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FERTILIZER TECHNOLOGY

Liquid Fertilizers from Wet-Process Phosphoric Acid. Suspension of Impurities

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Wet-process phosphoric acid has not been used extensively in liquid fertilizers because it contains impurities that precipitate during ammoniation; the precipitated impurities settle and thicken during storage. Moreover, crystals of magnesium ammonium phosphate (struvite) grow in the ammoniated products of some acids to a size large enough to plug spray nozzles. In tests of the production of liquid fertilizers from wet-process acid, a stable, nonsettling suspension was produced by adding 1 to 2% by weight of a swelling-type clay or by ammoniating at pH 7 or higher and adjusting the product to normal pH (6.7) for storage. Growth of struvite crystals was inhibited by quick cooling to room temperature or by ammoniating to a low pH (6.0); however, by the latter method, the settling rate was increased appreciably. Best results were obtained by a combination of processes involving ammoniation at a high pH and adjusting to a low pH for storage; the products were slow settling, highly fluid, and free of large crystals.

THE LIQUID mixed fertilizer industry in the United States had its beginning in California some 30 years ago. However, it was not until 1954 that the first bulk plant was built east of the Rockies. It is estimated that there are now over 350 plants producing about 200,000 tons per year of plant food as liquid mixed fertilizers. This is about 5% of the total applied as mixed goods.

The basic operation for the production of liquid mixed fertilizers is the neutralization of phosphoric acid with ammonia or ammoniacal solutions. Supplemental nitrogen may be supplied as urea, ammonium nitrate, or urea-ammonium nitrate solutions. Potash usually is supplied as potassium chloride. Most

producers use electric-furnace phosphoric acid as the source of phosphate. However, the lower cost of wet-process phosphoric acid in most areas has led to a major effort in finding ways of using it. The main difficulty is that the wet-process acid contains impurities that precipitate when the acid is ammoniated, and the resulting sludge may settle and cause handling problems. The precipitated impurities can be removed from the product or a sequestering agent can be used to keep them in solution. Another, and perhaps simpler, method is to suspend them in such a way as to give satisfactory handling and application properties; these properties are high fluidity, low degree of settling, and absence of par-

ticles large enough to clog spray nozzles.

Experience has shown that there are no serious problems, if liquid fertilizers produced by ammoniation of wet-process acid are applied to the field immediately after production. This is the basis on which several producers now use wet acid. However, difficulties may occur if the product is to be stored for more than a few days. The precipitated impurities settle and may require redispersion. Also, with some acids, struvite ($MgNH_4PO_4 \cdot 6H_2O$) crystals form and grow to a size large enough to clog spray nozzles.

This paper covers work at the Tennessee Valley Authority (TVA) aimed toward development of techniques and

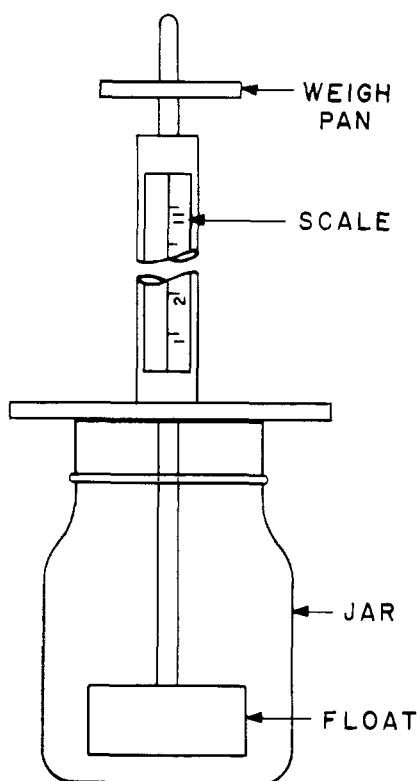


Figure 1. Sedimentation gage

procedures to minimize settling of precipitated impurities and to control growth of struvite crystals when it is a problem. The effects of several variables and procedures were studied. Use of clay as a suspending agent or control of pH during ammoniation was found to be effective as means of improving the stability of suspensions. Adjustment of terminal pH was found to be the best way of controlling struvite growth.

