Precipitated Impurities in 18-46-0 Fertilizers Prepared from Wet-Process Phosphoric Acid

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The use of marginal-quality phosphate rock and the increased use of the sludge fraction from wet-process phosphoric acid have created grade problems in the production of 18-46-0 fertilizers. Detailed solid-phase characterizations determined from chemical composition, optical microscopy, X-ray diffraction, and infrared spectroscopy made on 15 commercial 18-46-0 fertilizers are described and discussed. These characterizations are correlated with the process parameters to show the relationship of physical and chemical parameters on 18-46-0 grade. These samples represented a wide range of impurities from Florida, North Carolina, and western phosphate rock sources. Several reasons for grade problems and suggested methods for alleviating them were identified in this research study.

With the declining chemical quality of commercial phosphate raw materials, increasing amounts of metal impurities, which subsequently precipitate upon ammoniation, occur in the wet-process phosphoric acid. The compositional form and relative abundance of these metal salts depend upon both acid composition and operative parameters during ammoniation and granulation. Consequently, grade problems with respect to N or P_2O_5 content, or both, may have different origins, depending upon the particular controlling precipitation reactions. Characterization of the solid-phase components in fertilizer products of nominal 18-46-0 grade is an important step in the identification of specific causes of grade dilution. Certain solid-phase components precipitate and dilute the grade to a value less than the nominal grade of 18-46-0. It is important to recognize that 18-46-0 is 85% of the theoretical value for pure $(NH_4)_2HPO_4$.

The loss of acidity during ammoniation causes precipitation of dissolved metal impurities. The various types of precipitates depend on the pH, temperature, and retention time during ammoniation. The solubility properties of the diammonium phosphate fertilizer depend upon the total content of impurity solids and their specific compositional forms (Frazier et al., 1980).

For many years the iron and aluminum compounds that precipitate above pH 2, which were observed by optical microscopy and X-ray to be cryptocrystalline or amorphous, were assigned the composition $(Fe,Al)PO_4 \cdot nH_2O$ on the basis of their recognized constituents (Frazier et al., 1966). When crystallinity was observed, the identified compound was $(Fe,Al)NH_4(HPO_4)_2 \cdot 0.5H_2O$, and it was assumed that the amorphous material had largely crystallized as this compound. In fact, it was determined that high temperatures and long retention times in a preneutralizer at pH 3-6 would cause sufficient crystal development to allow for easy removal of the impurities by filtration.

Interest in 18-46-0 grade problems and the identification of fluorophosphates as components of ammoniated wet-process phosphoric acids have resulted in a refinement in the identification of the metallic precipitates. The identification of the components in 18-46-0 fertilizers has been complicated by the large number of impurities, the poor crystallinity of the precipitates, the lack of funda-

mental information, and the large number of process variables used in production processes. The poor crystallinity of the precipitates is sometimes due to the amorphous or cryptocrystalline nature of the original precipitates and at other times to the fact that the crystalline phases are decomposed to amorphous phases during drying of the 18-46-0 fertilizer product. The identification of these new fertilizer compounds, along with phase system studies and the use of argon plasma emission spectrometry for detailed chemical analysis, has provided a more thorough understanding of the composition of 18-46-0 grade fertilizers. Multielement determinations can be performed by emission spectrometry, whereas only single, or at most dual, elements can be performed by atomic absorption spectrometry. Also, microscopic, X-ray, and infrared techniques were required to confirm the presence of these compounds.

METHODS

Chemical Analysis and Component Analysis. For simplification of the problem, only the water-insoluble fraction from the 18-46-0 fertilizers was initially studied and characterized, and then the results were related to the total fertilizer composition. These samples, representing the range of impurities in different phosphate rock sources (Florida; North Carolina; western), are shown in Table I. The metals were analyzed by argon plasma emission spectrometry, with the remaining analyses done by AOAC methods. The component analysis for these samples as determined from chemical composition, optical microscopy, X-ray, infrared, and phase chemistry publications is presented in Table II; the process parameters for several samples are listed in Table III.

The data in Table I show that several impurity elements occur over wide concentration ranges, indicating the potential areas for applying purification treatments which will have the most effect on the fertilizer grade. The wide ranges of iron and aluminum were expected; however, calcium and fluorine, which were previously thought to be unimportant constituents, were sometimes highly significant. The solid-phase identifications in Table II reflect these chemical analyses and show the fate of each impurity element associated with the phosphoric acid. The process parameters in Table III show that there are significant differences in the operating conditions for moisture removal in the preneutralizer.

