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AMMONIATION REACTIONS OF WET-PROCESS PHOSPHORIC ACID

By

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A large amount of gel-like substance forms during the ammoniation of wet-process phosphoric acid and affects the granulation of solid fertilisers as well as the production of liquid and suspension fertilisers. The constitution of the gel-like substance, however, was not clear. It sometimes happens in production plants that the properties of the ammoniated slurry change considerably for no known reason, resulting in serious operational problems.

In the present study, wet-process phosphoric acids with various composition were ammoniated in a laboratory to pH 2 to 8 at temperatures between 50 and 270°C. The compounds formed were tested by X-ray diffraction, chemical analysis and electron microscope. It has been found that the main constituent of the gel-like substance is not so called iron and aluminium phosphate hydrate $(\text{Fe,Al})\text{PO}_4 \cdot n\text{H}_2\text{O}$ but is a compound 'S' whose composition has been determined as $(\text{Fe,Al})\text{NH}_4\text{HF}_2\text{PO}_4$. Several other compounds also form during the ammoniation. The conditions of the formation of those compounds and the relation between the compounds and the properties of the slurry, viscosity, filterability and the rate of sedimentation of the gel-like substance were studied.

A high temperature modification of $(\text{NH}_4)_2\text{HPO}_4$ has been newly found during the tests. Tests also were made on ammonium polyphosphate.

Acids Used for the Tests

The chemical composition of the acids used for the tests are shown in Table 1.

TABLE 1

Chemical Composition of the Acids Tested

Marks	Specific gravity	Composition (per cent)						Atomic ratio	
		P ₂ O ₅	SO ₃	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	F	F/(fe + Al)	F/Si
F-1	1.356	26.2	4.5	0.7	1.0	1.1	2.4	4.5	6.9
F-2	1.336	25.1	5.1	1.0	1.3	1.1	2.1	2.9	6.0
F-3	1.360	30.0	2.4	0.7	0.8	1.1	2.5	5.5	7.2
F-4	-	30.3	1.9	0.7	0.9	0.9	2.4	4.7	8.5
F-5	-	27.6	1.7	1.0	0.5	0.2	0.5	1.2	7.9
F-6	-	40.3	7.2	1.8	1.0	0.5	1.2	1.6	7.6
R-0	-	26.0	0	0	0	0	0	-	-
R-1	-	25.0	4.1	0.7	1.0	0	0	0	-
R-2	1.331	26.0	5.1	1.3	1.0	0	0	0	-

The acids F-1 and F-2 were produced with Florida phosphate ore by hemihydrate-dihydrate process. Their atomic ratios F/Si are close to 6 illustrating that most of the fluorine is present in the form of SiF_6^{2-} ; silica was added during the production to promote the hydration of hemihydrate. The acids F-3 and F-4 were produced with Florida ore by dihydrate process. The ratios of these acids are greater than 6 indicating that considerable amounts of fluorine are not tied to silica.

F-5 is a defluorinated product of an acid made by dihydrate process. Sodium hydroxide was added to the acid to precipitate $\text{Na}_2 \text{SiF}_6$ which was filtered off. Most of the silica in the acid was also removed by the treatment. F-6 is a concentrated product of an acid made by hemihydrate-dihydrate process. The acids R-0, R-1 and R-2 are composite acids prepared with chemical reagents.

For most tests, 100 ml each of the acids was put in a polyethylene bottle and ammoniated with gaseous ammonia at a rate of about 2g NH_3 per minute.

Water-insoluble Compounds Formed During Ammoniation

Figure 1 shows the change of water-solubility of each component of F-1 during the ammoniation at about 100°C. Insoluble compounds started to form around pH 2.5. The amounts of insoluble Fe_2O_3 and F reached maximum at pH of about 6 and that of insoluble Al_2O_3 at pH of about 5. Insoluble silica increased markedly above pH 6 indicating

the decomposition of SiF_6^{2-} ions. Tests with F-2 and F-3 gave similar results.

Figure 2 illustrates the relation between pH and the amounts of water-insoluble compounds formed during the ammoniation of F-1 at 100°C . The amounts were estimated by X-ray and chemical analysis. The water-insoluble phosphate first formed at pH 2.5 was gelatinous immediately after the ammoniation and crystallized gradually to form a compound $(\text{Fe,Al})\text{NH}_4\text{H}_2(\text{PO}_4)_2 \cdot 1/2\text{H}_2\text{O}$ (l) which will be called '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 this phosphate is not $(\text{Fe,Al})\text{PO}_4 \cdot n\text{H}_2\text{O}$ which has been generally assumed to be the major constituent of the gel but consists mainly of a compound 'S' which has been determined as $(\text{Fe,Al})\text{NH}_4\text{HF}_2\text{PO}_4$. The compound S is a solid solution of $\text{FeNH}_4\text{HF}_2\text{PO}_4$ and $\text{AlNH}_4\text{HF}_2\text{PO}_4$ (Table 2). S consists of very small round shaped particles about 20 millimicrons in diameter. X-ray tests have shown that the single crystals are much smaller than 20 millimicrons. The size varies with the conditions of formation, particularly by the temperature. Tests with synthetic $\text{AlNH}_4\text{HF}_2\text{PO}_4$ have shown that this crystal is likely to belong to the tetragonal system.

TABLE 2

X-ray Diffraction Peaks of the Samples
Prepared at 100°C . (28, Cu, Ko)

Compound	Main diffraction peaks	
$\text{FeNH}_4\text{HF}_2\text{PO}_4$	15.4	29.9
$\text{AlNH}_4\text{HF}_2\text{PO}_4$	15.8	30.8
$(\text{Fe,Al})\text{NH}_4\text{HF}_2\text{PO}_4^*$	15.7	30.2
Compound S (F-1)	15.7	30.2

*0.4 mole Fe salt and 0.6 mole Al salt.

Above pH 5, $\text{AlNH}_4\text{HF}_2\text{PO}_4$ decreased with the formation of $(\text{NH}_4)_3\text{AlF}_6$. Gelatinous silica increased substantially above pH 6.

Tests were made to study the effect of fluorine on the formation of those compounds. Acids with large F/(Fe+Al) ratios were prepared by adding H_2SiF_6 to F-1. Those with small ratios were prepared by adding small amounts of K_2CO_3 to F-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 Figure 3.

Only S was detected in a wide range above pH 3 with the acids whose ratios were larger than 1. The stoichiometric $F/(Fe+Al)$ ratio of S is 2. When the ratio of the acid was smaller than 2, up to about a half of fluorine ions of S was replaced by hydroxyl ions. When the ratio was smaller than 1, Q and S were present between pH 2 and 6 while gelatinous ferric and 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.

Similar results were obtained with composite acids prepared from R-1 and H_2SiF_6 . By using R-1 only Q formed below pH 6 and gelatinous phosphate above pH 6.

Figure 4 shows the results of the tests with composite acids prepared from R-1 and HF. In this case, Q did not form when the ratio was larger than 1 even at pH 2.5. $(NH_4)_3AlF_6$ formed at pH 3.5 when the ratio was larger than 6.

These results illustrate that F^- ions favour the formation of S inhibiting the formation of Q and that silica combines with fluorine at lower pH favouring the formation of Q and inhibiting the formation of $(NH_4)_3AlF_6$.

Change of Solubility

The change of citric solubility of P_2O_5 during the ammoniation is shown in Figure 5. 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 F-2 and F-3, but the amounts were much less than with R-2. Only small amounts of Q formed with F-3 which contained fluorine which was not combined with silica.

Figure 6 illustrates the change of water-solubility of P_2O_5 . The solubility was much lower with R-2 than with F-2 and F-3 although there is not much difference in the content and water-solubility of Fe_2O_3 and Al_2O_3 . R-2 formed much Q which contains 2 mole P_2O_5 per 1 mole Fe_2O_3 or Al_2O_3 while F-2 and F-3 formed much S which contain 1 mole P_2O_5 per 1 mole Fe_2O_3 or Al_2O_3 .

Viscosity of the Ammoniated Slurry

Figure 7 shows the viscosity of the ammoniated slurry of F-1. For the tests about 500 ml of F-1 was ammoniated to pH 8. Then the slurry was acidulated to pH 2.5 by adding the acid F-1. The viscosity was tested after the slurry was kept for about 5 minutes at various pH during the ammoniation and acidulation. The temperature of the slurries was between 90 and 100°C.

Relatively high viscosity was obtained around pH 2.7. Immediately after the 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 minutes 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 acidulation was higher than that during the ammoniation when the pH was above 5 and lower below pH 5.

Figure 8 shows the change of the viscosity on the ammoniation of F-1 at different temperatures. The viscosity was much higher when ammoniated at lower temperature due to the poor crystallinity of the insoluble substance. The viscosity was as high as 800 cp when ammoniated to pH 2.7 at 50°C. Such low-temperature ammoniation occurs in production plants where dilute ammonia gas such as coke-oven gas is used.