Equipment and Procedures

Most of the tests were made in a 10-gallon reactor tank, with auxiliary equipment consisting of raw material storage tanks, three weigh tanks for liquid feeding, a vibratory feeder for solids, and control equipment. Vigorous agitation and recirculation of product were provided. Cooling was obtained by circulating water through submerged cooling coils. Control was by measurement of pH and manual adjustment of acid or ammonia feeds as necessary. Agitation was provided in the acid storage and feed tanks to prevent settling of impurities and to ensure homogeneity of the acid fed. The feed pipes were positioned to inject acid and ammonia at the bottom of the reactor in as close proximity as possible to promote rapid reaction.

Normally, the equipment was operated in a semicontinuous batch manner. The water required by the formulation was weighed into the reactor first. When clay was used as a suspending agent, it was added with the water.

Wet-process phosphoric acid (50 to 54% P_2O_5) and aqua ammonia (20% N) then were added simultaneously, along with supplemental materials needed for the particular formulation.

The products had a specific gravity of about 1.2 to 1.3 (at 75° to 85° F.) and a viscosity, in most tests, between 20 and 185 centipoises. This is a somewhat higher viscosity range than that found for liquid fertilizers made from furnace-type phosphoric acid (up to about 25 centipoises). However, the suspensions gave no difficulty in subsequent pumping and handling operations.

Evaluation of Products

The products were evaluated by measurement of viscosity, rate of settling, particle size of crystals formed, and sprayability through standard spray nozzles. The apparent viscosity was measured with a Brookfield viscometer (RVT model); spindle No. 1 or 2 was used as appropriate for the viscosity of the particular sample.

The degree of settling was determined by measuring the depth of the two layers that developed during storage, a supernatant clear layer and a lower, thickened suspension. The proportion of total depth as settled suspension was reported as "sedimentation volume." A high sedimentation volume was indicative of minimum separation and a low degree of settling.

A sedimentation gage (Figure 1) similar to that used in the paint industry was used to characterize the products as to fluidity, thixotropy, and thickening in the lower portion of the settled layer. The rate of travel of a float down through the suspension was determined. The weight of the float system was such that no downward travel occurred until a weight was added. A 20-gram weight was added each 30 seconds and the position of the float at that point was recorded. Plots were made of the height of the float above the bottom of the container vs. the total weight of the float system (a function of time). Theoretically, all plots of such data should start at 100% of the depth as the initial reading; however, in only 1 or 2 seconds after addition of the first weight, the float dropped through the clear liquid portion of the suspension. There was a slight hesitation of float travel as it reached the suspension level; this hesitation was noted and the position of the float at that time was used as the initial point of all plots. A high initial point is indicative of slow settling. A steep slope of the curve indicates high fluidity, while a relatively flat portion of the curve followed by a change to a relatively steep slope indicates thixotropy. A flattened final portion shows thickening in the lower portion of the suspension, and hard caking—not encountered in the present

tests—would be indicated by failure of the curve to reach the lower axis.

Particle size of solids was determined by wet screen analysis. The sample was shaken and poured over a series of Tyler screens (20, 48, and 100 mesh). The material retained was flushed with water, partially dried with acetone, and dried further on a hot plate. Also, spray tests were made with a flat, jet-type nozzle (0.078-inch opening) and 25 to 30 p.s.i. discharge. This is the smallest of nozzles generally used in liquid fertilizer application.

Improvement in Stability of Suspension

Rate of Ammoniation. In previous work by Houston, Yates, and Haunschild (2) on production of diammonium phosphate from wet-process acid, the filtering rate of precipitated impurities decreased with increase in rate of ammoniation. Since low filtration rate and slow settling usually are concomitant, preliminary small-scale tests were made to check the effect of rate of ammoniation. Batch operation was tested first—i.e., all the acid for a batch was placed in a container and the ammonia then added. A high degree of settling was obtained in all these tests; the sedimentation volume ranged from 10 to 33 after a week.