RESULTS AND DISCUSSION

Calcium. Calcium is present in several forms, depending mainly on the total fluorine content. The chukhrovite $(Ca_4SiAlSO_4F_{13} \cdot 12H_2O)$, which ranges up to

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Table I. Chemical Analysis of 18–46–0 Fertilizers

	total		chemical analysis, wt %																	
sample	N	P₂O₅	Fe	Al	Mg	F	Ca	SO₄	Zn	V	Cr	Cd	U	Ni	Mn	Na	K	total H₂O	free H₂O	citrate-insoluble P₂O₅
DP no. 1	18.3	46.5	1.26	0.64	0.37	1.2	0.21	5.99	0.0082	0.0149	0.0082	0.0005	0.0074	0.0022	0.0330	0.05	0.06	1.9	1.7	0.37
DP no. 2	18.0	46.0	1.4	0.69	0.48	2.4	0.41	3.89	0.0065	0.0160	0.0076	0.0003	0.0170	0.0019	0.0294	0.15	0.11	3.0	2.0	0.32
DP no. 3	18.0	46.2	1.19	0.64	0.37	1.8	0.40	5.09	0.0080	0.0141	0.0080	0.0004	0.0161	0.0021	0.0322	0.10	0.12	2.8	2.3	0.18
DP no. 4	18.2	46.6	1.33	0.64	0.43	1.5	0.30	4.79	0.0060	0.0168	0.0083	0.0002	0.0148	0.0025	0.0270	0.10	0.11	2.6	2.2	0.04
DP no. 5	18.3	47.3	1.19	0.58	0.35	1.5	0.30	4.79	0.0058	0.0169	0.0077	0.0005	0.0180	0.0020	0.0329	0.09	0.11	1.7	1.4	0.84
DP no. 6	18.2	46.8	1.26	0.64	0.34	1.4	0.33	5.39	0.0070	0.0155	0.0082	0.0004	0.0046	0.0019	0.0311	0.07	0.09	2.4	1.7	0.10
DP no. 7	18.7	45.3	0.77	0.74	0.33	2.5	0.31	5.09	0.0095	0.0096	0.0092	0.0005	0.0060	0.0011	0.0350	0.09	0.09	2.6	1.9	0.08
DP no. 8	18.7	47.4	0.47	0.25	0.42	1.4	0.93	5.09	0.0284	0.0203	0.0277	0.0020	0.0146	0.0044	0.0111	0.16	0.09	1.8	1.2	nil
DP no. 9																				
DP no. 10	17.1	44.8	0.60	0.90	0.38	3.2	1.3	5.09	0.1470	0.1050	0.0645	0.0135	0.0120	0.0143	0.0082	0.37	0.24	3.1	2.3	0.01
DP no. 11	18.8	47.9	0.85	0.83	0.32	1.11	0.04	3.60	0.0069	0.0149	0.0082	0.0016	0.0187	0.0015	0.0351	0.04	0.05	3.4	2.3	0.01
DP no. 12	17.2	46.5	1.14	0.95	0.46	1.86	0.78	4.49	0.0068	0.0128	0.0084	0.0006	0.0152	0.0020	0.0285	0.26	0.15	3.4	2.7	0.21
DP no. 13	16.4	46.5	1.9	0.89	0.45	1.67	0.56	4.19	0.0110	0.0130	0.0092	0.0005	0.0083	0.0025	0.0357	0.20	0.13	3.6	2.7	0.46
DP no. 14	17.9	46.2	1.19	0.85	0.46	2.6	0.58	3.89	0.0090	0.0135	0.0100	0.0010	0.0217	0.0014	0.0295	0.20	0.16		1.9	0.27
DP no. 15	18.1	46.8	0.89	0.30	0.58	2.3	0.99	3.90	0.0497	0.0038	0.0220	0.0056	0.0103	0.0028	0.0068	0.21	0.14	1.5	1.1	0.58

Table II. Component Analysis (Weight Percent) of Compounds in 18–46–0 Fertilizers

compound	DP no. 1	DP no. 2	DP no. 3	DP no. 4	DP no. 5	DP no. 6	DP no. 7	DP no. 8 and 9	DP no. 10	DP no. 11	DP no. 12	DP no. 13	DP no. 14	DP no. 15
Ca₄SiAlSO₄F₁₃·12H₂O	0.24	0.21	0.26	0.53	0.20	0.45	0.10	1.67	0.47	0.07	1.06	0.53	0.078	0.17
CaF₂														1.14
ZnNH₄PO₄	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.08	0.40	0.02	0.02	0.03	0.025	0.14
CdNH₄PO₄	0.001	0.001	0.001	0.0004	0.001	0.001	0.001	0.004	0.03	0.003	0.001	0.001	0.002	0.01
UO₂NH₄PO₄	0.01	0.03	0.02	0.02	0.03	0.007	0.009	0.02	0.02	0.03	0.02	0.01	0.032	0.02
NiNH₄PO₄	0.006	0.006	0.006	0.007	0.006	0.006	0.003	0.01	0.04	0.004	0.006	0.007	0.004	0.01
MnNH₄PO₄	0.10	0.09	0.10	0.08	0.10	0.10	0.11	0.03	0.03	0.11	0.09	0.11	0.09	0.02
MgNH₄PO₄·H₂O	2.36	3.07	2.36	2.75	2.24	2.17	2.11	2.68	2.43	2.04	2.94	2.88	2.94	3.71
FeNH₄HPO₄F₂·xH₂O	0.73	3.36	1.90	0.65	1.61	0.82	2.86	1.20	2.23				3.54	3.31
AlNH₄HPO₄F₂·xH₂O	4.24	4.52	4.18	4.11	3.78	4.11	4.91	1.26	5.97	4.07	6.30	5.78	5.64	1.99
VNH₄HPO₄F₂·xH₂O	0.06	0.06	0.06	0.07	0.07	0.06	0.04	0.08	0.42	0.06	0.05	0.05	0.054	0.02
CrNH₄HPO₄F₂·xH₂O	0.03	0.03	0.03	0.03	0.03	0.03	0.04	0.11	0.25	0.03	0.03	0.04	0.039	0.09
FeNH₄(HPO₄)₂	5.22	2.46	3.35	5.71	3.74	5.12		0.74		4.18	5.61	9.35	1.18	
AlNH₄(HPO₄)₂										1.98				
Ca(NH₄)₃(HPO₄)₂·H₂O	1.14	2.57	2.43	1.29	1.86	1.64	2.08	4.15	5.08	0.20	3.93	3.15	4.02	2.59
(NH₄)₂SiF₆	0.12	1.16	0.71	0.49	0.51	0.33	1.40	0.50	1.20	0.33	0.23	0.39	1.16	0.97
(NH₄)₂SO₄	8.19	5.31	6.96	6.49	6.54	7.33	6.98	6.70	6.92	4.94	5.98	5.66	5.33	5.36
NH₄H₂PO₄	1.04		1.36		2.14	1.36		2.17				3.24		2.43
(NH₄)₂HPO₄	72.73	67.28	71.41	69.96	73.42	72.78	71.35	75.61	66.91	73.94	68.18	62.41	67.78	73.25
(NH₄)₃HPO₄		4.87		3.73			3.31			4.24			3.00	
NaH₂PO₄	0.26	0.78	0.52	0.57	0.47	0.37	0.47	0.89	1.93	0.21	1.36	1.04	1.04	1.10
KH₂PO₄	0.21	0.38	0.42	0.38	0.38	0.31	0.31	0.30	0.84	0.17	0.52	0.45	0.56	0.49
free H₂O	1.7	2.0	2.3	2.2	1.4	1.7	1.9	1.2	2.3	2.3	2.7	2.7	1.9	1.1
summation	98.41	98.21	98.40	99.09	98.55	98.71	98.01	99.40	97.47	98.93	99.03	97.83	98.41	97.92