Effects of MgO on Composition and Viscosity

The effect of MgO on the viscosity of the ammoniated slurry is shown in Figure 9. The MgO/P₂O₅ mole ratio was kept at 0.37 by dissolving 5 grams of reagent grade Mg(OH)₂ in 100 ml of F-1. The acid was then ammoniated at about 100°C to various pH and cured at about 90°C for 30 minutes. Very high viscosity, about 9,000 cp, was obtained at pH 6. The slurry had no fluidity at this viscosity. The viscosity was about 2,000 cp immediately after the ammoniation to pH 6, increased to 9,000 cp during the curing in about 20 minutes, and did not increase further. Magnesium formed much MgNH₄AlF₆ in very small crystals about 10 millimicrons in size; fluorine prevented the formation of crystalline magnesium compound such as MgNF₄PO₄·H₂O or MgHPO₄·3H₂O (2).

The viscosity of the slurry with F-5 also increased by the addition of Mg(OH)₂ but the maximum viscosity was less than one tenth of that with F-1. F-5 contained less fluorine and less silica; MgO formed crystalline MgNH₄PO₄·H₂O and MgHPO₄·3H₂O with some MgNH₄AlF₆.

Tests with fertiliser grade magnesium hydroxide obtained from sea water gave similar results.

Figure 10 illustrates the relation between the MgO/P_2O_5 ratio and the viscosity of the slurries from different acids. The acids in which reagent grade $Mg(OH)_2$ had been dissolved were ammoniated to pH 5.7 to 6.2 at about $100^\circ C$ and cured for 30 minutes at about $90^\circ C$.

The sample (R-0 + MgO) showed low viscosity. Fe_2O_3 , Al_2O_3 , F and SiO_2 all increased the viscosity. The effect of H_2SiF_6 was most intensive. The increase in the viscosity during the curing period occurred for F-4 and (R-0 + H_2SiF_6) as well as for F-1. All of these acids contained considerable amounts of silica. The increase was not observed for F-5, R-1 and (R-0 + HF) which contain less or no silica.

Addition of a small amount of magnesium to wet-process phosphoric acid would increase the viscosity of the ammoniated slurry and may help the granulation in some cases. Addition of too much magnesium must be avoided to maintain adequate fluidity of the slurry.

Effects of Other Additives

A few tests were made to study the effect of sodium. A small amount of sodium hydroxide was added to F-1 (Na_2O/P_2O_5 mole ratio 0.24) and ammoniated to pH 5.3. The viscosity was 15 cp soon after the ammoniation and increased to 25 cp after the curing for 30 minutes. In the other test, sodium hydroxide was added to F-4 (Na_2O/P_2O_5 mole ratio 0.24) and ammoniated to pH 6.3. The viscosity was 20 cp soon after the ammoniation and increased to 45 cp after the curing for 2 hours.

By the addition of sodium hydroxide to the acid, Na_2SiF_6 was precipitated and was then decomposed by ammoniation and curing. Both of the slurries contained S, Na_3AlF_6 and colloidal silica. Addition of less sodium resulted in the formation of $(NH_4)_2NaAlF_6$ instead of Na_3AlF_6 .

Two tests were made on the effect of nitrate. A mixture of 60 ml of F-1 and 46 ml of nitric acid (64 per cent HNO_3) was used for the tests. As the ammoniation of the mixed acid in the usual way resulted in a volatilization of much fume of ammonium nitrate including fluorine, the mixed acid and ammonia were charged simultaneously into a vessel in about 10 minutes maintaining pH at about 4 in one test and at about 6 in other test. The temperature of the reaction was 100 to $110^\circ C$.

The viscosity of the slurry was low - 8 cp at pH 4 and

10 cp at pH 6. The insoluble compounds formed were the same as those formed without nitric acid.

Rate of Sedimentation

F-1 was ammoniated to various pH at 100°C and diluted with equal amounts of water to prevent the crystallization of ammonium phosphate on cooling. About 50 ml 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 hours. The results are shown in Figure 11.

The rate of the sedimentation was higher 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 acidulated to pH 5.4 showed the lowest rate.

In other series of tests, F-1 was first diluted with equal amounts of water and then ammoniated to various pH to measure the rate of the sedimentation. The temperature of the ammoniation was between 80 and 90°C. The results are shown in Figure 12. The rate was considerably lower than that shown in Figure 11, possibly because of the lower crystallinity of S formed at lower temperature. The addition of a small amount of MgO prior to the ammoniation lowered the rate but the effect was not as remarkable as was shown for the viscosity.

Filterability

For the tests of filterability, 100 ml each of the acids were 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 in each 30 seconds. The overall amount of the filtrate was 65 to 70 ml in each test.

Figure 13 shows the amount of the filtrate in the first 1 minute with the slurries of F-1 and F-5. Maximum filterability was obtained at pH 4 for F-1. The filterability was poor for the slurries ammoniated at 50°C due to the poor crystallinity of the insoluble phosphate. The filterability was also poor for the slurries ammoniated to higher pH.

The filterability of the slurries with various acids ammoniated to pH 6.7 to 7.1 at 100°C is shown in Figure 14.

The addition of HF to R-1 improved the filterability markedly while the addition of H_2SiF_6 lowered the filterability. The F/ P_2O_5 ratios of those samples are the same as that of F-1. The water-insoluble compound formed with R-1 consisted of gelatinous ferric and aluminium phosphate hydrate. By the addition of HF the gel disappeared and S and $(\text{NH}_4)_3\text{AlF}_6$ formed improving the filterability. When H_2SiF_6 was added, gelatinous silica formed in addition to S and $(\text{NH}_4)_2\text{AlF}_6$ lowering the filterability. The difference in filterability between F-5 and F-1 may largely depend upon the difference in the silica content.

Reaction at Higher Temperature

The ammoniation of the acids between 120 and 170°C under ordinary pressure resulted in the loss of much water and the hardening of the products. Several tests were made under pressure to prevent the loss of water. Considerable growth of crystals of S occurred when the slurries ammoniated at 100°C were heated to 140 to 220°C under 2 to 20 kg/cm² pressure. The crystal growth should affect the properties of the ammoniated slurry prepared under such conditions.

X-ray tests of a commercial product of DAP by a spray tower ammoniation process showed that the major phase of the product was a previously unknown compound while the product contained small amounts of ammonium sulphate and S. The unknown compound has been identified as a high temperature modification of $(\text{NH}_4)_2\text{HPO}_4$. This modification can be prepared in a laboratory by heating the usual form of $(\text{NH}_4)_2\text{HPO}_4$ in a sealed glass tube at 160°C. The transformation occurred above 155°C, indicating that the ammoniation reaction in the spray tower occurred above this temperature. The high temperature 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 $(\text{NH}_4)_2\text{HPO}_4$.

Ammonium Polyphosphate

Ammoniation of the acid above 180°C under atmospheric pressure resulted in the formation of ammonium polyphosphate melt. The acid F-6, 60 g in each test, was preheated in a stainless steel beaker to 130°C to concentrate to 51 per cent P_2O_5 and then ammoniated rapidly by adding 7 g NH_3 per minute to minimize the formation of insoluble phosphates (3). The temperature was controlled to reach a desired level between 210 and 270°C in about one minute and to stay at the temperature for one minute (Figure 15) or for five minutes (Figure 16).

When reacted for one minute, total P_2O_5 of the product increased from 51 to 55 per cent and N of the product decreased from 13 to 12 per cent as the reaction temperature increased from 210 to 260°C. Fluorine content of the products was 0.5 to 0.6 per cent.

Figure 15 illustrates that as the temperature increased from 210 to 240°C, polyphosphate increased from 25 to 60 per cent of total P_2O_5 and the water-solubility from 94 to 99 per cent due to the increasing sequestering effect of polyphosphate. The water-insoluble phosphate consisted of a gelatinous substance which was soluble in alkaline citrate. Above 240°C, small amounts of $(Fe,Al)NH_4P_2O_7$ formed resulting in a slight decrease in the citrate solubility.

Figure 16 shows that when reacted for 5 minutes, a considerable amount of $(Fe,Al)NH_4P_2O_7$ formed above 240°C. Citrate solubility decreased to 86 per cent indicating that most iron and aluminium in the acid formed $(Fe,Al)NH_4P_2O_7$. Tests with a composite acid containing 56 per cent P_2O_5 and 3 per cent Fe_2O_3 have shown that the average crystal size of $FeNH_4P_2O_7$ was 30 millimicrons when formed at 240°C and 90 millimicrons at 270°C. The smaller crystals of $FeNH_4P_2O_7$ were partly soluble in the citrate while the larger crystals were essentially insoluble.

