

Clarification of Ammonium Polyphosphate Fertilizer Solutions

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Wet-process phosphoric acids contain metallic impurities—mostly magnesium, aluminum, and iron—that were dissolved in the acidulation of the parent phosphate rock. Ammonium polyphosphate fertilizer solutions prepared from these acids may deposit sludges of phosphates of the metallic impurities that interfere seriously with the mechanical handling of the liquids. Formation of the sludges

often can be prevented, however, by addition of fluorine as either fluoride or fluosilicate. The proper amount of fluorine is related to the amount of each of the metallic impurities present and to the fraction of the phosphate present as pyrophosphate. More highly condensed phosphates retard the formation of sludge, but their effect disappears when they hydrolyze to pyro- and orthophosphate.

Wet-process phosphoric acid is more economical than thermal-process acid as a source of phosphorus for ammonium polyphosphate fertilizer solutions. Wet-process acid, however, has the disadvantage that it usually contains considerable amounts of metallic impurities—mostly iron, aluminum, and magnesium—that may form precipitates in liquid fertilizers prepared from the acid that interfere seriously with mechanical handling of the fertilizers as fluids.

Superphosphoric acids are solutions of ortho-, pyro-, tri-poly-, and more highly condensed phosphoric acids. When it was observed that the mixed ammonium salts of the condensed phosphoric acids are more soluble in water than the ammonium orthophosphates (Farr and Williard, 1969; Hignett, 1968; Scott *et al.*, 1965), thermal-process superphosphoric acids were ammoniated to form concentrated fertilizer solutions, such as 11-37-0 (%N-%P₂O₅-K₂O). These solutions, however, were valued even more for their capacity to sequester the metallic impurities in 10-34-0 solutions prepared from wet-process acids (Scott *et al.*, 1965) than for their high concentration. Solutions of 10-34-0 or 11-37-0 grades prepared from thermal-process acid gave no trouble, but many of those prepared from wet-process acids that had been concentrated to about 70% P₂O₅ precipitated nuisance sludges, particularly after prolonged storage. Addition of relatively small amounts of ammoniated thermal-process superphosphoric acid lengthened the period during which the solution remained free of sludge. The fairly long period between the preparation of the fertilizer solution and the appearance of the sludge resulted in large measure from the sequestration of magnesium by tripoly- and more highly condensed phosphates; as these phosphates hydrolyzed to pyro- and orthophosphates, this sequestration capacity disappeared.

In another phase of the behavior of the impurities, some fertilizer solutions developed a gelatinous material that converted them into highly viscous, nonpourable masses with the peculiar property of increasing in viscosity on dilution with as much as an equal volume of water.

IDENTIFICATION OF SLUDGE COMPOUNDS

Fertilizer solutions prepared from wet-process acid are members of a complex multicomponent system comprising principally NH₃, MgO, Al₂O₃, Fe₂O₃, orthophosphate, polyphos-

phate, SO₃, F, and H₂O. The major sludge compounds are Al(NH₄)₂P₂O₇·OH·3H₂O, Mg(NH₄)₂P₂O₇·4H₂O, Mg(NH₄)₆-(P₂O₇)₂·6H₂O, Fe(NH₄)₂P₂O₇·2H₂O, and MgAl(NH₄)₆(P₂O₇)₂·F₂·6H₂O [erroneously identified previously as MgAl(NH₄)₆-H₂(PO₄)₄·6H₂O] (Frazier *et al.*, 1966). The amounts of the impurity metals in the initial solution usually determine the amount of sludge that can be formed, but the large amount of sludge in solutions containing the relatively small amounts of fluorine that remain after concentration of the acid is composed largely of MgAl(NH₄)₆(P₂O₇)₂·F₂·6H₂O in which Fe may replace as much as 5% of the Al. By establishing conditions that prevent its formation, most of the problems introduced by this sludge can be avoided.

In the course of this study it was observed that a water-soluble dimorph of MgAl(NH₄)₆(P₂O₇)₂·F₂·6H₂O formed in mixtures that contained unusually large amounts of magnesium and fluorine, whereas the usual troublesome sludge in ammonium polyphosphate solutions is the water-insoluble dimorph. The soluble dimorph is stable at higher concentrations of fluorine and magnesium and at lower temperatures than the insoluble dimorph. The compositions of these dimorphs and other new salts identified in the course of this study are shown in Table I, their X-ray diffraction patterns in Table II, their infrared absorption characteristics in Table III, and their optical properties in Table IV.