Table III. Process Parameters in 18–46–0 Production

	sample							
	DP no. 1	DP no. 2	DP no. 3	DP no. 4	DP no. 5	DP no. 6	DP no. 8 and 9	DP no. 14
production rate, t/h	37.5	50	77	110	44	55	75	37
preneutralizer operation number used	2	1	1	1	1	1	1	1
size of each, ft × ft high	(1) 11 × 15,25; (2) 12 × 10	12 × 20	14.75 × 22	17 × 25	14 × 25.5	12 × 20	11 × 25	12 × 25
retention time, min	(1) 101; (2) 29	74	61	48	98	49	31	128
slurry depth in preneutralizer, ft	(1) 15.25; (2) 3.5	12	10	8.5	10	9	9	15
mole ratio N:P	(1) 1.15; (2) 1.55	1.46	1.5	1.48	1.65	1.6	1.5	1.4
temperature, °F	240	225	250	245	230	232	235	240
specific gravity	1.5	1.56	1.57	1.56	1.625	1.52	1.56	1.58
granulator product temperature, °F	185	204	205	205	175	197	210	210

1.67%, is carried over from the wet-process acid because of incomplete removal during the acid filtration step. When fluorine is in excess of that required by aluminum, iron, chromium, and vanadium, it can precipitate as CaF_2, provided that the soluble silica also has been satisfied. This condition has been observed for sample DP no. 15. The stable calcium salt in diammonium phosphate solution between pH 5.3 and pH 8.0 is $Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$, which was used for the calculations in Table II even though a direct observation of its presence was not possible at the concentrations shown in Table II (Frazier et al., 1964). This salt dissolves incongruently in water, and its reaction product, $Ca_5(PO_4)_3OH$, was detected in the water-insoluble fraction. Investigation at several phosphoric acid plants showed that some of the acids contain higher calcium contents than normally expected; two possible sources of this are as follows: (1) the phosphoric acid unit was operated at high extraction temperatures, which caused an unusually large amount of calcium to be dissolved in the product acid from the plant; (2) the amount of calcium as gypsum in the acid was high because of the type of filter used or poor maintenance of the filter.

Magnesium. Like calcium, the magnesium ammonium phosphate was too poorly crystallized to be observed directly in the fertilizer. Since the calcium and magnesium salts shown in Table II could not be identified directly, it is possible that these cations precipitate as other forms, such as fluorophosphates. Ando et al. (1968) state "Fluorine forms a previously unknown compound, $MgNH_4HFPO_4$(MAFP), when monoammonium phosphate made from wet-process phosphoric acid is treated with magnesium hydroxide above about 75 °C in the presence of moisture. When preparation of MAFP was conducted at 90 to 100 °C in the presence of a small amount of water using a mixture of monoammonium and diammonium phosphates, magnesium hydroxide reacted very slowly releasing ammonia; the product contained $MgNH_4PO_4 \cdot H_2O$ and less MAFP in the same manner as in the test with commercial ammonium phosphate, indicating that only a small part of the fluorine forms MAFP at high pH". These results indicate that $MgNH_4HFPO_4$ could precipitate in the preneutralizer (lower pH) and $MgNH_4PO_4 \cdot H_2O$ could be formed in the granulator where the pH is high. However, TVA laboratory tests indicate that fluorine is precipitated as $(Al,Fe)NH_4HPO_4F_2 \cdot xH_2O$ and CaF_2 before magnesium can react with fluorine. The compound $MgNH_4PO_4 \cdot H_2O$ should be the precipitating phase in the preneutralizer slurry and the granulator, which would not cause any production problems with high magnesium acids since the $MgNH_4PO_4 \cdot H_2O$ (5–10 μ) is well crystallized and would not contribute significantly to viscosity problems. This compound can lose ammonia and water during drying of the product to produce an amorphous material. If the magnesium concentration in the DAP-grade acid ($\sim 40\%$ P_2O_5) is too high to make grade 18–46–0, it can be removed effectively from the acid by adding byproduct H_2SiF_6 to precipitate $MgSiF_6$ to reduce the magnesium concentration to an acceptable level.