In other series of tests, the acid F-6 was preheated to 150°C to concentrate to 56 per cent P_2O_5 . The reaction for one minute at 240°C gave a product which contained 12.6 per cent N, 56.7 per cent P_2O_5 , 60.3 per cent in polyphosphate form, 100 per cent soluble in the citrate, and 99.6 per cent soluble in water. The reaction for five minutes at 230°C gave a product which contained 13.2 per cent N, 55.2 per cent P_2O_5 , 55.8 per cent in polyphosphate form, 100 per cent soluble in citrate and 99.0 per cent soluble in water.

References

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DISCUSSION

PROFESSOR J. ANDO (Chuo University, Japan):
 In many fertiliser plants, wet process phosphoric acid is ammoniated to produce various types of fertiliser including ammonium phosphate in the powdered form of granular or granular NPK mixed fertilisers, slurry or liquid fertilisers. On ammoniation of wet process phosphoric acid, a large amount of gelatinous water insoluble material forms in the acid from slurry, and this is an important factor in fertiliser production. But the properties of the slurry sometimes vary markedly for unknown reasons. For example, I have heard that, not only in Japanese plants but also in several European plants, the viscosity of the slurry increases so much that it cannot be handled and the operation has to stop. The reason for these changes was a mystery and, as it happened on production plants, I started research on the make up of the slurry and its properties. It has generally been claimed that gelatinous iron or aluminium phosphate is the main constituent of this water insoluble material but this was by no means certain. My most important finding is that the main constituent of the gel is not in fact a simple iron or aluminium phosphate but a new type of compound which I called compound S. This has the formula $(Fe,Al)NH_4HF_2PO_4$ and is tied up with the fluorine and ammonia. Compound S is usually present in very small crystals of about 20 millimicrons in size. But sometimes on ammoniation at low temperature, crystal size is so far reduced that a true gel is almost formed, in which case viscosity increases quite remarkably. On the other hand, in cases of ammoniation at higher temperatures, crystal size may increase appreciably. This feature of compound S is the major influence on the characteristics of the slurry. In addition, at a lower pH, another compound, Q, is formed. It is insoluble in citric acid but soluble in neutral or alkaline citrate. We have also found several other iron and aluminium phosphates which are formed in ammoniated slurry, but are not referred to in the paper. One of these, which we call T, is soluble in citric acid but insoluble in neutral or alkaline citrate and has the formula $Fe(NH_4)_2H_2F(PO_4)_2$ with some crystallisation water. This compound T forms at pH of 6 to 7 and formation is quite slow unless there is some seed present in which case it will grow quickly. But without seed crystal or

some sort of nucleus, the formation of T is quite slow. But in large reaction tanks compound T does form and results in a decrease of the citrate solubility of P_2O_5 . Another compound, which we call U has the formula $Fe_2NH_4OH(PO_4)_2, 2H_2O$. It forms at a pH between 7 and 8 and is insoluble both in citric acid and citrate.

Most of the results of my work are set out in the paper. I will, however, just mention two things referred to in the text. One is the effect of calcium on the viscosity of the slurry. Figure 9 illustrates the effect of magnesium on the viscosity of slurry and small amounts of it increase the viscosity considerably. In the absence of magnesium, acid F-1, i.e. the normal acid produced from Florida phosphate rock, has a very low viscosity on ammoniation of 10 or 15 cps. But when there is a small amount of magnesium present in the F-1, the viscosity on ammoniation can rise to 6,000 or 7,000 cps which is quite viscous and the acid has virtually no fluidity. In cases when the acid does not contain fluorine, e.g. F-5 (which contains only small amounts of fluorine) the viscosity is not as high even when magnesium is added which is the result of the formation of $MgNH_4AlF_6$. Crystal growth is very weak and the formation of this compound increases the viscosity very considerably. When calcium is present instead of Magnesium, the result is different. When calcium is present with fluorine, viscosity does not increase much. But when calcium is present and fluorine is not, the viscosity rises up to about 4,000 or 5,000 cp at pH of 6 to 7. So the effects of calcium and magnesium are more or less contrary where fluorine is concerned.

Another point I would like to mention about this water insoluble compound is related to a peculiar property of granular mixed fertilisers. When used in paddy fields for rice in Japan and in many South East Asian countries, farmers frequently use the granular NPK mixed fertilisers. High analysis, mixed fertilisers are applied to paddy fields filled with water and the granules often sink to the bottom, but after about 30 minutes or an hour they rise to the surface and, if there is a wind, it blows all the fertiliser apparently still in its original form to a corner of the paddy field and the farmer becomes angry. This is one of the reasons why we have serious problems in Japan in using mixed high analysis fertilisers in paddy fields. Actually about 90% of the water soluble

portion has already dissolved when it comes to the surface, but this is not apparent to the farmer. The matter therefore is not really serious from the agricultural standpoint but, because it has exactly the same colour and shape as it had before application, farmers think it has all settled in one place. It is quite amusing and I would like to know if a similar problem has arisen in European countries. I have not found out why it floats nor how to prevent it. It bears a close relationship to the type of water insoluble compound formed on ammoniation. It would take a long time to deal with this problem in detail so if anyone is interested and wants to ask me. I will be glad to discuss the matter with him.

MR. E. PAVONET (Société de Prayon, s.a., Belgium): We are very grateful to Professor Ando, for his interesting presentation of a very immediate subject, closely linked to the day-to-day concerns of many of our members.

The ammoniation of phosphoric acid, with or without the formation of polyphosphates is current practice. It does, however, remain a little known field where trial and error predominate and where it is wiser to follow a well-tried process faithfully than to risk running into awkward complications.

This is hardly surprising when one considers that wet-process phosphate-acid is extremely variable in its composition with numerous organic and inorganic constituents.

An important experiment on phosphoric acid of the Florida type, synthetic acids, has revealed the formation of certain compounds either of a transitory nature like Q or more stable ones. The work has brought to light a relationship between the concentration of F and SiF ions and the nature of the precipitates formed. In addition it has led to further clarification of the role of magnesium and its influence on the viscosity of slurries. Finally, it pays particular attention to defining the relationship between the temperature and the duration of the reaction of ammoniation and the insolubilisation of P_2O_5 in the form of insoluble polyphosphates.

This well-conducted study based upon a great deal of advanced experimental and analytical work is very timely. It will elucidate matters for

many of us, permit us to ask more precise questions, help us to get out of our too narrow empirical routine and to evaluate in a more scientific way, the many possible hazards which can occur in ammoniation and to overcome them methodically.

To introduce the discussion, I would like to ask a few questions myself:

- I. (Figure 1) Portion of P insoluble in water.
What is the meaning of P?
How should the portion insoluble in water be determined?
Should the precipitate be washed with water?
- II. (Figure 2) How should the curves be interpreted?
Is the sum total of the precipitates represented by the upper curve?
What is the meaning of the curve in dotted lines?
- III. The precipitation of the Q compound, rich in P_2O_5 occurs at pH 2,5 for acids of which the ratio $F/Fe + Al$ is lower than 4,5 (see figure 3). Consequently, should not acid F-1 precipitate the compound Q?
- IV. In the tests which led to the curves of figures 2 and 3, ammonia has been progressively fed to the phosphoric acid.
We wonder what these figures would become if the ammoniation were effected continuously by simultaneous adding of acid and ammonia in the reaction tank. For instance, will phase Q still form itself at about pH3 above the line of ratio $F/Fe + Al = 1$?
- V. (Figure 7) What is the advantage of following the viscosity in the course of reacidifying?
How should the variation in viscosity in this part of the curve be explained?
- VI (Figures 15 and 16) The effect of the increase of the reaction temperature and of the duration of its maintenance at this temperature

is a reduction of water and citrate solubility of the P_2O_5 by the formation of insoluble pyrophosphates.

How is this explained?

Is the formation of insoluble pyrophosphates rather a slow reaction?

PROFESSOR ANDO: (slides were shown during these answers). The last question concerned the formation of insoluble polyphosphate. Is the formation of insoluble polyphosphates rather a slow reaction? My answer is that if the nucleus is already present in the system, crystal growth is very fast but the formation of the nucleus is slow. For example, at $240^\circ C$. it takes more than 1 minute for the nucleus to form so, if the ammoniation is over in one minute, without the presence of nucleus or seed crystal, it is all right. But if you use big tanks, one part of the product is always recirculated to the tank and so the seed crystal is present. Under such conditions the insoluble compound forms within 1 mn. so it is a matter of the presence of seed crystals. I think this is one of the reasons why TVA uses T reactors: to avoid the presence of seed crystal and to ensure very rapid reaction.

