September, 1972] BULLETIN OF THE CHEIMCAL SOCIETY OF JAPAN, VOL. 45, 2915—2920 (1972) 2915

Constituents and Properties of Ammoniated Slurry From Wet-process Phosphoric Acid

Takashi Akiyama and Jumpei Ando
Faculty of Science and Engineering, Chuo University, Kasuga Bunkyo-ku, Tokyo

(Received October 20, 1971)

A large amount of gel-like substance is formed during the ammoniation of wet-process phosphoric acid and affects the production of phosphate fertilizers. The authors have found that the main constituent of the gel-like substance is a compound "S" whose composition has been determined to be $(Al,Fe)NH_4HF_2PO_4$. Several other compounds, $Fe_3NH_4H_8(PO_4)_6 \cdot 6H_2O$, $(Fe,Al)NH_4H_2(PO_4)_2 \cdot 1/2H_2O$, $Fe(NH_4)_2H_2F(PO_4)_2 \cdot xH_2O$, $(NH_4)_3AlF_6$, gelatinous silica, *etc.*, are also formed during the ammoniation and curing of the ammoniated slurry, depending upon pH, atomic ratio of F/(Al+Fe) and temperature. Tests also were made on the properties of the ammoniated slurry; solubility, viscosity, filterability, and the rate of sedimentation. It has been found that the properties vary with the formation of the above compounds. A high-temperature modification of $(NH_4)_2HPO_4$ which is stable above 155°C has been newly found during the tests.

Wet-process phosphoric acid has been produced in large amounts in many countries. Most of the acid is ammoniated to pH 4—8 to give a slurry which is used for the production of granular, slurry, and liquid fertilizers.

Gel-like substance is formed in a large amount during the ammoniation and affects the properties of the slurry and consequently the production of the fertilizers. The constitution of the gel-like substance, however, was not clear. It sometimes happens in commercial scale plants that the properties of the slurry change seriously for some unknown reason causing much trouble in the operation of the plants. In the present study, tests were made on the constitution and the properties of the ammoniated slurry.

Acids Used for the Tests. The chemical compositions of the acids used for the tests are shown in Table 1.

The acids W-1 and W-2 were produced from Florida phosphate ore by the hemihydrate-dihydrate process with the addition of silica to promote the hydration of hemihydrate. Their atomic ratios F/Si are close to 6 illustrating that most of the fluorine is present in the form of SiF_6^{2-}. The acid W-3 was produced from Florida ore by the dihydrate process. The ratio of the acid is larger than 6 indicating that a considerable portion of the fluorine is not combined to silica. Other acids are composite acids prepared with chemical reagents.

Ammoniation and Measurement of pH. For most tests, 100 m*l* each of the acids was put in a polyethylene bottle and ammoniated with gaseous ammonia at a rate of about 2 g NH_3 per minute at about 100°C.

The pH of the ammoniated slurry was tested with a glass electrode pH meter after being diluted with 100 times as much water. The composition of the liquid phase corresponds to $NH_4H_2PO_4$ with $(NH_4)_2SO_4$ at pH 4.5 and $(NH_4)_2HPO_4$ with $(NH_4)_2SO_4$ at pH about 8.

Major Water-insoluble Compounds Formed During the Ammoniation. After the ammoniation to various

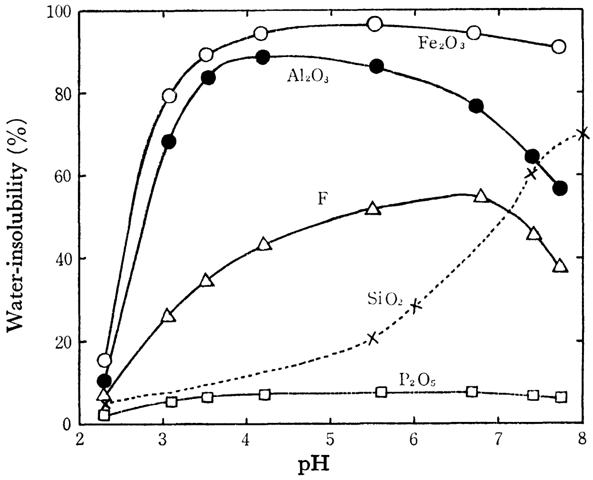

Fig. 1. Change of water-insolubility of each component of W-1 during the ammoniation at 100°C.