Further small-scale tests were then made in which the acid and ammonia were added simultaneously to the reaction vessel at rates proportioned to give a neutral product. Under this condition neutralization of the acid is practically instantaneous. This procedure markedly improved the suspensions produced, giving sedimentation volumes of 55 to 70. Since simultaneous feeding of acid and ammonia is a feasible and widely used procedure in making liquid fertilizers, it was adopted as standard procedure in subsequent tests.

Neutralization Temperature. The effect of temperature during neutralization was studied in tests in which the acid and ammonia were fed simultaneously to maintain a pH of 6.6 to 6.7 in the reactor. This is the pH commonly used in commercial plants and gives an N: P_2O_5 weight ratio of 1:3. The amount of water used was such as to give a product containing 8% of N and 24% of P_2O_5 , also a standard concentration in commercial practice. Results of tests in which reaction temperature was controlled at 160°, 180°, and 200° F. are given in Table I. Sedimentation volumes were higher at lower temperatures. The 160° F. level was used in subsequent tests; lower temperatures were not tested since they would require more cooling capacity than available in most liquid fertilizer plants. Although some of the precipitated solids failed to remain suspended during storage, they could be resuspended by agitation, and less agitation was required as the reaction temperature was decreased.

pH during Neutralization. Tests were made in which the pH during neutralization was higher than the normal of 6.7. This was done by feeding ammonia at a faster rate than usual. After all the ammonia had been fed, addition of acid was continued to bring the pH down to 6.7. Results (Table I) show that practically no settling occurred in 30 days when the neutralization was carried out at a pH of 7.0 or higher; the sedimentation volume was 98 to 100. In contrast, when the pH during ammoniation was 6.7 (normal), the sedimentation volume was 85. All the products of the high pH process were thixotropic in character, and the degree of thixotropy increased as the pH of ammoniation was increased.

Viscosity increased manifold in the pH range of 7.0 to 8.0. Thus, it appears desirable to control the process closely to hold the neutralization pH fairly close to 7.0. At lower levels, settling is increased and at higher values, the viscosity becomes so high that considerable loss in pump efficiency probably would be incurred. Use of a higher level also increases the possibility of ammonia loss during neutralization; however, a material balance indicated no loss of ammonia even at pH 8.0 under the conditions of the present tests.

Use of Suspending Agent. In tests with several suspending agents, best results were obtained with swelling-type clays such as those used in preparation of drilling muds. Attapulgite and sodium bentonite were used with good results. These materials were most effective when added as clay-water premixes that were allowed to stand at least 24 hours prior to use to develop suspending properties. Dispersion of the clay in water was accomplished by circulating the clay-water mixture through a gear pump or by use of a high-speed laboratory mixer, both of which imparted the necessary shearing action. Satisfactory premixes were formed with an attapulgite-water ratio of about 1:8 or slightly less; with the sodium bentonite-water premixes, the ratio had to be reduced to about 1:12 to obtain good mixing of clay and water. Typical data for tests with clays are given in Table I. The sedimentation volume of the product after 30 days of storage was 98% as compared with 85% without clay. The products were thixotropic and had a relatively high apparent viscosity. A few tests made by introducing dry clay during ammoniation indicated that, to obtain comparable increases in sedimentation volume, about twice as much dry clay was required as when the clay was added as a clay-water premix.

Repression of Crystal Growth

Most of the impurities in wet-process phosphoric acids precipitate during

Table I. Decreasing Settling of Suspension Fertilizers^a Made from Wet-Process Phosphoric Acid

Procedure	Conditions during Ammoniation		Apparent Viscosity, ^b Centipoises	Sedimentation Volume ^c
	pH	Maximum temp., ° F.		
Normal pH	6.7	160	40	85
	6.7	180	43	80
	6.7	200	23	68
High neutralization pH	8.0	160	325	100
	7.8	160	263	100
	7.4	160	176	100
	7.0	160	79	98
Clay added ^d	6.7	160	182	98

^a 8% N; 24% P₂O₅. Made from ammonia, acid, and water. Product pH, 6.7. Values given are the average of triplicate tests.