Iron and Aluminum. Previously the gelatinous materials from the ammoniation of wet-process phosphoric acid were described as amorphous iron and aluminum phosphate and assigned the formula $(Al,Fe)PO_4 \cdot nH_2O$. Chemical analyses of the water-insoluble components from commercial diammonium phosphate fertilizers show that the Fe and Al precipitate is much more complex than the $(Al,Fe)PO_4 \cdot nH_2O$ formula indicates.

Akiyama and Ando (1972) reported in their investigation that the main constituent of the gellike substance is a

Table IV. Citrate-Insoluble P_2O_5 in Commercial 18-46-0 Fertilizers as a Function of Retention Time in Preneutralizer

18-46-0 sample	retention time in preneutralizer, min	% $FeNH_4(HPO_4)_2 \cdot 0.5H_2O$ in 18-46-0	% citrate-insoluble P_2O_5 in 18-46-0	citrate-insoluble P_2O_5 as % of P_2O_5 in $FeNH_4(HPO_4)_2 \cdot 0.5H_2O$
DP no. 4	30	5.71	0.04	1.4
DP no. 8 and 9	31	0.74	nil	0.0
DP no. 6	49	5.12	0.10	3.8
DP no. 3	61	3.35	0.18	10.4
DP no. 2	74	2.46	0.32	25.2
DP no. 5	98	3.74	0.84	44.0
DP no. 14	128	1.18	0.27	44.3
pure $FeNH_4(HPO_4)_2$	150		22.4	45.9

compound having the composition of $(Al,Fe)NH_4HF_2PO_4$. This compound can be identified readily by X-ray powder diffraction techniques when sufficiently crystallized. It became apparent that the composition of $(Al,Fe)NH_4H$-F_2PO_4 was affected by the temperature and retention time during precipitation of the compound. This fact was confirmed by Pechkovskii et al. (1979), who state "The chemical analysis of the product showed a lower fluorine concentration in comparison with that calculated theoretically for the formula $AlNH_4HF_2PO_4$ in that the fluorine content was not constant for specimens obtained in different experiments, whereas the Al_2O_3 concentration varied within closer limits. This could be linked with a possible isomorphous replacement of a F^{1-} ion by an OH^{1-} ion in hydrothermal treatment". The compound was written as cryptocrystalline $(Al,Fe)NH_4HPO_4F_2 \cdot xH_2O$ to denote the variable chemical composition of the compound due to different temperatures and retention times encountered in 18-46-0 production (Table III). The Al end member of compound $(Al,Fe)NH_4HPO_4F_2 \cdot xH_2O$ precipitates first; the Fe end member precipitates if sufficient fluorine is present. For simplicity of calculations, the theoretical chemical composition of $(Al,Fe)NH_4HF_2PO_4$ was used instead of calculating the composition of the compound that would precipitate for each set of conditions (temperature and retention time).

Iron and aluminum also can precipitate as $(Fe,Al)N$-$H_4(HPO_4)_2$ when there is insufficient fluorine in the phosphoric acid to precipitate $(Al,Fe)NH_4HPO_4F_2 \cdot xH_2O$. The Fe end member of the compound $(Fe,Al)NH_4(HPO_4)_2$ precipitates first, with the Al end member precipitating next. When $(Fe,Al)NH_4(HPO_4)_2$ precipitates in the preneutralizer, it occurs as an amorphous gel which could contribute toward viscosity problems in the preneutralizer. This amorphous gel quickly dissipates with the temperature and retention times encountered in 18-46-0 production to produce large euhedral crystals of $(Fe,Al)NH_4(H$-$PO_4)_2$.

In the preneutralizer, conditions of slightly higher temperatures and longer retention times than normally encountered have resulted in citrate-insoluble phosphate. The citrate-insoluble phosphate problem in 18-46-0 fertilizer was found to be related to the $FeNH_4(HPO_4)_2$ but not always directly to its total quantity in the fertilizer (Hebbard, 1979). Microscopic observations showed that with increasing crystal size of the iron compound, the level of citrate-insoluble P_2O_5 also increased. To relate crystal size and citrate-insoluble P_2O_5, we chose three samples that differed widely in their reported content of citrate-insoluble P_2O_5 but had similar quantities of the iron ammonium phosphate.