Table 1. Acids tested

Marks	Composition (%)						Atomic ratio	
	P_2O_5	SO_3	Fe_2O_3	Al_2O_3	SiO_2	F	F/(Al+Fe)	F/Si
W-1	26.2	4.5	0.7	1.0	1.1	2.4	4.5	6.9
W-2	25.1	5.1	1.0	1.3	1.1	2.1	2.9	6.0
W-3	30.0	2.4	0.7	0.8	1.0	2.5	5.5	7.9
R-1	25.0	4.1	0.7	1.0	0	0	0	—
RF-1	25.0	4.1	0.7	1.0	0	2.5	4.6	—
RSF-1	25.0	4.1	0.7	1.0	1.3	2.5	4.6	6.0
R-2	26.0	5.1	1.3	1.0	0	0	0	—
RF-3	25.0	4.1	2.3	0	0	2.5	4.5	—
R-4	25.0	4.1	0	1.5	0	0	0	—
RF-4	25.0	4.1	0	1.5	0	2.5	4.6	—

pH, the slurries were kept at 95°C for 30 min, filtered, washed with water and acetone, dried at 50°C and tested by chemical and X-ray analyses. Some of the samples were tested by electron microscope.

The change of water-insolubility of each component of W-1 during the ammoniation at about 100°C is shown in Fig. 1. Insoluble compounds started to form around pH 2.3. The amount of insoluble Fe_2O_3 and F reached maximum at pH about 6, and that of insoluble Al_2O_3 at pH 4.5. The amount of insoluble silica increased markedly above pH 6 indicating the decomposition of SiF_6^{2-} ions. Tests with W-2 and W-3 gave similar results.

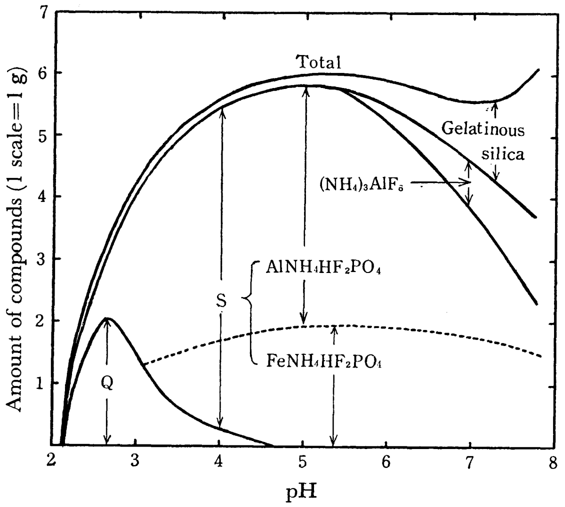

Fig. 2. Water-insoluble compounds formed from 100 g of W-1 during the ammoniation at 100°C.
(Amount of each compound is shown by the scale between 2 curves)
S: (Al, Fe)$NH_4HF_2PO_4$
Q: (Fe, Al)$NH_4H_2(PO_4)_2 \cdot 1/2\ H_2O$

The relation between pH and the amount of water-insoluble compounds formed during the ammoniation of W-1 at 100°C is shown in Fig. 2. The amounts are approximate values estimated by X-ray and chemical analyses. The water-insoluble phosphate first formed at pH 2.3 was gelatinous immediately after the ammoniation and crystallized gradually to form a compound (Fe,Al)$NH_4H_2(PO_4)_2 \cdot 1/2H_2O$[2] which will be referred to as "Q".

On further ammoniation "Q" decreased and a large amount of other gel-like phosphate formed. Tests with X-ray diffraction, electron microscope, and chemical analysis have shown that the main constituent of this gel-like substance is not (Fe,Al)$PO_4 \cdot nH_2O$ as was generally assumed but a compound "S" which has been determined as (Al,Fe)$NH_4HF_2PO_4$.[1] "S" is a solid solution of $AlNH_4HF_2PO_4$ and $FeNH_4HF_2PO_4$. "S" consists of very small round shaped particles about 20 millimicrons in diameter as shown in Fig. 3.