This slide illustrates Mr. Pavonet's fourth question. The question is why acid F-1 which has the F/Fe + Al ratio 4.5 should not produce compound Q? My answer is that the figure shows that, if the ratio is over 5, Q is not formed and, at the ratio 4,5, Q forms and once it does so it remains for some time. And in using acid, if you make use of the simultaneous reaction adding the ammonia and the phosphoric acid together in the reaction tank and with the pH above 4, then Q is not formed. But, if you have two stage ammoniation, in the first tank you ammoniate to pH of about 2.5 and at the next stage raise it to about 6, a considerable amount of Q is formed and it then decreases in the next stage. It can, however, still remain in the final product.

Mr. Pavonet's second question is related to this figure. The main point of his question is what does this dotted line mean? This compound S is a solid solution between the compound $AlNH_4HF_2PO_4$ and $FeNH_4HF_2PO_4$. Actually these two compounds are mixed to form uniform single crystals, so we can in fact separate these aluminium and iron compounds. This dotted line therefore just gives a rough idea of how much aluminium compound and how much iron compound is present. Below the dotted line is shown the iron compound and above it aluminium

This shows the water insoluble portion of the component on ammoniation of the acid to various pH. Mr. Pavonet's point is whether there is any change of the compound during washing with water? Essentially no change results from washing with water. I have confirmed this by various tests using X ray and electron microscope analysis.

There is another question about ammoniation to a high pH, up to 8, then acidulation down to 5. Is there any advantage in conducting ammoniation and acidulation of this sort? This is illustrated in figure 7 of my paper and, if the acid is first ammoniated to a high pH and then acidulated to pH 5 or 6, then sedimentation of the solid material is very slow, as is shown in figure 11. The sample with the mark pH 5.4 was prepared in this way and the slow sedimentation is caused by the formation of small amounts of gelatinous silica at high pH. I think this might have an advantage for the production of slurry fertilisers, which sediment very slowly.

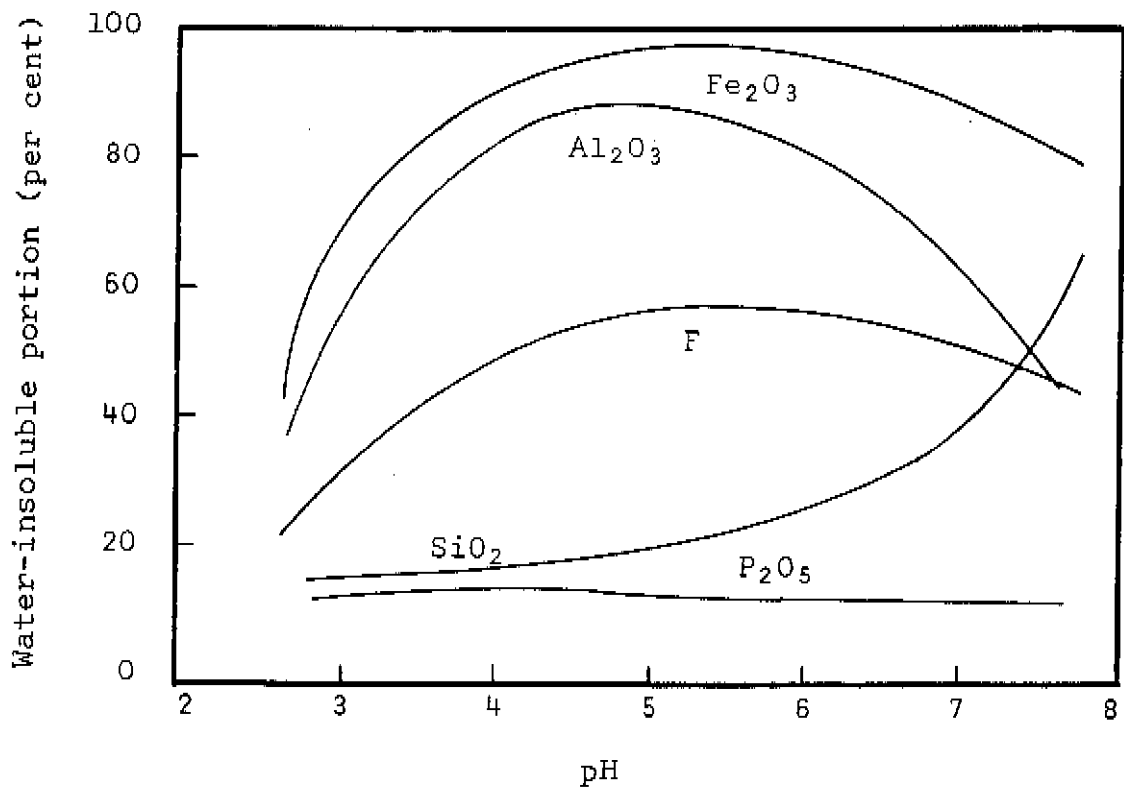


FIGURE 1

Change of Water-Solubility on Ammoniation
of the Acid F-1 at 100°C

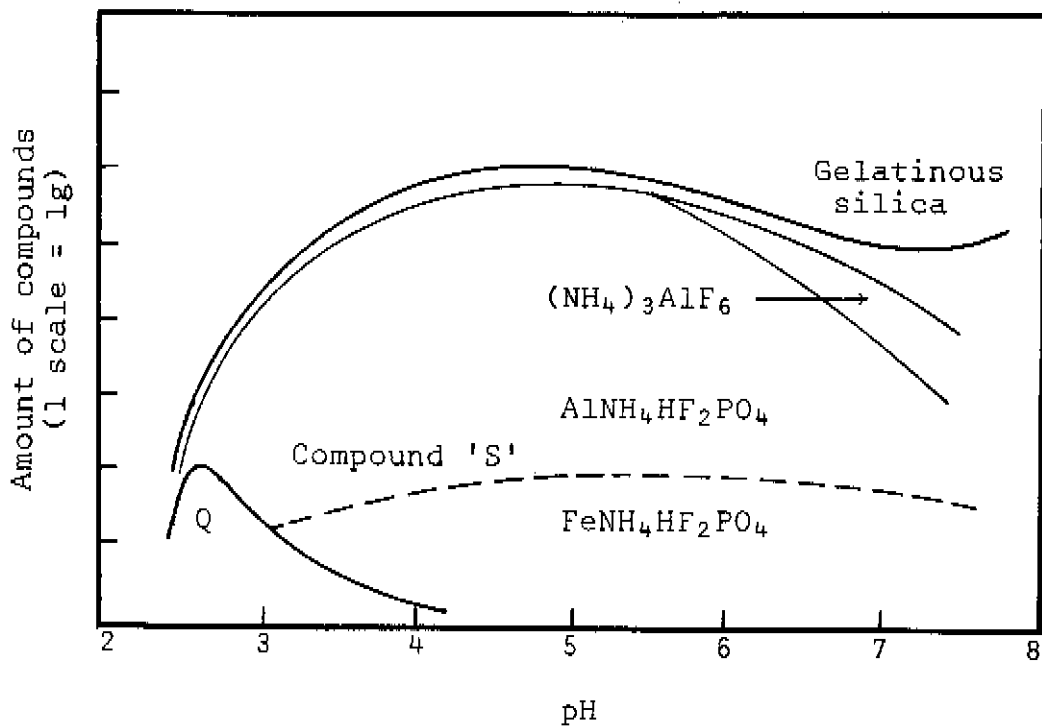


FIGURE 2

Water-Insoluble Compounds Formed from 100g of
F-1. Q = (Fe.Al)NH₄H₂(PO₄)₂ · ½H₂O



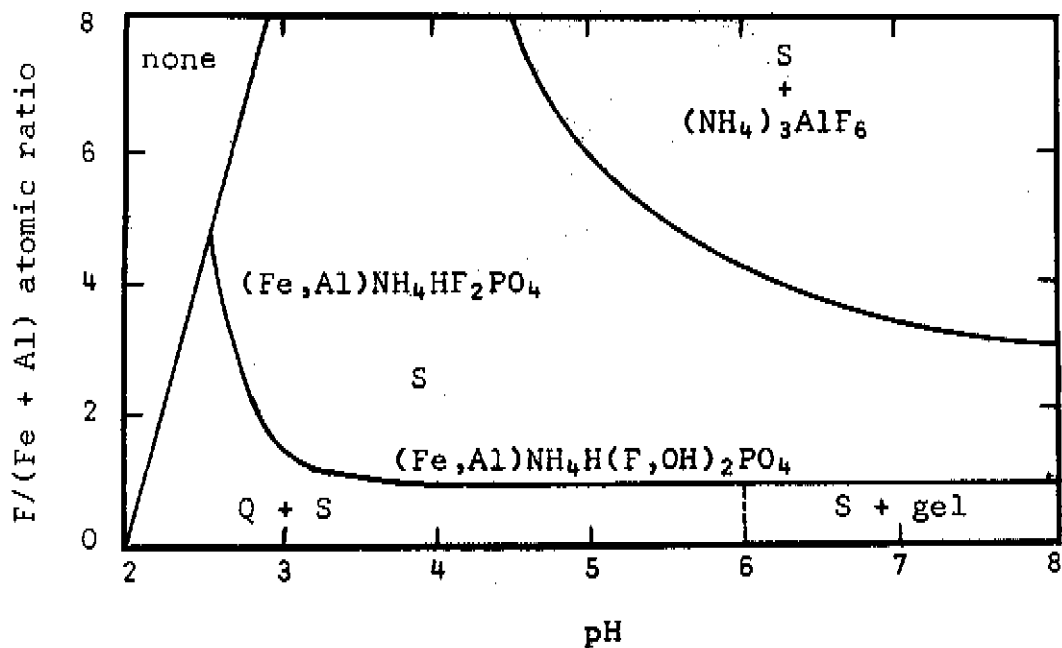


FIGURE 3

Water-Insoluble Ferric and Aluminium Compounds
Formed at Various F/(Fe + Al) Ratio and pH