The surface area of the three samples was determined on the water-insoluble fraction and compared to the citrate-insoluble P_2O_5 reported as percent of total P_2O_5 in the iron ammonium phosphate compound. These results (Figure 1) show a good correlation for surface area and citrate-insoluble P_2O_5 content. Reporting the citrate-in-
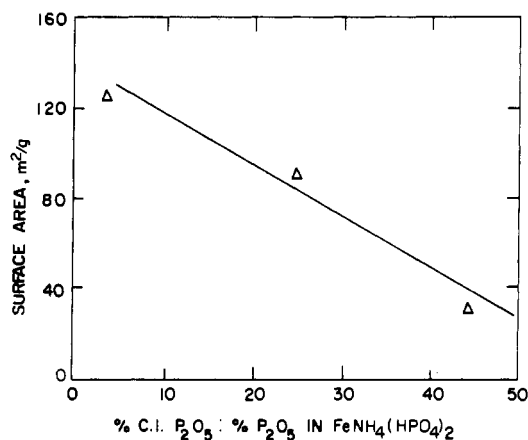

Figure 1. Effect of surface area on citrate-insoluble phosphate in 18-46-0 fertilizers.

soluble P_2O_5 as percent of total P_2O_5 present in the iron ammonium phosphate was necessary in order to compensate for the total quantity of this compound in the sample. For example, the weight percent citrate-insoluble P_2O_5 × 100 divided by the weight percent P_2O_5 reported as FeN-$H_4(HPO_4)_2$ provides an interaction term that relates the quantity of the citrate-insoluble compound to its effective solubility properties.

The citrate-insoluble fraction also was studied in a series of 18-46-0 fertilizers for which data for the retention time in the preneutralizer stage were available. These data are shown in Table IV. Again, the citrate-insoluble P_2O_5 was expressed as percent of total P_2O_5 in $FeNH_4(HPO_4)_2$. The pure sample of $FeNH_4(HPO_4)_2$ in Table IV was prepared in the laboratory under conditions similar to those encountered in commercial preneutralizers. These data show that crystal growth is complete after 100 min at 230-250 °F, where the citrate-insoluble P_2O_5 reaches a maximum of 45% of the P_2O_5 present as $FeNH_4(HPO_4)_2$. Thus, the citrate-insoluble P_2O_5 can be decreased by decreasing the total quantity of iron ammonium phosphate and by decreasing the retention time in the preneutralizer, which effectively decreases crystal size.

A detailed evaluation of the data in Tables I and II indicates that the quantity of the citrate-insoluble salt also can be decreased by maintaining a high fluorine content. This favors the formation of the more citrate-soluble iron fluorophosphate and also effectively releases a mole of H_3PO_4 for ammoniation to decrease the effect of iron on the nitrogen grade. There is no indication that the fluorophosphate compounds become a citrate-insoluble problem during normal retention times in the preneutralizer. For acids with insufficient fluorine contents, a very short preneutralizer period will be necessary to prevent crystal growth of the iron ammonium phosphate. Obviously, the preferable way to lower the retention time in the preneutralizer is to decrease the effective size of this tank. This can be accomplished by one of the following: (1) lower the depth of slurry in the existing preneutralizer, (2) install
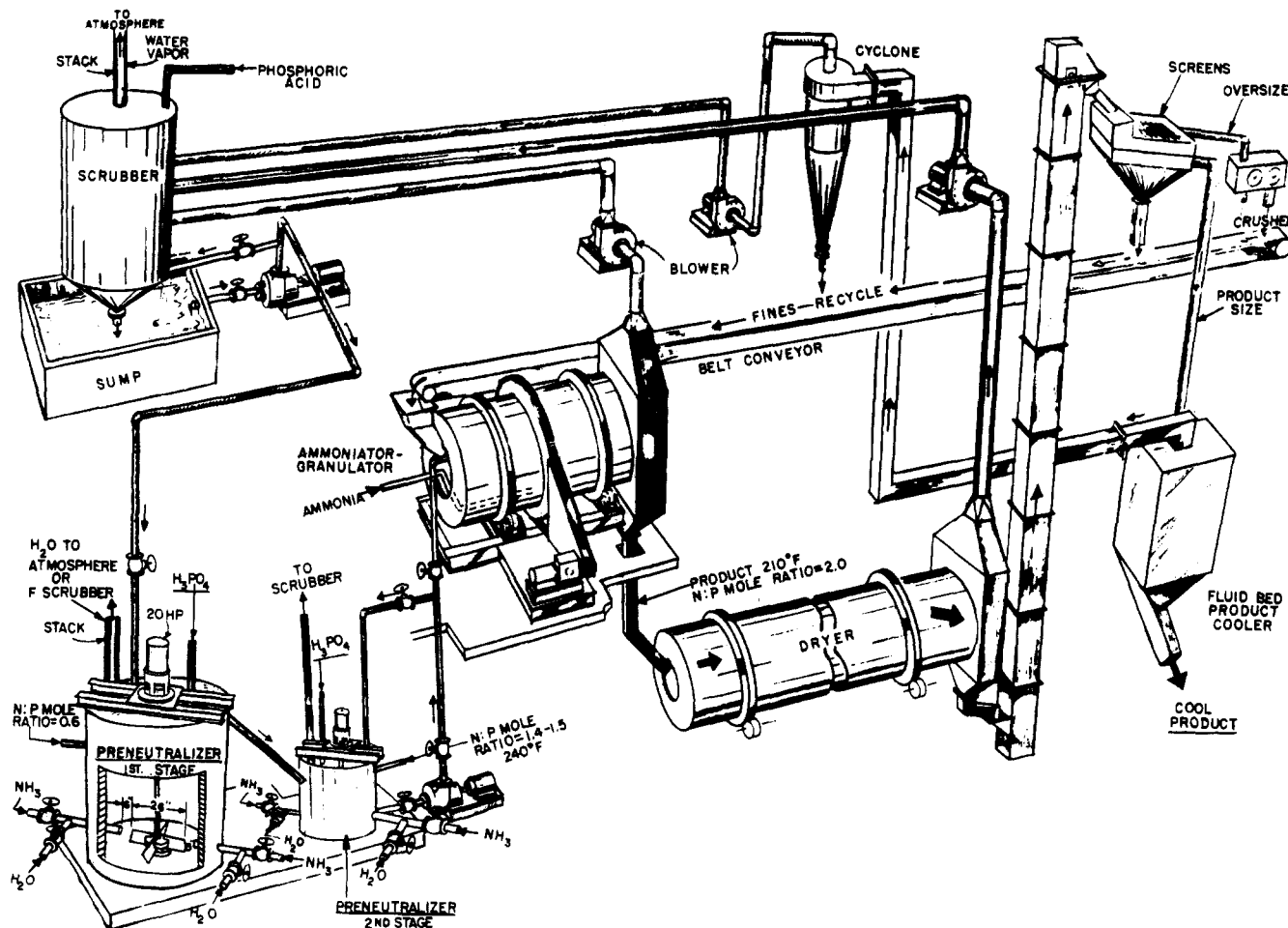
Figure 2. TVA process for production of granular diammonium phosphate.