The aluminum pyrophosphate that precipitates in synthetic 10-34-0 solutions in which aluminum is the only impurity and with pH above 7 is the dihydrate Al(NH₄)₂P₂O₇·OH·2H₂O (Frazier *et al.*, 1966) rather than the trihydrate, which is stable in less concentrated solutions at pH 6. Aluminum precipitates at about pH 6 from similar 10-34-0 solutions containing 1.5% Al₂O₃ as very thin, length-fast needles of unknown composition with a very weak birefringence and a mean refractive index of about 1.515. When these solutions are diluted with 10% of their volume of water, the needles alter to pseudomorphs of the trihydrate with a length-slow orientation, increased birefringence, and a refractive index in the range 1.465 to 1.470. The pseudomorphs are insoluble in water and remain unchanged when washed with water and dried with acetone. The data in Tables II, III, and IV are for the trihydrate Al(NH₄)₂P₂O₇·OH·3H₂O, as shown by the chemical analysis in Table I. The trihydrate forms directly as small needle crystals from the more dilute solutions with grades of about 8-25-0.

A brief study of the solubility of ferric iron in the fertilizer solutions showed that four ferric ammonium pyrophosphates

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Table I. Composition of Solid Phases

	Composition, wt %						
	P ₂ O ₅	NH ₃	MgO	Al ₂ O ₃	Fe ₂ O ₃	F	H ₂ O, diff.
MgAl(NH ₄) ₃ (P ₂ O ₇) ₂ F ₂ ·6H ₂ O I	45.3	13.3	6.3	7.9		5.6	24.0
MgAl(NH ₄) ₃ (P ₂ O ₇) ₂ F ₂ ·6H ₂ O II	44.4	13.6	5.9	8.0		5.2	25.1
Stoichiometric	44.67	13.40	6.34	8.02		5.98	24.10
Fe(NH ₄) ₃ (P ₂ O ₇) ₂ ·4H ₂ O	49.7	14.8			13.2		22.3
Stoichiometric	50.16	15.04			14.11		20.69
Fe(NH ₄) ₃ (P ₂ O ₇) ₂ ·9H ₂ O	49.5	15.2			7.8		27.5
Stoichiometric	47.20	16.99			8.85		26.96
Fe(NH ₄) ₂ P ₂ O ₇ ·OH·2H ₂ O	41.9	10.1			22.7		25.3
Stoichiometric	44.50	10.67			25.07		19.71
Al(NH ₄) ₂ P ₂ O ₇ ·3H ₂ O	45.9	11.0		16.1			27.0
Stoichiometric	46.08	11.06		16.55			26.32