^b Measurement with Brookfield viscometer with spindle speed of 50 r.p.m.; spindle No. 1 for 100 centipoises or less and spindle No. 2 for viscosity over 100 centipoises.

^c Per cent of volume as other than clear liquid after 30 days of storage at room temperature.

^d Attapulgite clay, 1% by weight, added as 10% clay-water premix.

Table II. Repression of Crystal Growth in Suspension Fertilizers^a Made from Wet-Process Phosphoric Acid

Procedure	pH		Apparent Viscosity, ^b Centipoises	Sedimentation Volume ^c after		Crystal Size, Tyler Mesh ^d			
	Neutralization	Product		7 days at 28° to 32° F.	30 days at room temp.	+20	+48	Total +100	
Normal pH, quick cooled	6.7	6.7	41	93	86	0.011	0.228	0.474	
	6.7	6.7	42	96	89	0	0.063	0.402	
Polyphosphate sequestering agent added ^e	6.7	6.7	42	96	89	<0.001	0.274	0.297	
	Low product pH	6.6	6.6	51	98	82	0.022	0.174	0.199
		6.4	6.4	39	92	67	0.005	0.011	0.018
		6.2	6.2	37	77	62	0	0.001	0.002
6.0	6.0	34	61	53	0	0.001	0.002		
Low product pH with clay added ^f	6.2	6.2	46	95	82	<0.001	0.005	0.007	
	High neutralization pH and low product pH	8.0	6.2	136 ^g	100	98	0.002	0.135	0.146
8.0		6.0	73	100	94	0	0	0.012	
8.0		5.8	48	98	87	0	0	<0.001	
7.6		5.8	52	98	89	0	0	<0.001	
7.0		5.8	53	98	89	0	0	<0.001	
6.8		5.8	45	96	82	0	0	<0.001	
6.6		5.8	45	95	85	0	0	<0.001	
6.4		5.8	43	92	77	0	0	<0.001	
6.2	5.8	38	84	72	0	0	<0.001		

^a Made from ammonia, acid, and water. Composition, % by weight: N, about 8, depending on pH; P₂O₅, 24. Neutralization temperature, 160° F.

^b Measurement made with Brookfield viscometer using spindle No. 1 at 50 r.p.m. except as noted.

^c Per cent of volume as other than clear liquid.

^d Per cent by weight retained on indicated Tyler screen; sample stored for 30 days at room temperature.

^e Ammoniated superphosphoric acid. Amount added: 1% by weight.

^f Attapulgite clay, 1% by weight, added as 10% clay-water premix.

^g Used spindle No. 2 at 50 r.p.m.

ammoniation as extremely fine particles and remain as such during storage; however, with some acids, struvite (MgNH₄PO₄·6H₂O) forms and grows in size during storage of the product. Results of test to control formation and growth of struvite are shown in Table II. When the acid was ammoniated at a normal pH and allowed to cool normally, a considerable amount of crystalline material was found in the product after 30 days of storage. Most of the crystals were quite fine, but there were enough of the larger sizes to clog rapidly the 0.078-inch nozzle in spraying tests.

Quick Cooling. A rapid rate of cooling was tried in an effort to increase crystallization rate and thereby decrease crystal size. In normal operation, the product was allowed to cool slowly to room temperature. In the quick cooling tests, the product was cooled to room temperature in less than 30 minutes. Typical data from these tests (Table II) show a minor reduction in total amount of +100-mesh crystals, but a major decrease in the larger sizes that cause nozzle clogging. There were no +20-mesh crystals; this usually ensures good sprayability through 0.078-inch nozzle.