a smaller preneutralizer, or (3) install a pipe-cross or pipe reactor.

Some producers fear that they will encounter high ammonia losses and low water evaporation from the preneutralizer if retention time is decreased. There is less heat loss from the tanks that have high retention time because of their large size. In the large tank there is less wall area per unit of slurry than in the smaller tanks. If these problems occur, it might be preferable to install two preneutralizers, as shown in the flow diagram (Figure 2). The first preneutralizer is relatively large and should be operated at a mole ratio N:P of 0.6. Microscopic and chemical analyses show that at this low degree of ammoniation there is no reversion of the P_2O_5 to an unavailable form. The exit gases from this preneutralizer may contain fluorine; however, they will not contain NH_3. Because of the low tank surface per unit of slurry in the first preneutralizer, there should be less heat loss and excellent evaporation efficiency. The degree of ammoniation in the second preneutralizer results in a slurry having a mole ratio N:P of 1.4–1.5. The citrate-insoluble $FeNH_4(HPO_4)_2$ forms at the higher degrees of ammoniation (Dillard et al., 1981). Since the retention time in this preneutralizer is low, the $FeNH_4(HPO_4)_2$ crystallizes as small crystals in which the P_2O_5 is available.

The total retention time for sample DP no. 1 (Table III) in two preneutralizers is relatively long (135 min); the retention in the second preneutralizer, in which the mole ratio N:P of the slurry is 1.45, is short (29 min). The citrate-insoluble P_2O_5 in this product was relatively low as compared with the citrate-insoluble P_2O_5 of some of the other products, which had relatively long slurry retention times in single preneutralizers. Data in Tables I and III

show that the temperature of the slurry from the preneutralizer or granulator seems to have little effect on the citrate-insoluble P_2O_5 of the product, provided that the product temperatures from the ammoniation units are less than 250 °F for the preneutralizers and 210 °F for the ammoniator–granulator. Additional data are needed to determine if there is an upper ammoniation temperature limit.

Excessive quantities of iron and aluminum can be decreased in the phosphoric acid by better clarification of the insoluble sludge components from merchant-grade acids. Iron and aluminum can be decreased to 0.2–0.3% Fe_2O_3 and 1.6–1.8% Al_2O_3 in wet-process acid containing 54% P_2O_5 by addition of a soluble source of potassium. This causes precipitation of $(Fe,Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$, which settles readily and permits decantation of the purified acid. The settled sludge fraction can be recovered in superphosphate or suspension fertilizer production where the high-impurity phosphate solid is not detrimental. The composition of the precipitating compound shows that addition of 0.1% K_2O to merchant-grade acid will decrease the Fe_2O_3 content of the acid by 0.50 percentage point and the Al_2O_3 by 0.32 percentage point.

Zinc, Cadmium, Nickel, Manganese, and Uranium. The divalent trace elements (Zn, Cd, Ni, and Mn) and the U^{6+} complex ion, UO_2^{2+}, most often precipitate as M^{2+}-NH_4PO_4 and were calculated as this anhydrous compound. Although each divalent trace element is relatively insignificant in quantity, their collective effect, particularly in western acids, is to neutralize a significant quantity of phosphoric acid as a low nitrogen content compound.