Table II. X-Ray Powder Diffraction Data^a

MgAl(NH ₄) ₃ (P ₂ O ₇) ₂ F ₂ ·6H ₂ O I, insoluble dimorph				MgAl(NH ₄) ₃ (P ₂ O ₇) ₂ F ₂ ·6H ₂ O II, soluble dimorph				Fe(NH ₄) ₃ (P ₂ O ₇) ₂ ·4H ₂ O					
d, Å	I/I ₀	d, Å	I/I ₀	d, Å	I/I ₀	d, Å	I/I ₀	d, Å	I/I ₀	d, Å	I/I ₀	d, Å	I/I ₀
14.78	3	2.932	7	12.33	100	3.493	15	14.51	7	4.287	15		
10.72	2	2.893	7	10.84	73	3.403	9	11.59	100	4.407	8		
8.75	100	2.787	7	9.70	46	3.072	40	10.41	52	4.125	8		
8.20	2	2.744	4	9.43	46	3.035	40	8.85	16	3.974	9		
7.42	65	2.699	5	9.16	20	3.015	15	8.64	18	3.877	8		
7.01	3	2.679	5	8.58	9	2.973	9	8.01	51	3.816	8		
6.47	2	2.639	3	8.38	21	2.953	9	7.76	10	3.740	11		
6.19	3	2.569	3	7.59	29	2.930	40	7.28	17	3.501	10		
6.09	8	2.521	1	7.20	16	2.903	9	7.01	69	3.453	22		
5.498	72	2.458	5 ^b	6.92	29	2.885	40	6.86	47	3.423	8		
5.022	4	2.375	6	6.73	48	2.817	15	6.62	6	3.375	21		
4.479	3	2.331	4	6.49	16	2.787	24	6.52	5	3.336	9		
4.274	7	2.272	4	6.17	55	2.737	9	6.29	23	3.295	14		
4.112	3	2.132	2	5.95	85	2.723	9	5.883	5	3.255	19		
3.627	6	2.110	3	5.73	42	2.695	9	5.772	10	3.202	9		
3.572	3	1.973	4 ^b	5.62	16	2.666	17	5.557	8	3.151	23		
3.545	17	1.954	2	5.44	17	2.565	10	5.502	10	3.111	12		
3.472	2	1.844	1	5.38	10	2.471	10	5.448	12	3.074	13		
3.230	8	1.830	<1	5.18	16	2.325	10	5.402	12	3.032	16		
3.191	13	1.816	1	5.11	10	2.057	25	5.240	21	3.003	33		
3.132	27	1.771	1	4.93	6	2.003	18	5.176	24	2.814	14		
2.954	30			4.82	61	1.983	10	5.068	21	2.759	10		
				4.580	25	1.913	5	4.940	16	2.730	14		
				3.965	15	1.837	5	4.856	9	2.666	11		
				3.958	18	1.770	5	4.713	22	2.640	9		
				3.873	20	1.738	5	4.683	15	2.593	9		
				3.729	18	1.684	15	4.433	5	2.362	7		
				3.654	21	1.635	12						
				3.614	10	1.437	15						
				3.532	15								
Fe(NH₄)₃(P₂O₇)₂·9H₂O^b				(Fe,Al)(NH₄)₂P₂O₇·OH·3H₂O				Fe(NH₄)₂P₂O₇·OH·2H₂O					
15.2	100	2.89	23	16.4	54	2.819	35	9.80	90	2.922	45		
8.76	95	2.84	15	9.46	48	2.721 ^b	17	9.16	23	2.889	30		
7.60	28	2.80	24	8.22	100	2.623	5	7.71	100	2.724	7		
5.71	39	2.76	8	5.64	68	2.398	2	7.50	60	2.616	13		
5.36	33	2.71	14	4.72	16	2.344 ^b	8	7.05	6	2.565	11		
5.07	52	2.55	12	4.64	36	2.238	8	5.79	61	2.544	13		
4.19	23	2.47	5	4.54	21	2.219	5	5.22	28	2.495	13		
4.14	13	2.45	7	3.57	12	2.070 ^b	5	5.13	25	2.419	8		
4.03	51	2.39	16	3.51	13	1.983	10	4.15	5	2.344	7		
3.79	75	2.30	9	3.31	34	1.921	2	3.745	12	2.174	10		
3.68	15	2.27	14	3.28	20	1.879	5	3.645	14	2.154	10		
3.45	13	2.20	21	3.185	13	1.751	6	3.597	16	2.095	12		
3.38	72	2.10	6	3.053	31	1.634	3	3.517	12	2.005	12		
3.29	56	2.09	7	2.949	14	1.590	5	3.396	8	1.975	10		
3.22	30	1.92	10	2.874	33			3.275	14	1.877	8		
3.20	41	1.88	4					3.084	24	1.817	8		
3.14	19	1.63	4					2.959	16				
3.05	18	1.56	9										
3.02	11												

^a Data obtained with X-ray diffractometer at 0.25° 20/min with Cu Kα radiation (1.54178 Å). Intensities measured as peak heights above background and expressed as percent of strongest line. ^b Powder data obtained from wet, undried crystals with a lacquer coating. Clean and dried crystals decompose slowly in several steps and approach Fe(NH₄)₃H₃(P₂O₇)₃·3H₂O in composition.

Table III. Infrared Absorption Bands

MgAl(NH ₄) ₅ (P ₂ O ₇) ₂ F ₂ ·6H ₂ O I (insoluble dimorph)		MgAl(NH ₄) ₅ (P ₂ O ₇) ₂ F ₂ ·6H ₂ O II (soluble dimorph)		Fe(NH ₄) ₅ (P ₂ O ₇) ₂ ·4H ₂ O		Fe(NH ₄) ₅ (P ₂ O ₇) ₃ ·9H ₂ O	
cm ⁻¹	I ^a	cm ⁻¹	I ^a	cm ⁻¹	I ^a	cm ⁻¹	I ^a
3430	M	3420	M	3400	sh	3200	S, b
3190	S	3190	S	3170	M, b	2800	sh
3044	M	3040	S	2820	sh	1430	sh
2860	sh	2850	sh	1435	M	1393	M
1650	W, b	1610	W ^b	1400	M	1140	S
1585	W			1129	S	1067	S
1434	M	1430	M	1063	S	1017	M
		1395	M	1024	S	890	M
1163	S	1154	S	890	M	732	W
1080	S	1090	S	768	W	580	M
1024	S	1019	S	731	W	523	M
897	S	883	S	579	M		
750	W	749	W	512			
610	M	600	M				
570	M	545	M				
508	M	471	M				
460	W	400	W				
Fe(NH ₄) ₂ P ₂ O ₇ ·OH·2H ₂ O		Fe(NH ₄) ₂ P ₂ O ₇ ·OH·3H ₂ O		Al(NH ₄) ₂ P ₂ O ₇ ·OH·3H ₂ O		MgNH ₄ P ₂ O ₇ ·F·H ₂ O gel	
3420	M, b	3420	sh	3420	M, b	3420	M, b
3160	S, b	3130	S, b	3165	S, b	3160	S, b
1620	W	1600	W, b	1620	W	1620	W, b
1440	sh	1394	S	1455	sh	1430	sh
1397	M	1154	S	1394	M	1395	M
1157	S	1138	S	1169	S	1150	S
1059	S	1030	S	1100	S, b	1100	S
1025	S	892	M	1037	S	1040	M
992	sh	745	W	902	M	910	S
908	M	570	M	762	W	719	W
754	W	480	W	582	M	590	sh
624	W			520	W	537	M
580	M			488	W	520	M
487	M					420	W