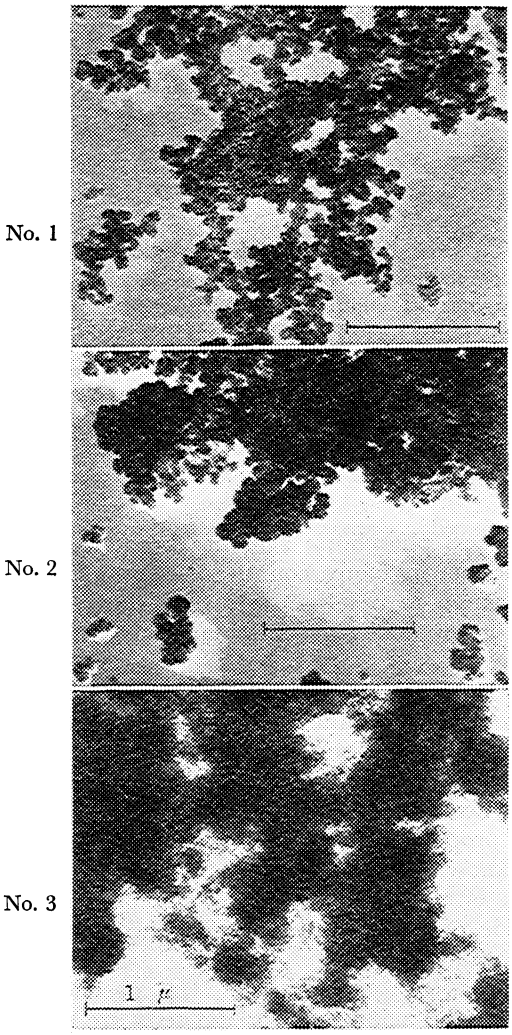

Fig. 3. Electron microscopic photographs of water-insoluble gel-like compounds formed during ammoniation at 100°C.
No. 1: RF-1 at pH 3.5, (Al, Fe)$NH_4HF_2PO_4$
No. 2: W-1 at pH 3.5, mainly (Al, Fe)$NH_4HF_2PO_4$
No. 2: R-1 at pH 6.5, gelatinous ferric aluminium phosphate

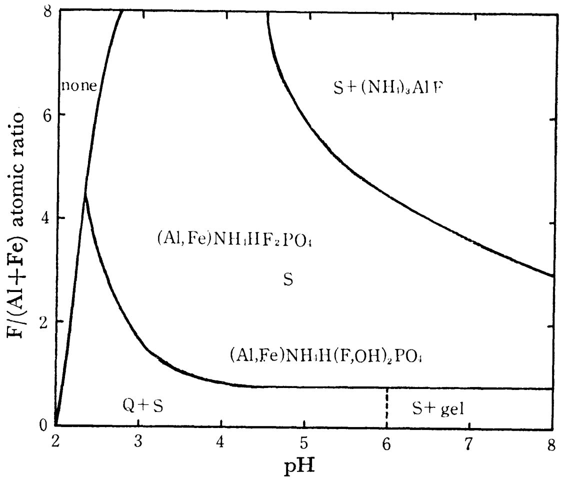

Fig. 4. Water-insoluble ferric and aluminium compounds formed at various F/(Al+Fe) ratio and pH (from W-1).

Above pH 5, $AlNH_4HF_2PO_4$ decreased with the formation of $(NH_4)_3AlF_6$; "S" became richer in $FeNH_4HF_2PO_4$. Gelatinous silica increased substantially above pH 6. When a small amount of Na^+ ion was added to W-1 and ammoniated, $(NH_4)_2NaAlF_6$ formed above pH 5.

Tests were made to study the effect of fluorine on the

---

[1] T. Akiyama, M. Hashimoto, H. Muraoka, and J. Ando, *Kogyo Kagaku Zasshi*, **74**, 1774 (1971).

formation of these compounds. Acids with large F/(Al+Fe) ratios were prepared by adding H_2SiF_6 to W-1. Those with small ratios were prepared by adding small amount of K_2CO_3 to W-1 to precipitate and separate K_2SiF_6. The relation between the ratio of the acid and the compounds formed at various pH is shown in Fig. 4.

Only "S" was detected in a wide range above pH3 with the acids whose ratios were larger than 1. The stoichiometric F/(Al+Fe) ratio of "S" is 2. When the ratio of the acid was smaller than 1, "Q" and "S" were present between pH 2 and 6 while gelatinous ferric aluminium phosphate hydrate and "S" were present above pH 6. $(NH_4)_3AlF_6$ formed at pH 4.5 when the ratio was 8 and at higher pH as the ratio decreased.