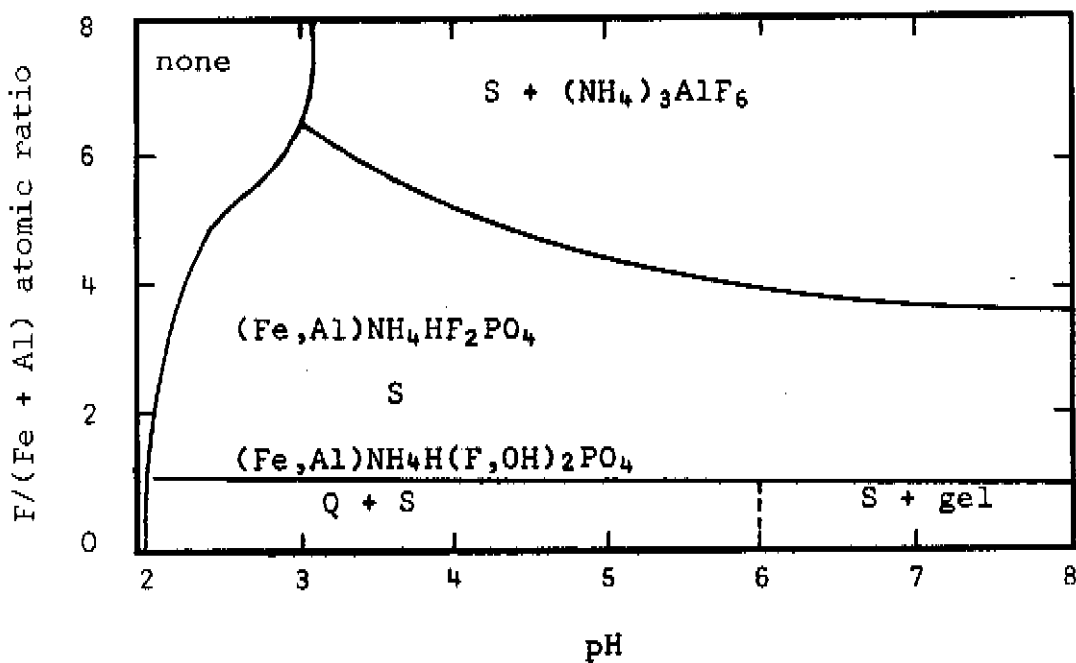


FIGURE 4

Water-Insoluble Ferric and Aluminium Compounds
(R-1 and HF, Without Silica)