^a S = strong; M = medium; W = weak; b = broad; sh = shoulder.

Table IV. Optical Properties

Compound	Crystal system, class, habit	Refractive indices	Optical properties ^a
MgAl(NH ₄) ₅ (P ₂ O ₇) ₂ F ₂ ·6H ₂ O II	Orthorhombic, <i>mmm</i> . Second-order rods elongated along <i>Z</i>	$N_{\alpha} = 1.470$ $N_{\beta} = 1.472$ $N_{\gamma} = 1.474$	Biaxial (-). $2V = 70^{\circ}$ (80°). $d = 1.74$
Fe(NH ₄) ₅ (P ₂ O ₇) ₂ ·4H ₂ O	Monoclinic, <i>2/m</i> . Small plates tabular on (100) or (001)	$N_{\alpha} = 1.524$ $N_{\beta} = 1.531$ $N_{\gamma} = 1.540$	Biaxial (+). $2V = (84^{\circ})$. $OAP \perp (010)$, $X = b$. $d = 1.79$
Fe(NH ₄) ₅ (P ₂ O ₇) ₃ ·9H ₂ O	Orthorhombic, <i>mmm</i> . First-order plate crystals tabular on <i>X-Z</i> plane and elongated along <i>X</i>	$N_{\alpha} = 1.481$ $N_{\beta} = 1.482$ $N_{\gamma} = 1.490$	Biaxial (+). $2V = (40^{\circ})$. $d = 1.66$
Fe(NH ₄) ₂ P ₂ O ₇ ·OH·2H ₂ O	Orthorhombic, <i>mmm</i> . Blades elongated along <i>Z</i> and tabular on <i>X-Z</i> plane	$N_{\alpha} = 1.520$ $N_{\beta} = 1.535$ $N_{\gamma} = 1.590$	Biaxial (+). $2V = (66^{\circ})$. $OAP =$ tabular plane. $d = 1.88$
Fe(NH ₄) ₂ P ₂ O ₇ ·OH·3H ₂ O	Orthorhombic, thin needles elongated along <i>Z</i>	$N_{\alpha} = 1.502$ $N_{\beta} = 1.510$ $N_{\gamma} = 1.551$	Biaxial (+). $2V = (48^{\circ})$ $d = 1.77$
Al(NH ₄) ₂ P ₂ O ₇ ·OH·3H ₂ O	Orthorhombic, thin needles elongated along <i>Z</i>	$N_{\alpha} = 1.465$ $N_{\gamma} = 1.470$	$d = 1.70$

^a Values for $2V$ in parentheses are calcd. All values for densities calculated by Gladstone-Dale equation (Larsen and Berman, 1934).

exist in the pH range 5 to 9. These salts were prepared by treating with H₂O₂ a thick slurry of the ferrous salt Fe(NH₄)₂P₂O₇·H₂O in a saturated solution of (NH₄)₃HP₂O₇. At pH 6 the solid phase was Fe(NH₄)₅(P₂O₇)₂·4H₂O, at pH 7 it was Fe(NH₄)₅(P₂O₇)₃·9H₂O, and at pH 8.5 both the di- and trihydrates of Fe(NH₄)₂P₂O₇·OH·*n*H₂O appeared. These may not be the equilibrium solid phases, however, because the viscous solutions in which they were found had been equilibrated for only 1 week. Study of the iron ammonium pyrophosphate system is being continued.