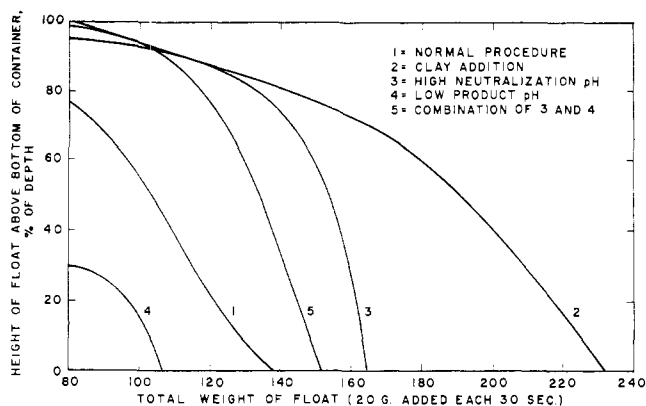


Figure 2. Sedimentation gage data for ammoniated wet-process phosphoric acid

Table III. Effect of Acid Type on Properties of Suspension Fertilizer^a

Acid Type ^b	Procedure	Apparent Viscosity, ^c Centipoises	Sedimentation Volume, ^d %	Crystal Size, Tyler Mesh ^e		
				+20	-20 +48	Total +100
I	Normal pH	74	92	0.001	0.001	0.004
II	Normal pH	46	75	0	<0.001	0.001
	Clay added ^f High neutralization pH	80	95	0	<0.001	0.001
III	Normal pH	163 ^g	96	0	<0.001	<0.001
	High neutralization pH and low product pH	40	85	0.001	0.140	0.450
IV	Normal pH	56	95	0	0	0.007
	High neutralization pH and low product pH	41	70	0.002	0.042	0.201
		48	86	0	<0.001	0.001

^a Made from ammonia, acid, and water. Composition, % by weight: N, about 8, depending on pH; P₂O₅, 24. Neutralization temperature, 160° F.

^b Results given for one acid of each type.

^c Measurement made with Brookfield viscometer using spindle No. 1 at 50 r.p.m. except as noted.

^d Per cent of product as other than clear liquid after storage for 30 days at room temperature.

^e Per cent by weight retained on indicated Tyler screen; sample stored for 30 days at room temperature.

^f Dry attapulgite clay, 1% by weight, added as 10% clay-water premix.

^g Used spindle No. 2 at 50 r.p.m.

Sequestration. Wilbanks, Nason, and Scott (3) have shown that impurities in wet process acid can be prevented from precipitating by use of a polyphosphate sequestering agent; it was necessary to supply about 20% of the phosphate as sequesterant to repress precipitation completely. In the present work, a few tests were made in which a small amount (1%) of an ammonium phosphate solution (ammoniated superphosphoric acid) containing about half the phosphate in a polyphosphate form was added in an effort to sequester magnesium preferentially and prevent formation of struvite. Results indicated some reduction in crystal growth. However, the products contained unsuspended solids that stuck to the containers, and vigorous agitation was required to redisperse them.

Effect of Product pH. Tests were made in which the pH during ammoni-

ation and storage was lower than the normal level of 6.7. This was found to be a very effective method for repressing struvite growth. At 6.2 and lower, practically no +100-mesh crystals were found after 30 days of storage. However, the sedimentation volumes of the products were drastically reduced at the lower pH values (25 to 35 percentage points lower than at normal product pH).

Since use of clay or high neutralization pH had been found effective in improving sedimentation volume at normal product pH, these methods were tried in conjunction with low product pH. When 1% by weight of an attapulgite clay was used and ammoniation was carried out at a pH of 6.2, crystal formation was controlled effectively and the sedimentation volume was increased to a level slightly below that obtained by normal neutralization procedure. However, results were not as good as in tests

in which clay was used in conjunction with normal product pH.

High neutralization pH and low product pH were combined by neutralizing at a pH of 8.0 and adjusting the product to 6.2 or lower. This method was superior to use of clay as a means of getting a combination of high sedimentation volume and low crystal growth. At a product pH of 6.2 there was practically no settling in 30 days and the crystal size was reduced enough to make the suspension sprayable through most nozzles. At pH 6.0, there was slight settling (94% sedimentation volume) but +48-mesh crystals were eliminated. Thus, it appears possible to get both low settling and low crystal growth by careful adjustment of product pH.

