerals, such as wavellite, dufrenite and saldanah. In Japan, calcined aluminum phosphate rock from South Daito Island was in common use as commercial fertilizer. When the synthesised phosphates were heated, the reduction of manurial value was observed by some investigators.<sup>10</sup>

In order to clarify this phenomenon, the following experiments were performed.

#### Materials

*At first,  $FePO_4$ ,  $AlPO_4$  and  $Ca_3P_2O_8$  was prepared.*

$FePO_4$  was synthesised by mutual precipitation of sodium monohydrogen phosphate and ferric chloride.<sup>4</sup> The colloidal precipitate was centrifuged and washed throughly with water.  $AlPO_4$  was synthesised from the solution of sodium monohydrogen phosphate and aluminum sulphate.<sup>4</sup>  $Ca_3P_2O_8$  was prepared by mixing sodium monohydrogen phosphate and calcium chloride solution.<sup>4</sup>

The  $FePO_4$  was creamy yellow, and the  $AlPO_4$  white, translucent, gelatinous, colloidal gels. The  $Ca_3P_2O_8$  was a white opaque colloidal salt. The following seven samples of each were given the following treatment:

- (1) The colloidal salt, left in original state.
- (2) Air dried.

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Contribution from the Laboratory of Soil and Fertilizers.

- (3) Heated for three hours at 60°C.
- (4) Heated for three hours at 100°C.
- (5) Heated for three hours at 200°C.
- (6) Ignited for three hours at 500°C.
- (7) Ignited for three hours at 900°C.

$\text{Ca}_3\text{P}_2\text{O}_8$  and  $\text{FePO}_4$  are easily dehydrated and pulverized by heating while  $\text{AlPO}_4$  is not easily dehydrated.

The analysis of the prepared samples are shown in the below ;

Table 1.

	$\text{FePO}_4$			$\text{AlPO}_4$			$\text{Ca}_3\text{P}_2\text{O}_8$		
	$\text{P}_2\text{O}_5$	$\text{Fe}_2\text{O}_3$	$\text{H}_2\text{O}$	$\text{P}_2\text{O}_5$	$\text{Al}_2\text{O}_3$	$\text{H}_2\text{O}$	$\text{P}_2\text{O}_5$	$\text{CaO}$	$\text{H}_2\text{O}$
(1) Newly precipitated	8.06	12.69	79.25	11.26	10.95	77.78	8.59	10.07	81.34
(2) Air-dried	31.16	49.06	19.78	26.80	26.08	49.12	42.12	49.40	8.46
(3) Heated at 60°C	32.28	50.82	16.90	35.38	34.44	30.18	43.80	51.36	4.84
(4) " 100°C	35.63	51.11	8.26	39.54	38.48	21.98	44.71	52.43	2.86
(5) " 200°C	38.84	61.16	—	50.68	49.32	—	46.03	53.97	—
(6) " 500°C	38.84	61.16	—	50.68	49.32	—	46.03	53.97	—
(7) " 900°C	38.84	61.16	—	50.68	49.32	—	46.03	53.97	—

It will be observed that there was no change in the ratio of  $\text{P}_2\text{O}_5$  to the metal oxides in the samples heated or ignited.

X-ray analysis showed that  $\text{FePO}_4$  is almost amorphous, this agrees with the results of report I, which was not crystallized by heating and dehydrating;  $\text{AlPO}_4$  is slightly crystalline as stated in the last report, and is not changed by heating;  $\text{Ca}_3\text{P}_2\text{O}_8$  is crystalline, showing no remarkable change by heating, this corresponds to  $\text{Ca}_3\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$  in crystal constitution, and not to  $\text{Ca}_3\text{P}_2\text{O}_8$ .

### Experimental

The solubilities in some of the habitual solutions used for determining manurial value are shown in the table 2.

The solubility of these heated samples in the ammoniacal solution of ammonium citrate after Petermann and in 2% solution of citric acid were observed. It was found that  $\text{AlPO}_4$ ,  $\text{Ca}_3\text{P}_2\text{O}_8$  and  $\text{FePO}_4$  show a particular change in the solubility in that order. Further, the solubility of  $\text{FePO}_4$  in 2% solution of citric acid decreases considerably when heated to a high temperature, while the solubility of  $\text{AlPO}_4$  and  $\text{Ca}_3\text{P}_2\text{O}_8$  does not decrease so remarkably. The decrease in solubility is not caused by an essential change of the crystal structure, but is due chiefly to the change of physical

properties caused by heating, which decrease the intrusion and osmosis rate of the solution.