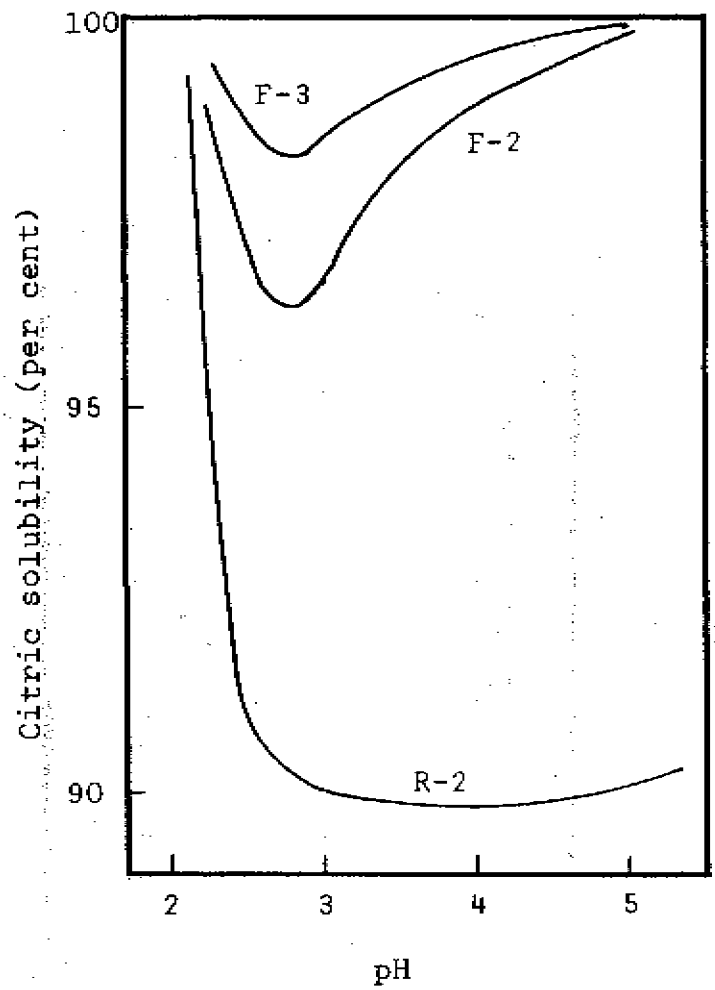


FIGURE 5

Change of Citric Solubility
of P₂O₅ During Ammoniation

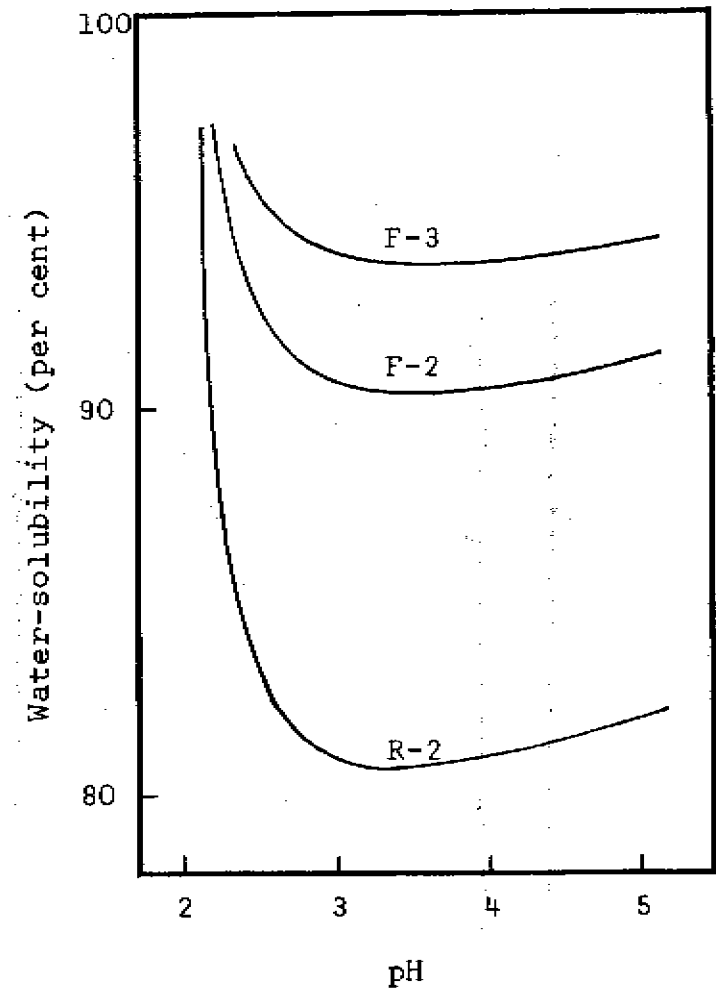


FIGURE 6

Change of Water-Solubility
of P₂O₅ During Ammoniation

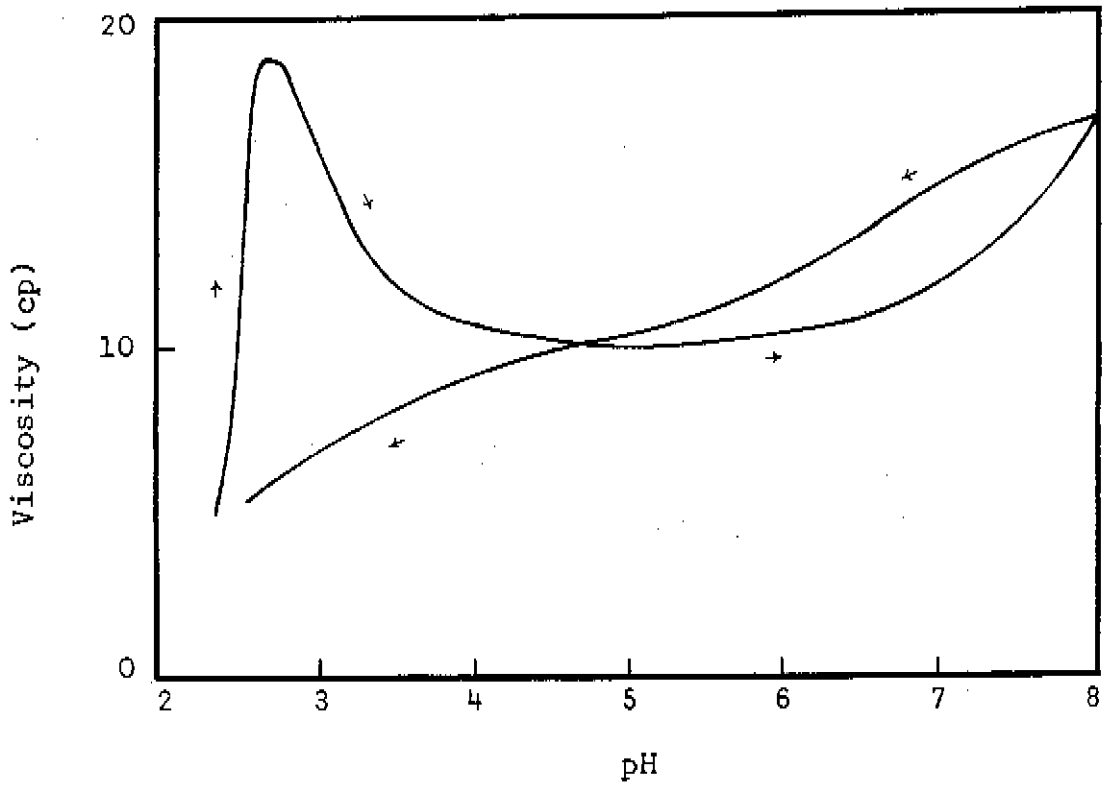


FIGURE 7

Change of Viscosity of Ammoniated Slurry of F-1 (100°C)

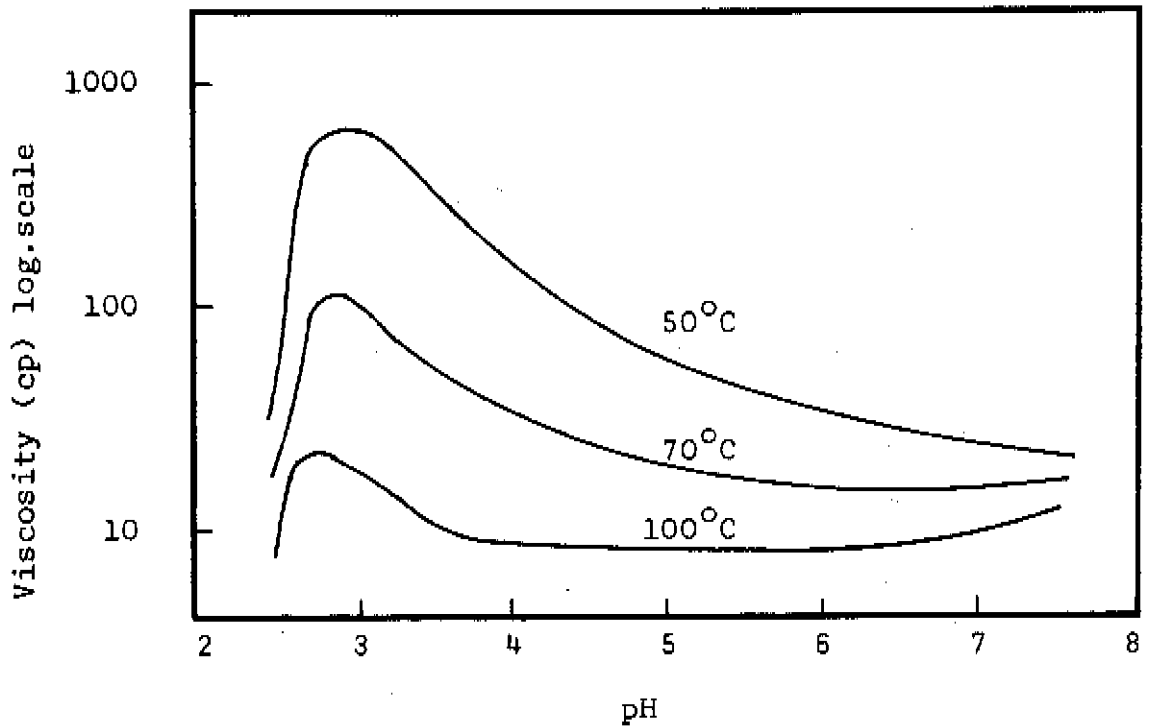


FIGURE 8

Change of Viscosity of F-1 on Ammoniation

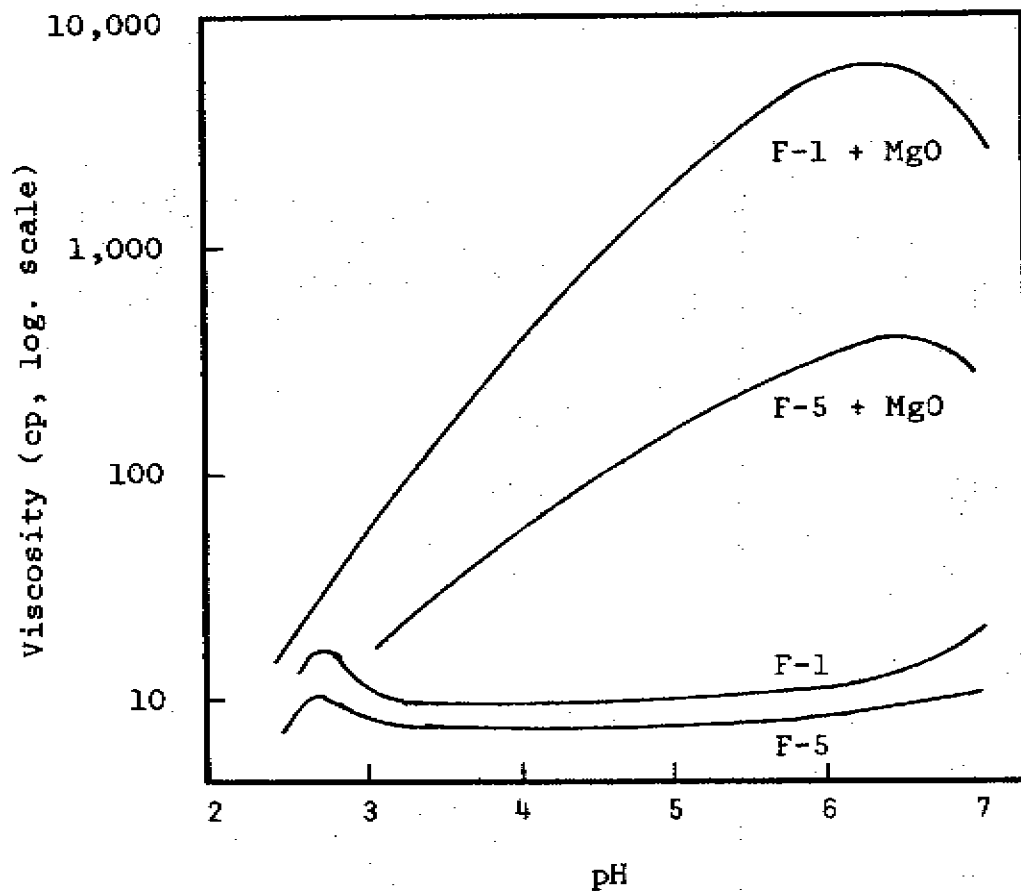


FIGURE 9

Effect of MgO on Viscosity
(100°C MgO/P₂O₅ Mole Ratio 0.37)