Further tests were made to find the lowest neutralization pH practicable in conjunction with low product pH. Results (Table II) show that the minimum neutralization pH should be about 7.0. However, close control at this level should not be necessary, since viscosity was not increased by higher pH. Apparently, the low product pH eliminated the effect of neutralization pH on viscosity, as compared to results obtained when the product pH was adjusted to the normal level of 6.7 (Table I).

Viscosities of products made by the combination high-low pH procedure generally were somewhat lower than those of products made at high neutralization pH and normal product pH. However, for neutralization at pH 7.0, which was shown to be adequately high, the difference was not very great.

In tests on repression of crystal growth, sedimentation volume was measured also after 7 days of storage at 28° to 32° F., a condition that might be encountered in practice. The general effect of variables was the same as for 30 days of storage at room temperature; however, less settling occurred at this time-temperature combination (sedimentation volume about 10 points higher).

Sedimentation Gage Data. Typical data obtained with the sedimentation gage on products stored for 30 days at room temperature are plotted in Figure 2. The products were made by the procedures discussed above. The curve for the normal procedure (both neutralization and product pH at 6.7) has an initial point below 80, which indicates a clear or relatively thin upper layer. The steep slope of the curve indicates high fluidity, and the slight flattening near the end indicates some thickening near the bottom of the container. A high degree of settling is indicated by the curve for low product pH; however, the thickened slurry at the bottom was fluid and no hard, settled cake was present. The other curves—for clay addition, high neutralization pH, and combination of high neutralization pH and low product pH—all show by their high initial point

the improvement in homogeneity obtained by these procedures. All show a thixotropic nature by the flattened initial portion. The two involving high neutralization pH show high fluidity after the thixotropy was broken. For clay addition, however, relatively low fluidity is indicated over the full curve.

Effect of Supplemental Materials

All tests described thus far were on products made from ammonia, acid, and water to give a grade of approximately 8-24-0 (% by weight of N-P₂O₅-K₂O). Although this is one of the standard grades in liquid fertilizer practice, many other grades are made by incorporation of potash and supplemental nitrogen. A few tests were made to determine whether the presence of supplemental materials would affect settling and crystal growth. Urea-ammonium nitrate solution was used to supply supplemental nitrogen and potassium chloride to supply potash. When the normal procedure was used (pH 6.5 to 6.7), the products had relatively low sedimentation volumes and contained crystalline material of sufficient size to cause plugging of spray nozzles. The following tabulation gives average values from settling tests on products made by the high neutralization-low product pH procedure.

Grade	Neutralization Temperature, ° F.	Sedimentation Volume after 30 Days at Room Temperature
8-24-0	160	92
6-18-6	160	83
7-14-7	145 ^a	85
7-7-7	100 ^a	74

^a Heat of reaction not sufficient to give higher temperature.

Struvite growth was repressed satisfactorily in all these products.

These results show that use of supplemental materials increases settling somewhat, but does not interfere with the beneficial effect of low product pH on struvite formation.

Comparison of Wet-Process Phosphoric Acids

The tests reported above were made with acid obtained from one commercial producer. Since wet-process phosphoric acid is known to vary widely in composition and characteristics, further tests were made with acids from several other producers. The results indicated that acids can be classified roughly into four types as listed in Table III. A few acids (Type I) gave satisfactory suspensions when a normal pH was used; they could be substituted for electric-furnace acid

in liquid fertilizer production without any change in procedure. Acids classified as Type II gave no difficulty with crystal formation, but sedimentation volumes could be improved considerably by use of clay or high neutralization pH. Acids of Type III behaved similarly to the one used in the tests discussed earlier in this paper. These acids, ammoniated by a normal procedure, gave products with fairly high sedimentation volume, but with excessive crystal growth. With acids of Type III, ammoniation by the high neutralization-low product pH process not only controlled crystal growth, but also increased sedimentation volume to over 90%. Acids of Type IV were similar to Type III, except that a sedimentation volume higher than 90% could not be obtained. These acids required lower product pH for repression of crystal growth than did those of Type III. The low product pH appeared to be the cause of the lower sedimentation volume.