Table 2.

	P. P.	C. P.	P.P./T.P.	C.P./T.P.
FePO <sub>4</sub> newly precipitated	33.60	18.52	86.45	47.67
" air-dried	37.26	15.42	95.91	39.69
" Heated at 60°C	38.05	12.79	97.94	32.92
" " 100°C	38.37	9.51	98.75	24.48
" " 200°C	38.29	7.80	98.58	20.08
" " 500°C	38.13	6.31	98.14	16.23
" " 900°C	23.35	2.42	60.13	6.22
AlPO <sub>4</sub> newly precipitated	44.36	24.21	87.56	47.79
" air-dried	42.96	4.33	84.80	8.54
" Heated at 60°C	50.11	8.03	98.80	15.85
" " 100°C	48.25	17.35	95.27	34.27
" " 200°C	49.09	18.71	96.89	36.92
" " 500°C	50.10	21.81	98.79	43.05
" " 900°C	44.71	21.30	88.22	42.03
Ca <sub>3</sub> P <sub>2</sub> O <sub>8</sub> newly precipitated	13.64	32.50	29.53	70.57
" air-dried	18.97	33.21	40.75	72.12
" Heated at 60°C	17.57	31.41	38.16	68.21
" " 100°C	15.73	25.35	34.16	55.05
" " 200°C	12.12	22.87	26.32	49.68
" " 500°C	5.86	19.96	12.72	43.34
" " 900°C	6.22	19.93	13.52	43.38

#### Manurial effect

A precise cultivation test on paddy rice and barley was made. The method of experiment was as reported previously, and the cropping results are shown in the table below.

In the case of paddy-rice, the newly precipitated FePO<sub>4</sub> colloid has the highest manurial effect among all tested samples, this chemical loses its availability rapidly with heating. Sample ignited at 500°C and 900°C have only half manurial value of the newly precipitated colloid.

In AlPO<sub>4</sub>, too, the availability is lowered by heating, though not so remarkably as in FePO<sub>4</sub>. The manurial value of the salt ignited at high temperature is two-third of that of the newly precipitated colloid. Ca<sub>3</sub>P<sub>2</sub>O<sub>8</sub> is least affected by heating.

These tendencies are all the more severe with barley. This is quite in accord with the crystallinity of salts mentioned in the above.

Table 3.