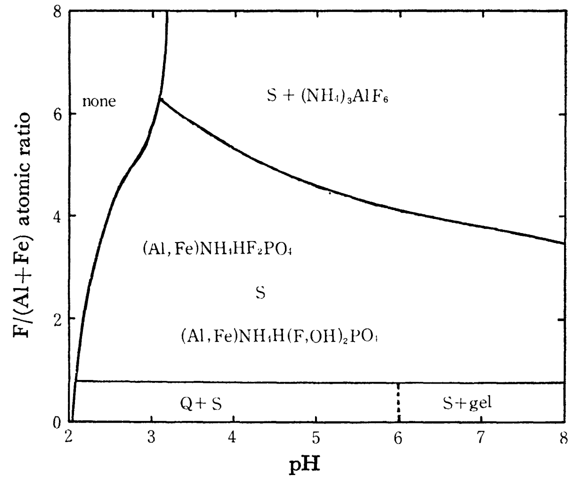

Fig. 5. Water-insoluble ferric and aluminium compounds formed at various F/(Al+Fe) ratio and pH (R-1 and HF, without silica).

The results of similar tests with the acid R-1 to which various amounts of HF were added are shown in Fig. 5. Silica was absent in the system. In this case, "Q" did not form when the ratio was larger than 1 even at pH 2.3. $(NH_4)_3AlF_6$ formed at pH 3.5 when the ratio was larger than 6.

These results illustrate that F^- ions favor the formation of "S" to depress the formation of "Q" and that silica combines with fluorine at lower pH to favor the formation of "Q" depressing the formation of $(NH_4)_3AlF_6$.

X-Ray Diffraction Patterns and Data. X-Ray powder diffraction patterns of the water-insoluble residues of the six samples of the ammoniated slurries are shown in Fig. 6. Each acid was ammoniated to pH 3.5 or 6.5 at 100°C, filtered, washed with water, dried and tested by means of X-ray diffraction. Nos. 1 and 3 of Fig. 6 show the diffraction patterns of "S". Nos. 2 and 4 show those of $AlNH_4HF_2PO_4$ and $FeNH_4HF_2PO_4$, respectively. The diffraction peaks are very broad illustrating the low crystallinity of the compounds. X-ray tests on crystal size have indicated that the single crystals are much smaller than 20 mμ.

No. 5 indicates the pattern of $(Fe,Al)NH_4H_2(PO_4)_2 \cdot 1/2H_2O$ ("Q") formed on ammoniating the acid R-1 to pH 3.5 and No. 6 gelatinous ferric aluminium phsophate hydrate formed on ammoniating the acid to pH 6.5.

The crystallinity of "S" was found to vary widely with the conditions of the formation, particularly with the temperature. The diffraction patterns of $AlNH_4$-

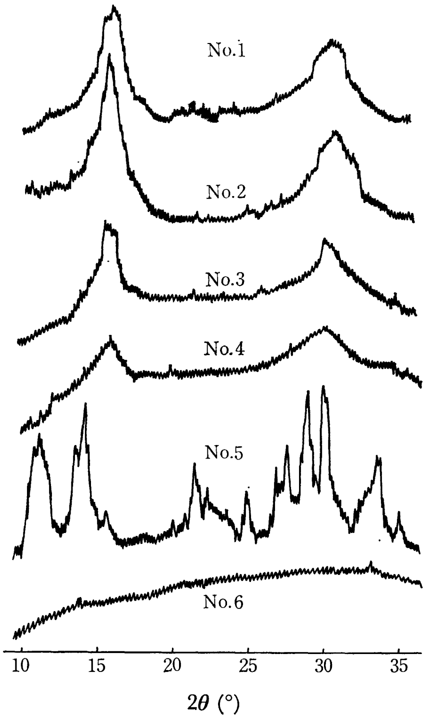

Fig. 6. X-Ray diffraction patterns of water-insoluble compounds formed during the ammoniation at 100°C (Cu, K_α).