Fe(NH₄)₅(P₂O₇)₂·4H₂O is very stable when washed with a mixture of 80 parts of methanol and 20 parts of water and then dried with acetone. When washed and dried in the same manner, Fe(NH₄)₅(P₂O₇)₃·9H₂O loses water and ammonia on subsequent exposure to the atmosphere, and the composition of the residue approaches that of Fe(NH₄)₆H₃(P₂O₇)₃·3H₂O. Fe(NH₄)₅(P₂O₇)₃·9H₂O dissolves incongruently in water with precipitation of Fe(NH₄)₅(P₂O₇)₂·4H₂O. Both the di- and trihydrates of Fe(NH₄)₂P₂O₇·OH·*n*H₂O have aluminum analogs with which the respective iron salts form isomorphous

series (Frazier *et al.*, 1966). As indicated by the formula for the single entry in Table II, the X-ray powder patterns of the iron and aluminum analogs of the trihydrate are identical, but the pattern of the iron dihydrate, shown separately in Table II, is shifted significantly from that of its aluminum analog (Frazier *et al.*, 1966). The dihydrate of the iron salt has been identified as a product of the reaction of ammonium pyrophosphate solution with soil minerals (Philen and Lehr, 1967).

Divalent iron and manganese in these fertilizer solutions are not sequestered by pyrophosphate, and the isomorphous salt $(\text{Fe,Mn})(\text{NH}_4,\text{K})_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (Frazier *et al.*, 1966) precipitates almost quantitatively when either or both of these cations are present. Ferrous iron is a rather common but minor impurity, and in 10-34-0 solutions it can be converted easily to less troublesome ferric iron by oxidation with small amounts of hydrogen peroxide. Divalent manganese is not a significant impurity in phosphate rocks and it is encountered in precipitates in ammonium polyphosphate liquid fertilizers only when it has been added as a micronutrient.

Ferrous iron may be present in solutions prepared from calcined phosphate rock, but its presence may be avoided if the rock is calcined in an excess of air. Alternatively, the iron may be oxidized to the ferric state by adding small amounts of ammonium nitrate or nitric acid to the hot wet-process acid before ammoniation. In studies on a commercial acid made from calcined rock, addition of 0.25% NH_4NO_3 to the hot (140° C) partially neutralized acid containing 0.5% ferrous iron oxidized the iron and prevented the formation of $\text{Fe}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ which otherwise would have precipitated as a significant sludge fraction in 10-34-0 solutions prepared from the untreated acid. Although ferrous iron is sequestered by the tripolyphosphate in ammonium and potassium polyphosphate fertilizer solutions, this effect is temporary and the ferrous iron is precipitated when the tripolyphosphate is hydrolyzed to pyro- and orthophosphate.

The gels that form in solutions relatively high in magnesium (0.4-0.6% MgO) and with intermediate fluorine contents (0.1-0.3% F) are so variable in composition that they have no measurable constants and so cannot be completely characterized, but typical compositions of washed and dried gels are shown in Table V. The gels were washed with large volumes of water in an ultrasonic cleaning bath and allowed to dry in the laboratory atmosphere for 10 to 14 days. The gels did not change in appearance during the washing, but on drying they shrank markedly to glassy amorphous materials with refractive indices in the range 1.44 to 1.51. They have a fairly distinctive infrared spectrum, however, as shown in Table III.

SEQUESTRATION BY POLYPHOSPHATE

Aluminum and ferric iron are more readily sequestered by pyrophosphate than magnesium, and the primary sludge compound in fertilizer solutions that contain little fluorine is usually the magnesium pyrophosphate $\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ (Frazier *et al.*, 1966). This compound precipitates from solutions that contain more than 0.15% MgO, and the precipitate appears when the higher polyphosphates have hydrolyzed almost completely to pyro- and orthophosphate.

The precipitation of this magnesium sludge from ammoniated wet-process superphosphoric acids can be prevented, or at least delayed, by adding to the fertilizer solution a small amount of a high-polyphosphate fertilizer solution prepared from electric furnace superphosphoric acid (Farr and Walters, 1970). This treatment both adds tripolyphosphate and decreases, by dilution, the concentration of MgO in the ferti-

Table V. Compositions of Washed and Dried Gels

Composition, wt %							
P_2O_5		NH_3	MgO	Al_2O_3	Fe_2O_3	F	H_2O diff.
Total	Ortho ^a						
39.7	3.6	6.8	10.0	4.3	...	3.7	37.1
40.6	0.4	5.2	11.2	7.2	3.7	8.3	27.3
44.8	12.3	7.6	3.9	10.9	3.3	4.2	27.1

^a P_2O_5 present as orthophosphate.

lizer solution, thereby delaying the precipitation and decreasing the relative amount of sludge. Further development of electric furnace acid technology has produced 11-37-0 and 12-44-0 solutions in which about 80% of the phosphate is present as polyphosphate, and small amounts of these solutions are highly effective in minimizing the formation of sludge in fertilizer solutions produced from wet-process acid. Both wet-process superphosphoric acids and electric furnace 12-44-0 solutions, however, require the expenditure of considerable amounts of energy in their production, and less expensive methods of producing satisfactory fertilizer solutions are being sought.