Chemical analyses were made on acids of all four types (Table IV), and attempts were made to correlate composition with characteristics of the ammoniated products. No valid correlations were found. The composition of Type III acid was adjusted in a further attempt at correlation. Two per cent of sodium (as Na₂CO₃) was added to determine whether crystal formation would be reduced to that encountered with acid of Type II; however, no appreciable decrease was obtained. When magnesium (as MgSO₄·7H₂O) was added to increase the Mg content to 1%, the crystal content of the ammoniated product was not increased.

Spray Tests

All products from present tests could be sprayed without difficulty. The spraying rates were about the same as for water. The thixotropy noted in some products was not sufficient to interfere with flow.

Segregation of Nutrients

One of the disadvantages of settling in the products is segregation of nutrients. The composition of the dry precipitated solids is about 10-50-0 (unwashed), so that settling gives some segregation of nutrient between top and bottom of the

Table IV. Chemical Analyses of Typical Wet-Process Acids

Constituent	Indicated Constituent, % by Weight			
	Type I	Type II	Type III	Type IV
Ca	0.02	0.1	0.01	0.2
Fe	0.9	0.8	0.7	0.9
Al	0.7	0.3	0.7	0.3
Mg	0.3	0.2	0.3	0.5
Cr	0.01	0.01	0.03	0.01
V	0.02	0.01	0.04	0.02
Na	0.05	1.9	0.03	0.2
K	0.08	0.1	0.07	0.08
F	1.0	0.3	0.7	0.7
SO ₃	3.2	1.8	3.0	3.6
SiO ₂ (acid insoluble)	0.2	0.2	0.2	0.3
C	0.3	0.04	0.1	0.3
Total solids ^a	3.3	5.1	1.7	5.1

^a Filtered material, not washed, dried for 1 hour at 220° F., and weighed.

suspension and also between nitrogen and phosphate content. Suspensions that had settled to varying degrees were carefully sampled from points near the top and bottom and analyzed. Another portion of each suspension was stirred thoroughly and analyzed to get over-all composition. Results are given in the tabulation below.

Nitrogen contents of the layers and the stirred suspension were about the same, as would be expected because the nitrogen contents of the suspension and of the precipitated solids were about the same. There was considerable segregation of phosphate, however, in samples that had settled. The clear, top layers contained about 4% less phosphate than did the stirred samples, a deficiency that would be tolerated in some states, but not in others. It should be noted that degree of settling does not affect the deficiency, if clear liquor is sampled; the latter has the same composition regardless of the degree of settling. Thus, a poor sample will be obtained even at high sedimentation volume if it is taken from the clear layer. A good sample is obtained at 100% sedimentation volume, as shown in the tabulation.

Another disadvantage of nutrient segregation is the changing composition as product is withdrawn from storage tanks. The composition of the lower, settled layer is important in this respect, since product normally is withdrawn

Sedimentation Volume	Composition, % by Wt.					
	Top Layer		Lower Layer		Over-all	
	N	P ₂ O ₅	N	P ₂ O ₅	N	P ₂ O ₅
52	7.5	24.3	7.6	26.1	7.6	25.2
59	7.8	23.9	7.8	25.7	7.8	25.2
60	7.5	24.3	7.5	26.0	7.5	25.3
65	7.7	24.0	7.8	26.0	7.7	25.2
70	7.6	23.7	7.7	25.1	7.9	24.5
73	8.3	23.9	8.3	25.0	8.2	24.6
100	8.0	24.2	8.0	24.1	8.0	24.1

from the bottom of the tank. Data in the tabulation above show a decreasing difference between the phosphate contents of the lower layer and the stirred suspension as the sedimentation volume is increased.

Discussion and Conclusions

Production of a satisfactory liquid fertilizer of the suspension type from wet-process phosphoric acid appears to depend on several factors, of which the major ones are those associated with handling and application of the product. If the situation is such that the product can be applied to the soil with little delay after production, it should be feasible to substitute wet-process acid for the furnace type without any change in procedure. Immediate settling is much less severe, if the acid and ammonia are added to the reactor simultaneously, as is done in many commercial plants. However, even stepwise addition should give a product of sufficient fluidity for immediate application.