No. 1: W-1 at pH 3.5, mainly (Al, Fe)$NH_4HF_2PO_4$
No. 2: RF-4 at pH 3.5, $AlNH_4HF_2PO_4$
No. 3: RF-1 at pH 3.5, (Al, Fe)$NH_4HF_2PO_4$
No. 4: RF-3 at 3.5, $FeNH_4HF_2PO_4$
No. 5: R-1 at pH 3.5, (Fe, Al)$NH_4H_2(PO_4)_2 \cdot 1/2H_2O$
No. 6: R-1 at pH 6.5, gelatinous ferric aluminium phosphate

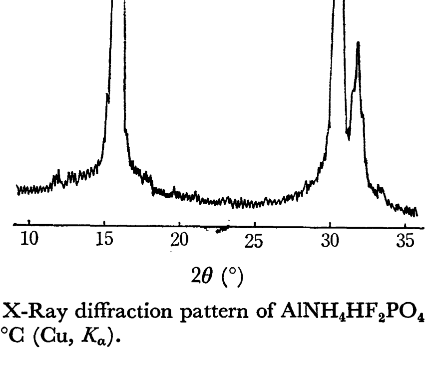

Fig. 7. X-Ray diffraction pattern of $AlNH_4HF_2PO_4$ prepared at 210°C (Cu, K_α).

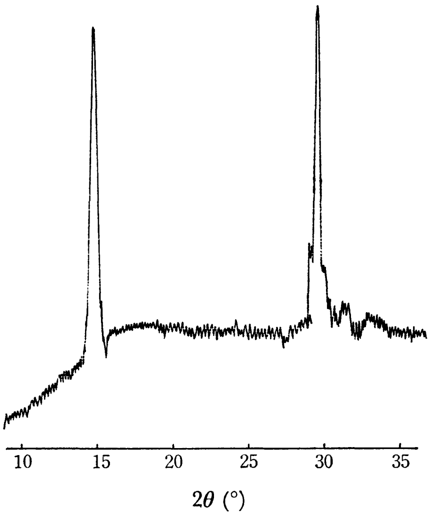

Fig. 8. X-Ray diffraction pattern of $FeNH_4HF_2PO_4$ prepared at 170°C (Cu, K_α).

HF_2PO_4 and $FeNH_4HF_2PO_4$ with high crystallinity prepared in an autoclave at 210 and 170°C respectively are shown in Figs. 7 and 8. The data of these compounds are shown in Table 2. The data indicate that the crystals belong to tetragonal system.

TABLE 2. X-RAY DIFFRACTION DATA OF THE COMPOUNDS PREPARED AT ELEVATED TEMPERATURE

$AlNH_4HF_2PO_4$ tetragonal $(a=5.64, c=4.34)$				$FeNH_4HF_2PO_4$ tetragonal $(a=6.05, c=4.35)$		
I/I_{100}	$d_{obs.}$, Å	$d_{calc.}$, Å	h k l	I/I_{100}	$d_{obs.}$, Å	$d_{calc.}$, Å
100	5.64	5.64	1 0 0	100	6.05	6.05
70	2.94	2.94	1 1 1	60	3.05	3.05
35	2.82	2.82	2 0 0	90	3.025	3.025
4	1.99	1.99	2 2 0			
11	1.88	1.88	3 0 0			
17	1.72	1.72	2 0 2	10	1.765	1.765
5	1.65	1.65	2 1 2			
3	1.469	1.469	2 2 2			
4	1.270	1.269	2 1 3			

Other Minor Water-insoluble Compounds. A very small amount of compound "R", $Fe_3NH_4H_8(PO_4)_6\cdot 6H_2O$[2] was found to form when the ammoniated slurry of W-1 at pH 2 was kept at 100°C for 2 hr. Another compound "T"[3] formed in a small amount when the slurry of W-1 at pH 6 was kept at 100°C for several hours. Similar results were obtained with a composite acid RSF-1. The composition of "T" has been determined to be nearly $Fe(NH_4)_2H_2F(PO_4)_2$; "T" might contain some water of crystallization.

A very small amount of "R" formed when the acid R-1 was ammoniated at pH 2, but disappeared above pH 2 to form "Q". On further ammoniation of R-1, "Q" disappeared above pH 6 to form gelatinous ferric aluminium phosphate hydrate whose electron microscopic photograph is shown in Fig. 3.