Chromium and Vanadium. Stability constants for complex ion formation of fluorine with chromium and
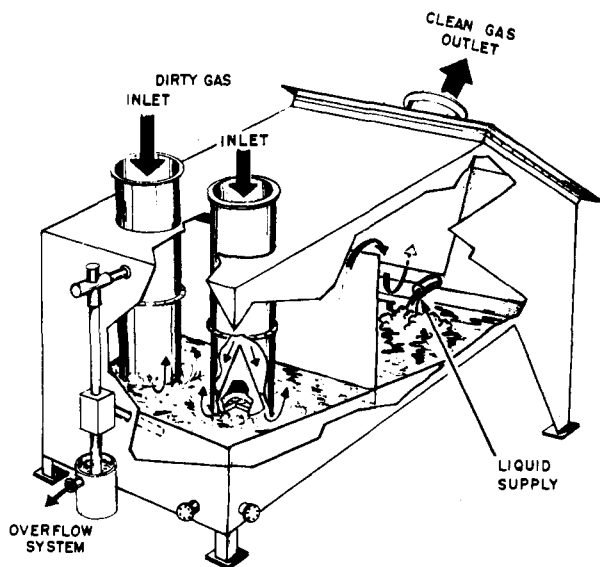
Precipitated Impurities in 18-46-0 Fertilizers

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Figure 3. Impingement-type scrubber.

Figure 4. Effect of cation impurities on nitrogen content of 18-46-0 fertilizers.

vanadium are similar to those for fluorine and iron. Therefore, these trivalent cations were calculated as the fluoride compounds. Further characterization work is necessary to accurately predict the correct composition of matter of the precipitating solids.

Silica. The silica content was associated with the water-soluble fluorine and was calculated as $(NH_4)_2SiF_6$. At first, the water-soluble fluorine was suspected to be $(NH_4)_3AlF_6$; however, the absence of a significant water-soluble aluminum component eliminated this possibility.

Sulfate. Only two sulfate-containing compounds have been detected, namely, $(NH_4)_2SO_4$ and $Ca_4SiAlSO_4F_{13}\cdot12H_2O$, which is an insoluble component carried over in the wet-process phosphoric acid. Phase studies indicate that the metal ammonium sulfates, $M(NH_4)_2(SO_4)_2\cdot xH_2O$, formed by divalent metals are possible solid components over a wide pH range. However, essentially all of these double sulfate compounds have a much higher solubility than the comparable metallic ammonium phosphate. Thus, $(NH_4)_2SO_4$ is the stable sulfate in equilibrium with the ammonium phosphates. Double salts comprising ammonium sulfate and phosphate exist only in the acid region below pH 1 and thus are not present in 18-46-0 fertilizers (Frazier et al., 1971).

Fluorine. Other than ammonia and phosphate, fluorine is the most widely distributed element in 18-46-0 fertilizers. Fluorine occurs as $Ca_4SiAlSO_4F_{13}\cdot12H_2O$, CaF_2, $(Al,Fe)NH_4HPO_4F_2\cdot xH_2O$, $(V,Cr)NH_4HPO_4F_2\cdot xH_2O$, and $(NH_4)_2SiF_6$. Precipitation of the complex metal ammonium fluorophosphates presents a potential method for converting residual fluorine derived from wet-process phosphoric acid to an insoluble form in the 18-46-0 grade product rather than scrubbing the fluorine by expensive pollution abatement processes. Some commercial 18-46-0 producers are using their ammonia scrubbers for fluorine scrubbing by operating at a low mole ratio of N:P, which is effectively the same as a preneutralizer slurry, only a little lower in pH. The producers report that the mole ratio N:P in the slurry from the scrubber is between 0.6 and 0.7. At this degree of ammoniation of the acid, most of the fluorine remains in the acid when using a Doyle impingement-type scrubber (Figure 3), and there is no difficulty with loss of fluorine from the process. Usually about one-third of the acid used in the process is added to the scrubbers, and the remaining acid is added directly to the preneutralizer. When all of the acid was added to the scrubbers and the mole ratio N:P was less than 0.6,
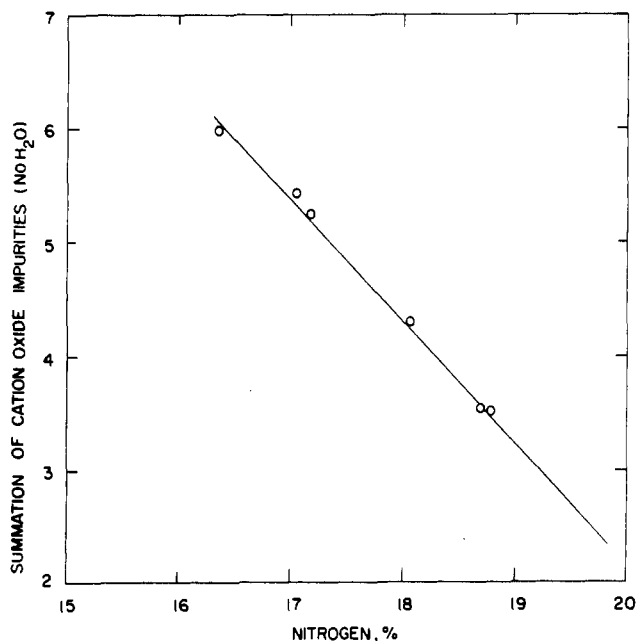
there was a significant loss of fluorine from the scrubbers. For this reason, the amount of acid added to the scrubbers was limited.