If the product is to be stored for several days, settling and crystal growth become problems. Batch ammoniation is likely to give a product difficult to remove from storage tanks. Continuous ammoniation gives much better fluidity, but settling and crystal growth give rise to other problems in use.

The problem resulting from settling is difficult to evaluate. Assuming continuous ammoniation and storage not longer than 30 days, the present tests indicate that most products would be fluid enough for pumping and spraying although somewhat settled. The main problem from settling may be segregation

of plant nutrients, either from variation in composition as product is drawn from storage tanks or from difficulty in sampling for official inspection. This can be avoided by stirring before withdrawal or sampling. However, it would be desirable to avoid the need for stirring or minimize the degree of stirring needed.

Settling can be kept to a low level either by using clay as a suspending agent or neutralizing at a pH of 7.0 rather than the usual value of 6.6 to 6.7. Of the two, the latter appears preferable in the continuous ammoniation process because it does not require an additional raw material or special mixing equipment. For batch ammoniation, where neutralization pH cannot be held constant, clay addition is the only alternative.

Whether or not struvite crystal growth is a problem depends on the type of application equipment. Squeeze pump applicators, which do not have small openings in the flow path of the suspension, should handle the largest crystals formed in the present tests without difficulty. However, most of the applicators in general use are equipped with spray nozzles of one type or another, and the openings are therefore relatively small. For the range of orifice sizes normally used, the larger ones should be able to handle the crystals, but the smaller ones would not.

Crystal growth can be repressed adequately by using a product pH of roughly 5.8 to 6.2, depending on characteristics of the acid. Low pH aggravates settling, however, so high neutralization pH should be used also. Possible disadvantages of the low product pH are that corrosion may be increased and that the N:P₂O₅ weight ratio will be a little lower

than 1:3. The latter is a problem only if a 1:3 ratio is desired in the product. However, this ratio can be obtained by adding a small amount of supplemental nitrogen. Available data on corrosion (7) indicate little effect of pH in the range in question. These data were for solutions made from reagent materials; however, similar results were obtained in unpublished work with solutions made from wet-process acid.

Tests indicated that quick cooling is also an effective method. However, the rate of cooling required is higher than could be accomplished in most existing plants.

It should be noted that acids from some sources gave satisfactorily low settling and crystal growth without any adjustment of manufacturing procedure. Products from other acids varied widely in the degree of objectionable characteristics. This indicates that, in practice, a testing procedure might be desirable for routine checking of incoming acid to determine the best procedure for using it. Alternatively, the combination high neutralization-low product pH might be adopted in a plant as standard procedure to ensure against trouble from a change in the character of the acid.

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FERTILIZER TECHNOLOGY

Wet-Process Phosphoric Acid in Mixed Fertilizers

PHOSPHORIC ACID is a well known commodity in the fertilizer industry. For many years it has been used in the manufacture of high analysis triple superphosphate, and to a much lesser extent as a phosphate material for direct application in the irrigated areas of the West. In recent years, while its use in these two areas has increased greatly, the acid has also become a basic raw material in the manufacture of both solid and liquid mixed fertilizers. These changes are

causing a sizable expansion in facilities for producing phosphoric acid (7).

Two types of phosphoric acid are marketed—a purified acid made by the electric furnace method and a less pure, dark acid made by the wet-process method. The information presented here relates primarily to wet-process phosphoric acid made from Florida pebble phosphate by the Dorrco process (7a).

While wet-process phosphoric acid has

been used in the fertilizer industry for a number of years, its advent as an important raw material for mixed fertilizers dates back only a few years. Its use in solid mixed fertilizers began about 1955 (6); its use in liquid mixed goods, first reported in 1957 (70), is only now coming into prominence. The growth in the use of wet-process phosphoric acid in mixed fertilizers and for direct application has been phenomenal—from less than 50,000 tons of P₂O₅ in 1957-58 to an

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