During the concentration of the slurry at pH 7 containing the gelatinous phosphate by evaporation at 110°C, another compound "U" formed in a small amount. The X-ray diffraction pattern of "U" resembles that of $KFe_2(PO_4)_2(OH)\cdot 2H_2O$.[4] When ammonium fluoride was added at 100°C to the ammoniated slurry of R-4 at pH 6 to give the F/Al ratio of 1, another compound formed in a very small amount. The X-ray pattern of this compound is similar to that of $K_2O\cdot 2Al_2O_3\cdot 2P_2O_5\cdot 1.6HF\cdot 6.2H_2O$.[2]

Change of Solubility. The change of citric solubility of P_2O_5 during the ammoniation of three acids is shown in Fig. 9. With R-2 which does not contain fluorine only "Q" formed in a large amount above pH 2 and the citric solubility decreased. "Q" is soluble in alkaline citrate but less soluble in citric acid, while "S" is soluble in both citrate and citric acid. "Q" also formed with W-2, but the amount was much less than with R-2. Only a small amount of "Q" formed with W-3 containing fluorine which was not combined with silica.

Tests also were made on the solubility of other phosphates. Like "Q", "R" is soluble in alkaline citrate but less soluble in citric acid. "T" is less soluble in alkaline citrate but soluble in citric acid, contrary to "Q" and "R". "U" is less soluble in both citrate and citric acid.

The change of water-solubility of P_2O_5 during the ammoniation is shown in Fig. 10. The solubility was much lower with R-2 than with W-2 and W-3 although all these acids contain nearly equal amounts of Fe_2O_3+Al_2O_3. The difference in solubility is caused by the difference of compounds formed. "Q" containing 2 mol P_2O_5 per 1 mol Fe_2O_3 or Al_2O_3 formed in a large amount with R-2, while "S" containing 1 mol P_2O_5 per 1 mol Fe_2O_3 or Al_2O_3 formed in similar amount with W-2 and W-3.

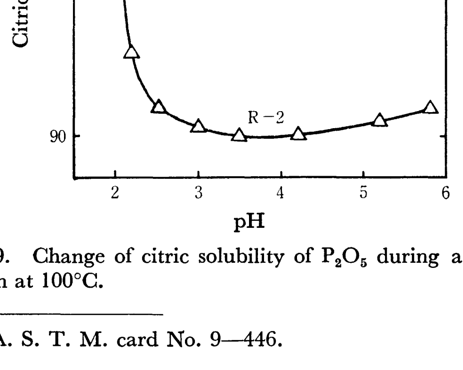

Fig. 9. Change of citric solubility of P_2O_5 during ammoniation at 100°C.

---

[2] J. F. Haseman, J. R. Lehr, and J. P. Smith, *Soil Science Soc. Proceeding*, **15**, 76 (1950).

[3] J. Ando and T. Akiyama, *Kogyo Kagaku Zasshi*, **68**, 1056 (1965).

[4] A. S. T. M. card No. 9—446.

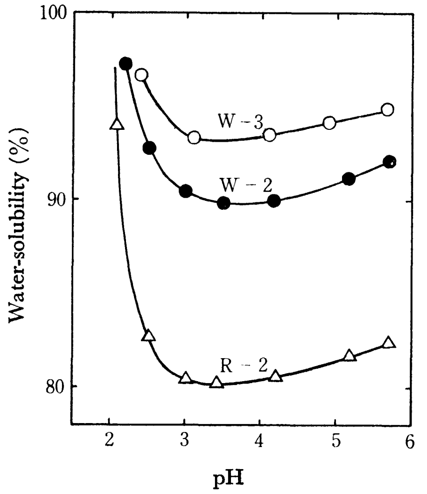

Fig. 10. Change of water-solubility of P_2O_5 during ammoniation at 100°C.

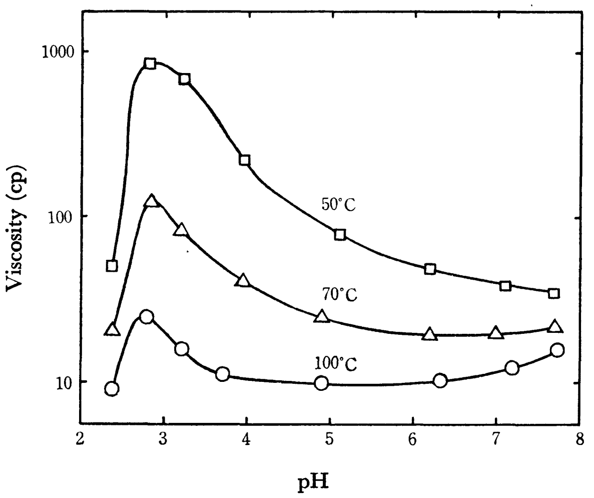

Fig. 12. Change of viscosity of ammoniated slurry during ammoniation at different temperatures.