	Paddy-rice plant						Barley							
	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	Content of $\text{P}_2\text{O}_5$ in ear (%)	Content of $\text{P}_2\text{O}_5$ in straw (%)	$\text{P}_2\text{O}_5$ re-covered by plants (mg)	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	Content of $\text{P}_2\text{O}_5$ in ear (%)	Content of $\text{P}_2\text{O}_5$ in straw (%)	$\text{P}_2\text{O}_5$ re-covered by plants (mg)
iron- $\text{P}_2\text{O}_5$	8.5	6.74	12.06	22.0	0.30	0.06	27.5	6.0	1.22	2.46	3.3	0.50	0.40	15.9
$\text{CaH}_4\text{P}_2\text{O}_8$	37.5	30.52	45.44	100.0	0.35	0.06	134.1	21.5	36.97	25.90	100.0	0.44	0.06	178.2
$\text{FePO}_4$ newly precipitated	39.5	33.02	48.08	108.2	0.33	0.06	137.9	20.5	23.89	13.66	64.6	0.48	0.13	132.2
" air-dried	38.0	31.23	47.54	102.3	0.37	0.06	144.1	16.0	14.60	9.89	39.5	0.60	0.19	106.4
" heated at 60°C	33.5	29.21	50.91	95.7	0.37	0.06	138.6	20.0	16.99	11.75	46.0	0.64	0.17	128.7
" " 100°C	26.0	27.39	41.62	89.7	0.38	0.06	129.1	9.0	5.25	8.48	14.2	0.62	0.30	58.0
" " 200°C	28.5	24.36	43.29	79.8	0.38	0.06	118.5	14.5	7.67	10.96	20.7	0.61	0.37	81.9
" " 500°C	22.0	17.39	34.15	57.0	0.40	0.07	93.5	8.5	2.43	4.09	6.6	0.55	0.37	28.5
" " 900°C	20.5	17.36	28.80	56.9	0.37	0.06	81.5	8.5	2.25	4.15	6.1	0.53	0.37	27.3
$\text{AlPO}_4$ newly precipitated	34.5	30.25	45.24	99.1	0.34	0.06	150.0	21.0	25.64	14.81	69.4	0.48	0.13	142.4
" air-dried	32.0	26.69	43.02	87.5	0.38	0.06	116.6	17.0	15.30	11.10	41.4	0.56	0.20	107.9
" heated at 60°C	27.0	25.13	34.83	82.3	0.38	0.05	112.9	15.0	14.46	11.48	39.1	0.64	0.22	117.8
" " 100°C	23.5	24.05	34.53	78.8	0.34	0.06	102.5	19.0	16.81	12.85	45.5	0.54	0.22	119.5
" " 200°C	23.0	19.34	33.82	63.4	0.36	0.06	89.9	18.0	12.68	12.49	34.3	0.69	0.27	123.7
" " 500°C	20.5	20.20	30.50	66.2	0.32	0.08	89.0	17.0	13.60	11.85	36.8	0.57	0.26	108.3
" " 900°C	19.5	19.75	30.28	64.7	0.36	0.07	92.3	18.0	11.92	12.34	32.2	0.61	0.28	107.3
$\text{Ca}_3\text{P}_2\text{O}_8$ newly precipitated	35.5	28.89	43.52	94.7	0.34	0.06	124.3	21.0	30.86	14.94	83.5	0.41	0.07	145.9
" air-dried	33.0	30.60	46.45	100.3	0.35	0.04	125.7	21.5	25.48	12.98	68.9	0.40	0.12	118.7
" heated at 60°C	37.0	30.34	44.79	99.4	0.35	0.06	133.1	19.0	21.91	12.94	59.3	0.51	0.13	128.5
" " 100°C	37.0	31.01	47.45	101.6	0.32	0.06	127.7	22.0	32.64	15.84	88.3	0.56	0.07	193.9
" " 200°C	34.0	29.21	45.85	95.7	0.31	0.07	127.7	22.0	26.64	16.08	72.1	0.54	0.11	161.6
" " 500°C	26.5	23.15	39.25	75.9	0.32	0.07	101.6	17.0	19.50	12.95	52.7	0.60	0.14	135.1
" " 900°C	28.5	24.63	39.58	80.7	0.35	0.06	110.0	22.5	22.46	15.12	60.8	0.59	0.19	161.2

Taking a sample the crystal of  $\text{FePO}_4$  and  $\text{AlPO}_4$ , prepared on the basis of literature cited,<sup>1, 2, 3, 4, 5, 13, 14</sup> we investigated the relationship between heating and manurial effect.

Table 4.

	$\text{P}_2\text{O}_5$ mg Amount absorbed by rice seedling	rate of recovering %
Ignited crystalline $\text{FePO}_4$	1.1	4.4
Non-treated crystalline $\text{FePO}_4$	0.6	2.4
Ignited crystalline $\text{AlPO}_4$	1.3	5.2
Non-treated crystalline $\text{AlPO}_4$	1.0	4.0

Seedling method ; the salt was used 25 mg as  $\text{P}_2\text{O}_5$ , each pot.

The results showed that the solubility and the manurial effect of these crystalline salts could be promoted when heated and properly dehydrated. This result is in accord with that of Marais<sup>12</sup> adopted to the natural crystalline phosphate mineral.

### Discussions

To sum up these results and those achieved by other researches, it is concluded that when the original phosphatic salt is amorphous, even if the crystal constitution does not change by heating and dehydrating, the solubility and the manurial effect decrease due to the physical decrease of intrusion and osmosis rate of the solution, contrary to this, when the salt is crystalline, there are cases in which the solubility and the manurial effect are promoted, due to the inactivation of metal oxides and the physical destruction of the crystal constitution through the loss of crystallization water or combined water. To obtain the best result requires special care in roasting or igniting phosphate rock.

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