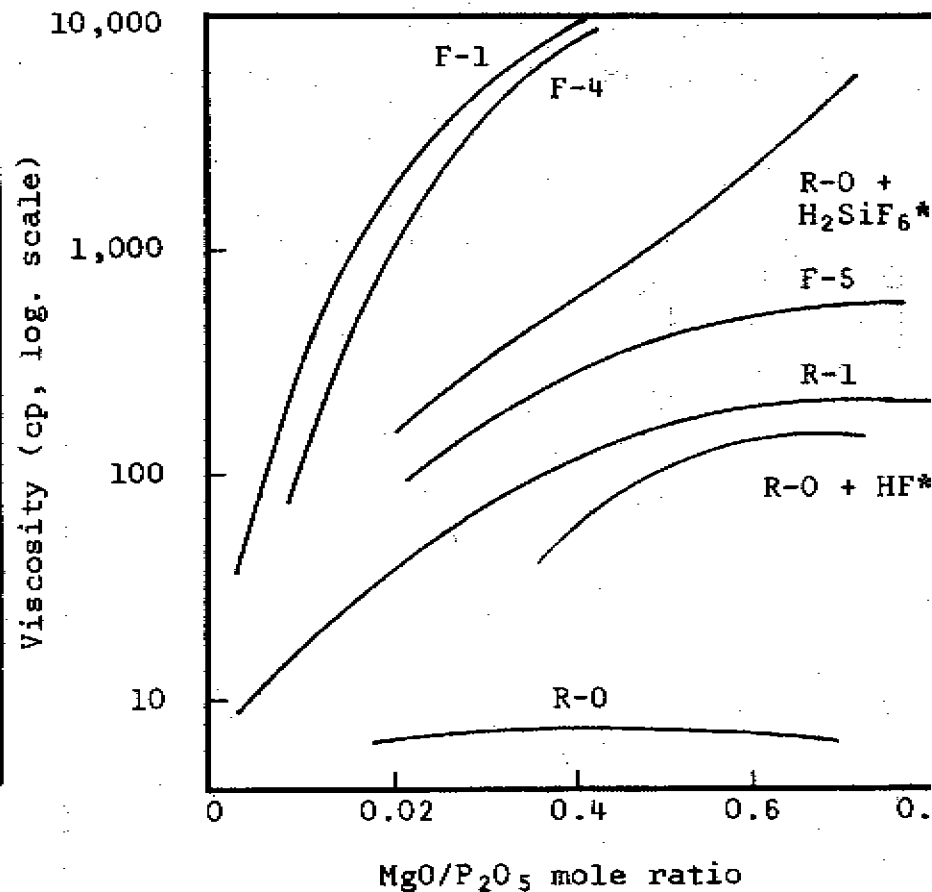


FIGURE 10

Effect of MgO on Viscosity
(100°C, pH 5.5 to 6. *Ratio of
F/P₂O₅ is Equal to that of F-1)

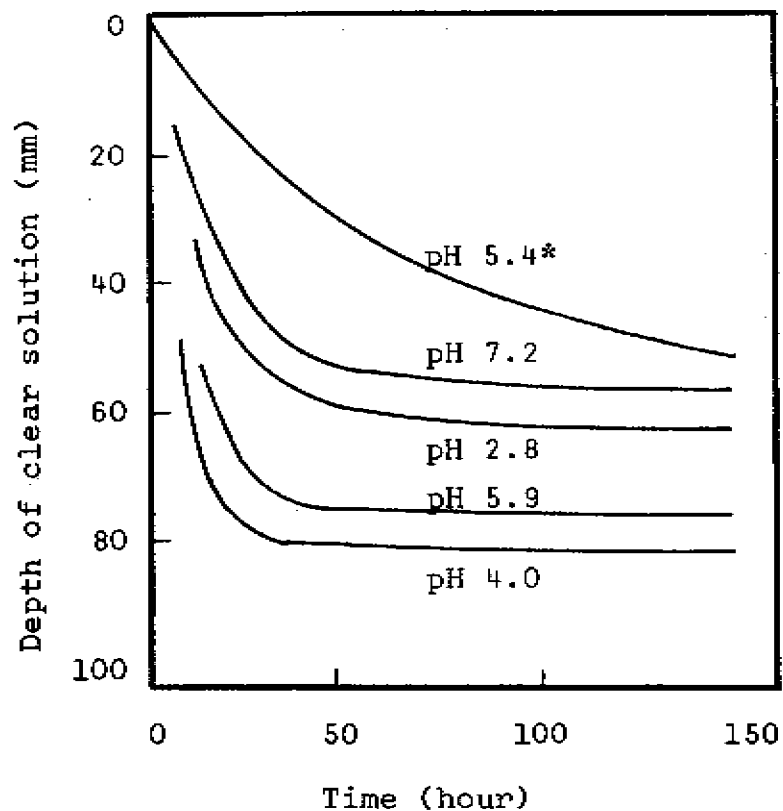


FIGURE 11

Sedimentation of Gel-Like Substance
In Ammoniated Slurry of F-1
(Ammoniated and then Diluted. *The
Sample Ammoniated and then Acidulated
to pH 5.4)

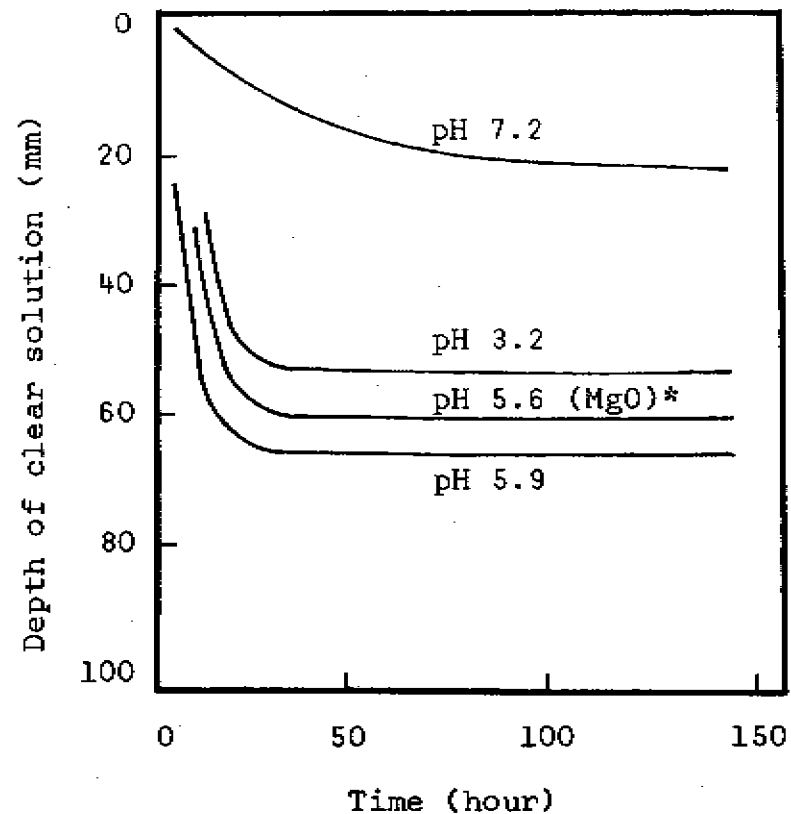


FIGURE 12

Sedimentation of Gel-Like
Substance in Ammoniated Slurry
of F-1.
(Diluted and then Ammoniated.
*MgO/P₂O₅ Mole Ratio = 0.15)