Viscosity of the Ammoniated Slurry. The viscosity of the ammoniated slurry of W-1 is shown in Fig. 11. For the tests about 500 m*l* of W-1 was first ammoniated to pH 8. The ammoniated slurry was then acidified to pH 2.5 by adding the acid W-1. The viscosity was tested after the slurry was kept for about 5 min at various pH during the ammoniation and acidification. The temperature of the slurries was 90—100°C.

Relatively high viscosity was obtained around pH 2.7. Immediately after ammoniation to this pH the water-insoluble substance formed was gelatinous and the viscosity was as high as 100 cp. The viscosity decreased to about 20 cp by curing for 5 min as "Q" crystallized with the decrease of the gel. On further ammoniation "S" formed and the viscosity decreased to 10 cp. The viscosity increased above pH 6, presumably because of the increase of gelatinous silica. The viscosity during the acidification was higher than that during the ammoniation when the pH was above 5 and lower below pH 5.

The change of viscosity on the ammoniation of W-1 at different temperatures is shown in Fig. 12. The viscosity was much higher when ammoniated at lower temperature due to the poor crystallinity of the insoluble substance and was as high as 800 cp when ammoniated to pH 2.7 at 50°C. Such low-temperature ammoniation occurs in commercial scale plants where dilute ammonia gas such as coke-oven gas is used.

Rate of Sedimentation. W-1 was ammoniated to various pH at 100°C and diluted with an equal amount of water to prevent the crystallization of ammonium phosphate on cooling. About 50 m*l* of the diluted slurry was put in a glass cylinder to a depth of 140 mm and kept at room temperature. The depth of the clear solution layer which formed on the surface of the slurry due to the sedimentation of the insoluble substance was measured several times in 150 hr. The results are shown in Fig. 13.

The rate of sedimentation was larger for the slurries at pH 4.0 and 5.9 which had lower viscosity than for the slurries at pH 2.8 and 7.2. The slurry ammoniated to pH 8 and then acidified to pH 5.4 showed the smallest rate.

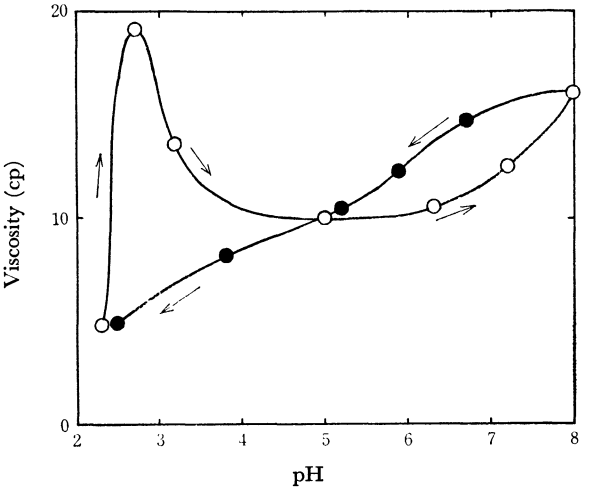

Fig. 11. Change of viscosity of ammoniated slurry of W-1 during ammoniation and acidification at 100°C.

○: in case of increasing pH on ammoniation

●: in case of decreasing pH on acidification

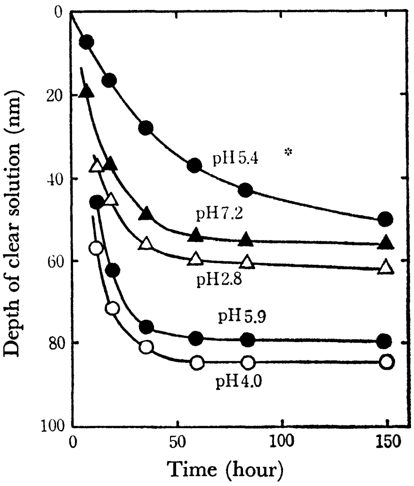

Fig. 13. Rate of Sedimentation of gel-like substance in ammoniated slurry of W-1 (Ammoniated and then diluted. *The sample ammoniated and then acidulated to pH 5.4).