Much of the expense of concentrating merchant grade (54% P_2O_5) wet process acid to superphosphoric acid (70% P_2O_5) can be avoided by ammoniating merchant grade acid by the direct ammonium polyphosphate process in which the solution is concentrated by the heat of ammoniation (Getsinger, 1968). Addition of a small amount of external heat (Meline *et al.*, 1970) produces a solution in which as much as 50% of the phosphate is present as polyphosphate. In another approach, 10-34-0 fertilizer solutions are prepared at lower cost by adding ammoniated high-polyphosphate superphosphoric acids (80% P_2O_5) to ammoniated merchant grade wet process acids.

In still another approach, some producers are lowering the cost of their fertilizer solutions by using small amounts of aluminum pickling liquors as an inexpensive phosphate source. These liquors contain about 3% Al_2O_3 and 20 to 22% P_2O_5 ; they are concentrated to about 54% P_2O_5 and added to other solutions in relatively small amounts that raise the aluminum content no higher than to about 1.5% Al_2O_3 in the final fertilizer solution. The aluminum is expected to be sequestered by the polyphosphate in the solution.

SEQUESTRATION BY FLUORINE

The fertilizer solutions containing these less expensive phosphate sources are satisfactory if they are applied in the field soon after they are prepared. When these solutions are stored, however, sludges form more rapidly than in solutions prepared from wet process superphosphoric acids alone, and the sludges are both larger in amount and more difficult to handle. Thus, instead of a small amount of $\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ as the precipitating phase, large amounts of slow-settling needle crystals of $\text{MgAl}(\text{NH}_4)_3(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$ are deposited.

Results of earlier studies showed that these badly sludged or gelled solutions can be made pourable by lowering the pH to 3 or 4 by addition of wet-process phosphoric acid. This method is inconvenient, however, and a more practical solution of the sludge problem was sought.

Three impurities—Mg, Al, and F—are the major components of this sludge phase, and the effects of these impurities were explored in a factorial arrangement of tests. Simulated

Table VI. Precipitation of Impurities From Simulated 10-34-0 Solutions (50% of P₂O₅ Present as Pyrophosphate)

No.	Initial concn, wt %, of soln			Precipitate, g/100 g soln ^a			Final concn, wt %, of soln ^b		
	F	MgO	Al ₂ O ₃	MgAl(NH ₄) ₅ (P ₂ O ₇) ₂ F ₂ ·6H ₂ O	Mg(NH ₄) ₂ P ₂ O ₇ ·4H ₂ O	(NH ₄) ₃ AlF ₆	F	MgO	Al ₂ O ₃
1	0.0	0.1	0.2	0.0	0.0	0.0	0.0	0.1	0.2
2	0.0	0.1	0.8	0.0	0.0	0.0	0.0	0.1	0.8
3	0.0	0.3	0.4	0.0	0.1	0.0	0.0	0.3	0.4
4	0.0	0.5	0.2	0.0	2.5	0.0	0.0	0.17	0.2
5	0.0	0.5	0.8	0.0	2.5	0.0	0.0	0.17	0.8
6	0.2	0.1	0.4	1.42	0.0	0.0	0.12	0.01	0.29
7	0.2	0.3	0.2	1.51	0.0	0.0	0.11	0.21	0.08
8	0.2	0.3	0.4	3.42	0.0	0.0	0.0	0.08	0.13
9	0.2	0.3	0.8	3.82	0.0	0.0	0.0	0.06	0.5
10	0.2	0.5	0.4	1.73 ^c	1.73 ^c	0.0	0.10	0.16	0.26
11	1.0	0.1	0.2	Nil ^c	0.8 ^c	0.8 ^c	0.53	0.0	0.0
12	1.0	0.1	0.8	1.57	0.0	1.5 ^c	0.04	0.0	0.28
13	1.0	0.3	0.4	0.0	0.0	1.00	0.42	0.3	0.14
14	1.0	0.5	0.2	Nil ^c	0.0	0.1 ^c	0.94	0.5	0.17
15	1.0	0.5	0.8	0.0	0.0	1.00	0.42	0.5	0.54

^a After standing 20 days at 25° C. ^b Estimated from initial concentration and amount of precipitate. ^c Estimated by microscopic examination.

fertilizer solutions with grade 11-37-0, pH 6.2, and 50% of the phosphate present as ortho- and 50% as pyrophosphate were prepared from reagent chemicals and ammonium pyrophosphate that had been recrystallized from a pilot plant product. The mixtures were equilibrated at room temperature for 20 days with frequent agitation, after which the solid phases were filtered off, washed with water, dried, and weighed. Water-soluble (NH₄)₃AlF₆ was present as very small crystals from which all the mother liquor could not be removed; the amount of this material was estimated to be half the weight of the wet solids. The amounts of the precipitated solids and the calculated compositions of the supernatant liquor are shown in Table VI.