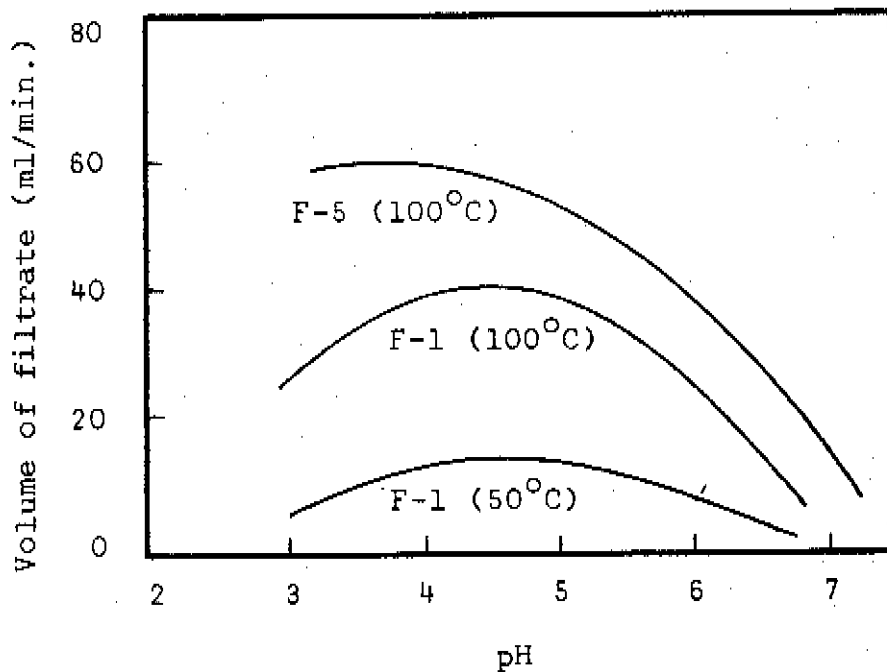


FIGURE 13

Relation between Filterability, Temperature, and pH

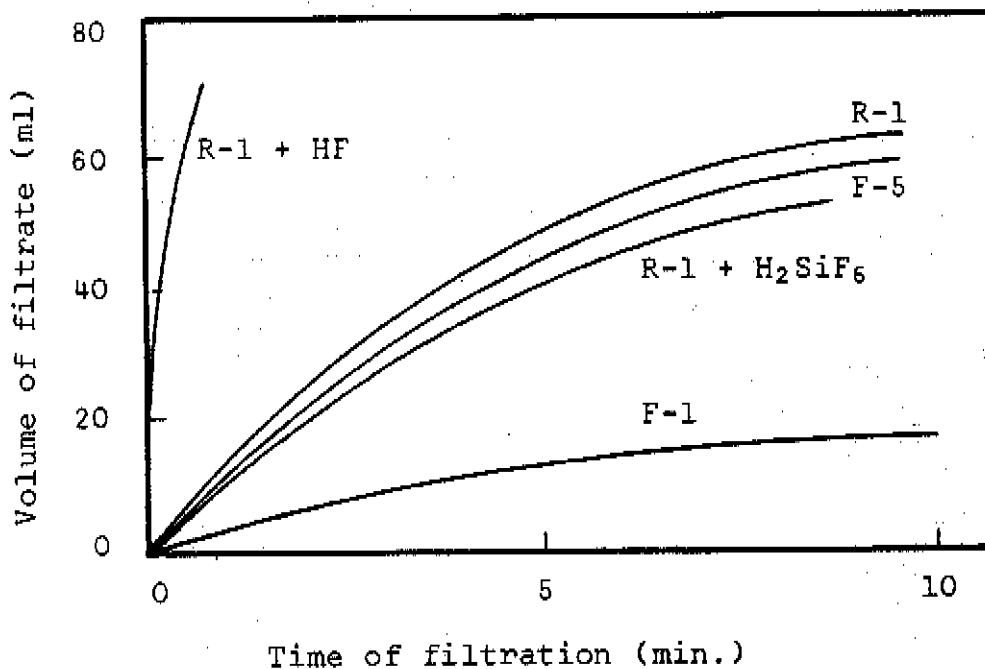


FIGURE 14

Comparison of Filterability of the Slurries
 from Various Acids. (100°C pH 6.8 to 7.0)

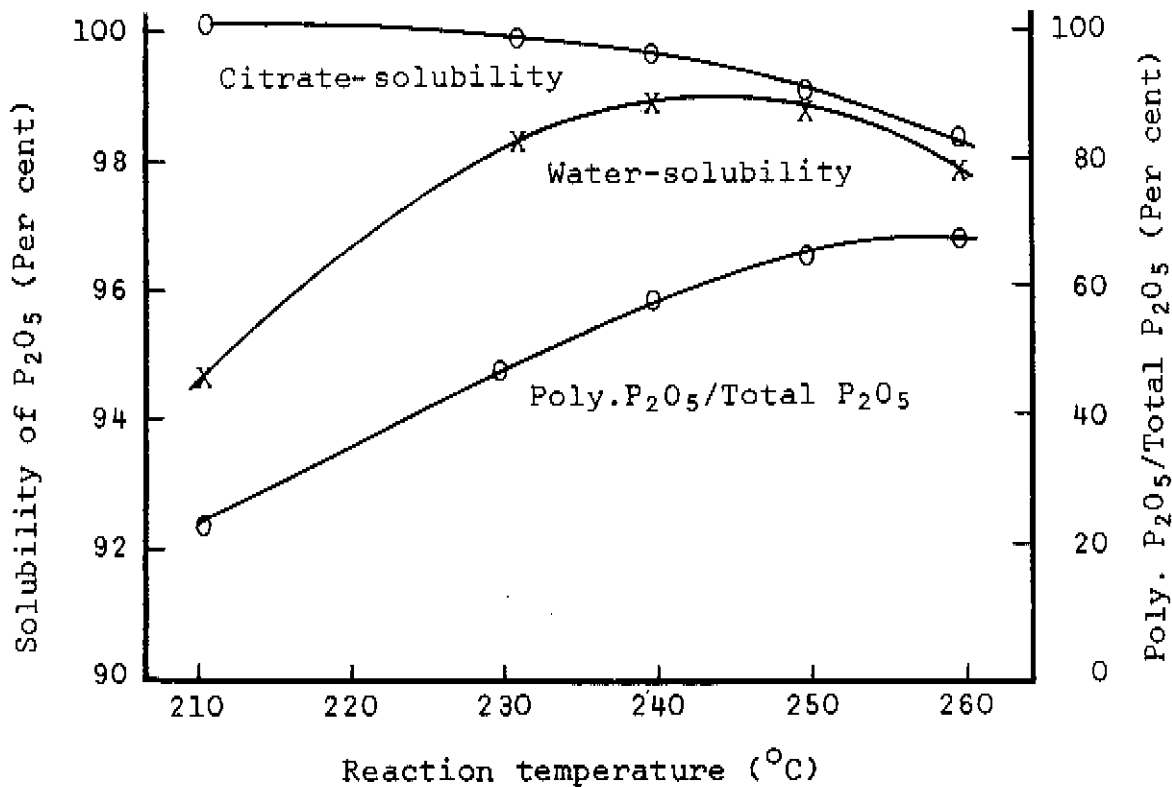


FIGURE 15

Effect of Reaction Temperature on Polyphosphate Content and Solubilities. (Retention Time 1 Min. Total P₂O₅ 51 to 55 Per Cent. N 12 to 13 Per Cent)

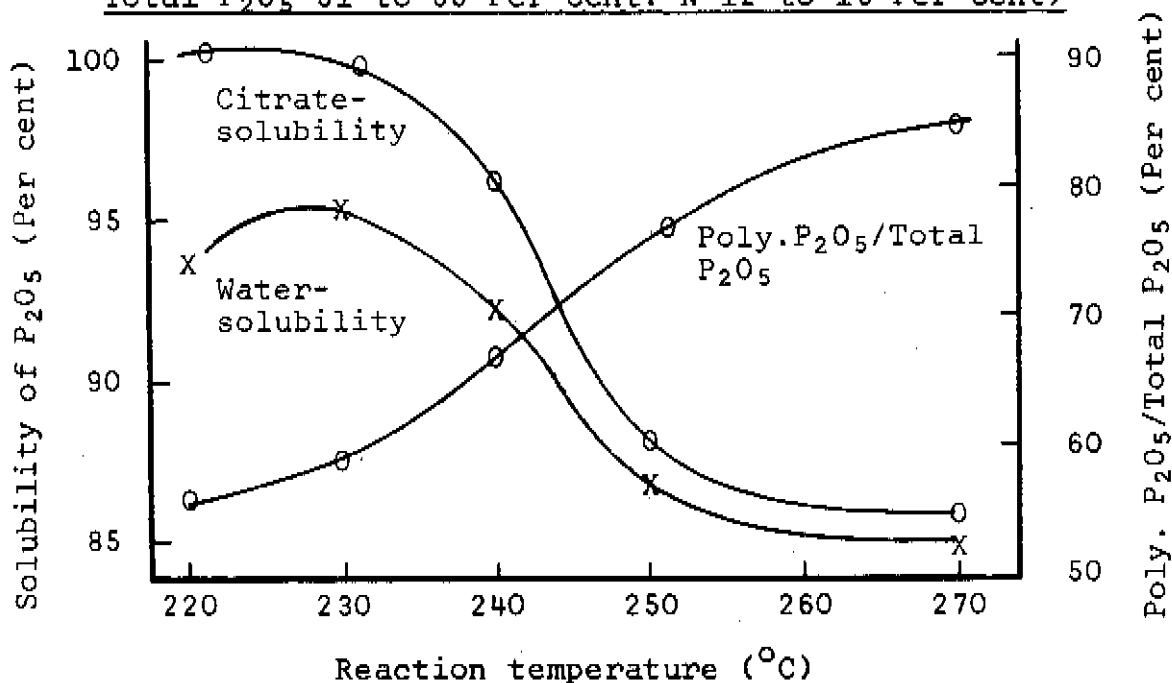


FIGURE 16

Effect of Reaction Temperature on Polyphosphate Content and Solubilities. (Retention Time 5 Min. Total P₂O₅ 53 to 57 Per Cent, N 12.5 to 13.5)