In other series of tests, W-1 was first diluted with an equal amount of water and then ammoniated to various pH for measurement of the rate of sedimentation. The results are shown in Fig. 14. The rate was considerably smaller than that shown in Fig. 13, possibly because of the lower crystallinity of "S" formed at lower temperature.

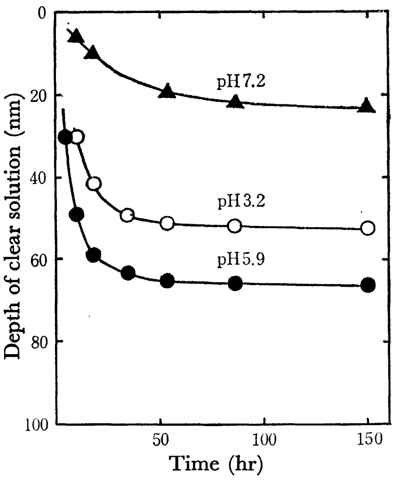

Fig. 14. Rate of sedimentation of gel-like substance in ammoniated slurry of W-1 (Diluted and then ammoniated).

Filterability. For the tests of filterability, 100 m*l* each of the acids was ammoniated to various pH at 100°C in most tests and at 50°C in some tests. The slurry was filtered with a filter paper (diameter 11 cm) in a Buechner funnel (diameter 12 cm) applying a vacuum of 100 mmHg below atmospheric pressure. The amount of the filtrate was recorded every 30 sec.

The best filterability obtained with the slurry at pH about 4 is shown in Fig. 15. The poor filterability with slurry ammoniated at lower temperature is in good agreement with the results shown in Figs. 12 and 13.

High Temperature Modification of $(NH_4)_2HPO_4$.
X-Ray tests of a commercial product of diammonium phosphate manufactured by ammoniation of wet-process phosphoric acid in a spray tower showed that the major phase of the product was a previously unknown compound while the product contained small amounts of ammonium sulfate and the compound "S". The unknown compound has been identified as a high temperature modification of $(NH_4)_2HPO_4$. This modification can be prepared in a laboratory by heating the usual form of $(NH_4)_2HPO_4$ at 160°C in a sealed tube to prevent the loss of ammonia during the heating. The inversion occurred above 155°C indicating that the ammoniation reaction in the spray tower occurred above this temperature. The presence of ammonium sulfate and "S" did not appreciably affect the inversion temperature. X-Ray diffraction data of the modification are shown in Table 3. This modification can stay at room temperature as long as it is dry. Addition of moisture at room temperature resulted in an instantaneous conversion into the usual form of $(NH_4)_2HPO_4$.

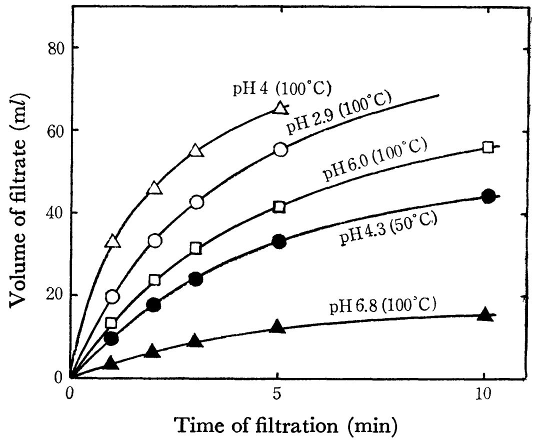

Fig. 15. Effect of pH and temperature on the filterability of ammoniated slurry of W-1.

TABLE 3. X-RAY DIFFRACTION DATA OF HIGH TEMPERATURE MODIFICATION OF $(NH_4)HPO_4$

d, Å	I/I_{100}	d, Å	I/I_{100}
6.27	3	2.71	3
5.46	53	2.64	10
4.54	100	2.50	15
3.85	30	2.485	10
3.32	20	2.320	3
3.29	23	2.267	12
3.02	11	2.165	5
2.93	52	2.092	9
2.79	15		