Small changes in composition of the solutions caused marked changes in the amounts and composition of the precipitates. In solutions containing small amounts of both fluorine and tripolyphosphate, such as 10-34-0 solutions prepared from wet process superphosphoric acids, the MgO concentration that could be tolerated without precipitation was 0.2 to 0.3% (entry 3). In solutions prepared from reagent chemicals in which fluorine was the limiting component (entries 8 and 9), precipitation of MgAl(NH₄)₅(P₂O₇)₂F₂·6H₂O removed practically all the fluorine from solution; when aluminum (entry 7) or magnesium (entry 6) was the limiting component, the limiting metal also was precipitated almost completely. In the presence of a relatively large amount of fluorine, aluminum precipitated first as (NH₄)₃AlF₆; if all the aluminum was precipitated as this salt, magnesium then precipitated as Mg(NH₄)₂P₂O₇·4H₂O, as in entry 11. When the amounts of both fluorine and aluminum were markedly larger than that of magnesium, as in entry 12, both (NH₄)₃AlF₆ and MgAl(NH₄)₅(P₂O₇)₂F₂·6H₂O were precipitated, and the magnesium was completely precipitated. These conditions, however, were established in simulated fertilizer solutions and probably would not be encountered in commercial solutions. Precipitation of magnesium can be prevented by a small amount of fluorine, as shown by entries 13, 14, and 15; with an excess of fluorine above that required to maintain the magnesium in solution, the fine-grained, water-soluble (NH₄)₃AlF₆ (entries 13 and 15) was precipitated.

In other tests it was observed that, as fluorine was added to a low-fluorine 10-34-0 fertilizer solution prepared from wet-process acid, an increasing amount of the water-insoluble dimorph, MgAl(NH₄)₅(P₂O₇)₂F₂·6H₂O I was formed until the

mixture had the appearance of a suspension instead of a solution, after which a very small increase in fluorine content produced a clear liquid that contained almost no solid phase. Further addition of fluorine then caused a slight precipitation of water-soluble (NH₄)₃AlF₆ as very small, slow-settling crystals, and sometimes small amounts of the water-soluble dimorph MgAl(NH₄)₅(P₂O₇)₂F₂·6H₂O II or the soluble magnesium salt Mg(NH₄)₂(P₂O₇)₂·6H₂O. At any combination of the usual MgO and Al₂O₃ contents in merchant grade acids, a very small amount of fluorine causes the abrupt change from a suspension to a clear solution. To determine the amount of fluorine required to sequester the impurities in a liquid fertilizer, a second series of solutions was prepared from reagent chemicals and allowed to stand at room temperature with occasional manual agitation. After about 20 days, when equilibrium appeared to be established, the mixtures were allowed to settle and the supernatant liquids were analyzed. The results are shown in Table VII.

As part of the same series, increasing amounts of fluorine were added to portions of several commercial fertilizer solutions and the mixtures were seeded with MgAl(NH₄)₅(P₂O₇)₂F₂·6H₂O and allowed to stand at room temperature for 4 months with occasional manual agitation. The mixture from each solution that formed a clear solution with the smallest amount of fluorine was analyzed as representative of a well-sequestered solution; the results are shown in Table VII. When these sequestered solutions were stored at 4° C for 6 weeks there was no significant precipitation of the impurity components, but there were a few crystals of (NH₄)₂HPO₄ in some of the samples.

To express the amount of fluorine in a liquid fertilizer in relation to its effect on the major cation impurities, the expression

$$SR = F / (MgO + 2.5 Al_2O_3 + 0.33 Fe_2O_3) \quad (1)$$

was derived empirically from the data in Table VII. In this expression, *SR* is termed the "sequestration ratio," and the chemical formulas represent concentrations in weight units of the indicated components. The proper value of *SR*, then, is that which provides a clear, stable solution.