Phosphate. The N:P adjustment can be used to augment either the nitrogen or phosphate level in the 18-46-0 product at the expense of the other component by precipitating $NH_4H_2PO_4$ (low N; high P_2O_5) or $(NH_4)_3PO_4$ (high N; low P_2O_5). The precipitation of $(NH_4)_3PO_4$ was observed on a recent plant trip, confirming earlier microscopic findings. During operation of the ammoniator-granulator, it was observed that there were several lumps of material which had stuck to the ammonia spargers. When the material was broken down, it contained large quantities of ammonia. By addition of a small quantity of water with the ammonia, this caking around the sparger could be practically eliminated, resulting in less loss of ammonia from the ammoniator-granulator. Microscopic analyses show that some of the 18-46-0 products contained triammonium phosphate which was present in these lumps off the ammonia spargers in the ammoniator-granulator.

Water. Free water, which decreases both fertilizer components, is decreased by slightly higher temperatures and much longer retention times in the preneutralizer. Moisture can be decreased before complete ammoniation (first-stage preneutralizer) if the fluorine concentration is low or in the preneutralizer if the fluorine is sufficiently high to prevent the precipitation of $FeNH_4(HPO_4)_2$.

Grade Limitations. A few 18-46-0 products were selected from Table I to represent the range of impurities and nitrogen and phosphate values. The effect of these impurity levels on the fertilizer grade is shown in Figures 4 and 5, where the summation of metallic oxides is compared with the nitrogen values and the fluorine plus sulfate is compared with phosphate. For simplification of the nitrogen curve, only the major impurities of iron, aluminum, calcium, and magnesium oxides were used. The same effect was observed when all the metallic oxides were included. The data used in Figures 4 and 5 show that the fertilizer grade is affected to the extent that each percent increase of impurity oxide and fluorine plus sulfate will lower the grade level by 1%. When the average value for hydrated and free water is added to the other impurities, the total impurities are limited to 15% in order to maintain
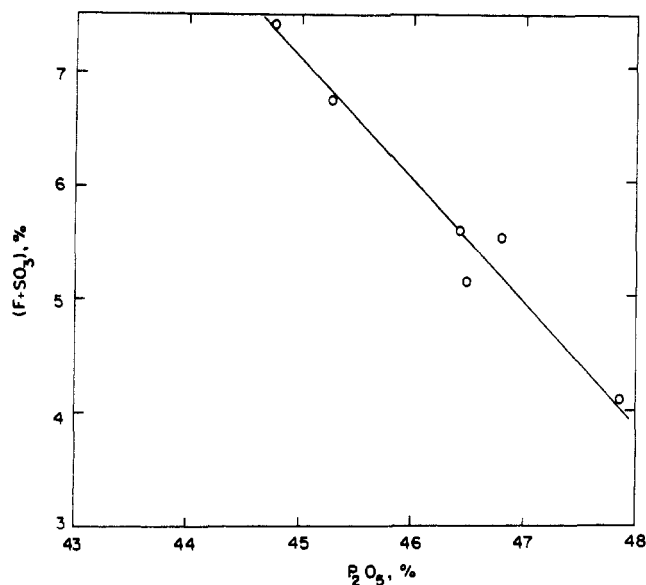
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Figure 5. Effect of anion impurities on phosphate content of 18-46-0 fertilizers.

an 18-46-0 grade. When the maximum level of impurities (15%) is present, the 18-46-0 process will require close pH control to compensate for the ratio of total cation to anion impurities by precipitating $NH_4H_2PO_4$ (low N; high P_2O_5) or $(NH_4)_3PO_4$ (high N; low P_2O_5). Above this maximum level (15%), purification processes will be required to maintain 18-46-0 grade.

In summary, this study identifies the main problems in meeting 18-46-0 grade specifications and suggests some possible solutions to these problems.

Calcium was the major cause of grade deficiency in the commercial samples which were investigated. Possible solutions to this problem are to maintain filter cloths in the phosphoric acid unit in good condition, operate the phosphoric acid unit at as low an acid temperature as is consistent with good operation of this unit, and partially clarify the acid before it is used.

In the production of 18-46-0, the amount of Fe_2O_3 and F in the acid affects the content of citrate-insoluble P_2O_5 in the product. If the weight ratio F:Fe_2O_3 in the product can be kept above 2.3:1, the citrate-insoluble P_2O_5 content of the product will be less than 0.1%. At lower weight ratios F:Fe_2O_3, it is advantageous to have lower retention

times in the preneutralizer and ammoniator–granulator when the mole ratio N:P is 1.4:1 or higher.

The mole ratio N:P in the slurry coming from the preneutralizer to the granulator must be above 1.4:1 to avoid nitrogen deficiencies. At lower ratios the product will contain some MAP; this causes nitrogen deficiency in the product.

The Mg and Al contents of the acids have less effect on grade deficiency than Ca and Fe.

To avoid highly viscous preneutralizer slurries when low preneutralizer retention times are used, ensure that there is sufficient fluorine available (weight ratio F:Fe_2O_3 > 2.0:1) to combine with the Fe_2O_3 to form cryptocrystalline Fe–NH_4–PO_4–F–H_2O instead of an $FeNH_4(HPO_4)_2$ gel. An alternative to this latter suggestion is to replace the preneutralizer with a TVA pipe reactor installed so that it discharges viscous slurry directly onto the bed of material in the granulator (Dillard et al., 1981).

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