As shown by entries 21 to 24 in Table VII, increase in the pyrophosphate content increases the value of *SR* that is required for sequestration of the impurities. This effect, which is shown in Figure 1, is to be expected, because all the precipi-

Table VII. Compositions of 10-34-0 Fertilizer Solutions Sequestered by Fluorine

No.	pH	Pyro-, % of total phos- phate ^a	Compn, % of liquid phase					F	Wt ratio MgO:Al ₂ O ₃	SR ^b	Solid phase ^c
			P ₂ O ₅	MgO	Al ₂ O ₃	Fe ₂ O ₃					
Solutions prepared from reagent chemicals ^d											
21	6.0	10	34.0	0.70	0.40	0.5	0.25	1.75	0.13	None	
22	6.0	30	37.0	0.51	0.70	0.0	0.90	0.73	0.40	N ₃ Al	
23	6.0	50	37.1	0.51	0.46	0.0	0.78	1.11	0.47	N ₃ Al	
24	6.0	70	34.5	0.90	0.90	0.0	1.53	1.00	0.49	N ₃ Al + MgAl I	
25	5.5	50	34.2	1.70	1.80	0.0	2.5	0.94	0.40	MgAl II	
26	6.0	50	35.6	1.45	1.50	0.0	2.1	0.97	0.40	MgAl II	
27	6.5	50	31.6	0.55	0.56	0.0	0.82	0.98	0.42	MgAl II	
28	6.0	50	35.6	1.45	1.50	0.0	2.1	0.97	0.40	MgAl II	
29 ^e	6.0	50	38.8	1.75	1.80	0.0	2.3 ^e	0.97	0.37	MgAl II	
30	6.0	50	32.6	1.80	1.45	0.0	2.4	1.24	0.44	N ₃ Al + MgAl II	
31	6.0	50	35.0	1.50	1.00	0.0	2.9	1.50	0.73	MgN ₆	
32	6.0	70	32.6	1.37	0.77	0.0	3.3	1.78	1.00	N ₃ Al	
33	6.0	50	37.3	0.52	0.27	0.0	1.3	1.93	1.08	MgN ₆ + N ₃ Al	
34	6.0	50	30.2	1.08	0.36	0.0	2.6	3.00	1.31	N ₃ Al	
35	6.0	50	35.4	1.60	0.45	0.0	3.6	3.56	1.32	MgN ₆ + N ₃ Al + MgAl II	
Commercial solutions											
41	6.0	44	33.6	0.40	0.80	0.40	1.10	0.50	0.43	None	
42	6.0	46	34.3	0.46	0.71	0.81	1.10	0.65	0.44	None	
43	6.0	35	33.7	0.60	0.43	0.90	0.85	1.40	0.43	vm N ₃ Al	
44	6.0	38	35.0	0.27	0.45	0.70	0.68	0.60	0.42	vm N ₃ Al	
45	6.0	35	33.4	0.32	0.64	0.91	0.81	0.50	0.37	None	
46	6.0		32.2	0.16	0.34	0.90	0.50	0.47	0.38	None	
47	6.0		34.0	0.22	0.60	0.90	0.77	0.37	0.38	None	

^a Rest of P₂O₅ present as orthophosphate. ^b SR = F/(MgO + 2.5 Al₂O₃ + 0.33 Fe₂O₃), where formulas denote concentration in weight units of components. ^c N₃Al = (NH₄)₃AlF₆; MgAl = MgAl(NH₄)₃(P₂O₇)₂F₂·6H₂O, I = insoluble dimorph, II = soluble dimorph; MgN₆ = Mg(NH₄)₆(P₂O₇)₂·6H₂O; vm = very minor. ^d F added as NH₄F, unless otherwise specified. ^e F added as H₂SiF₆.

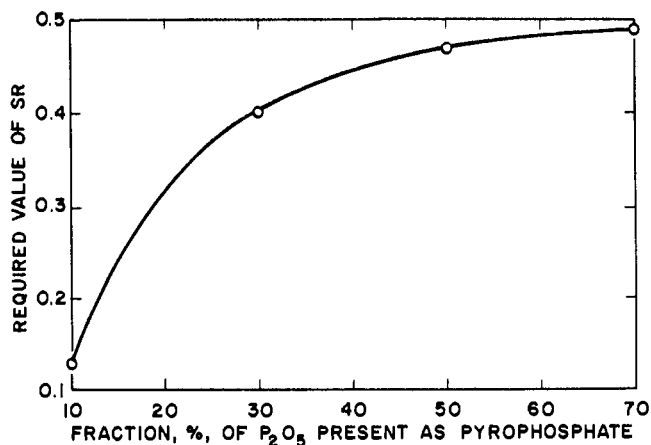


Figure 1. Effect of pyrophosphate content on required value of sequestration ratio

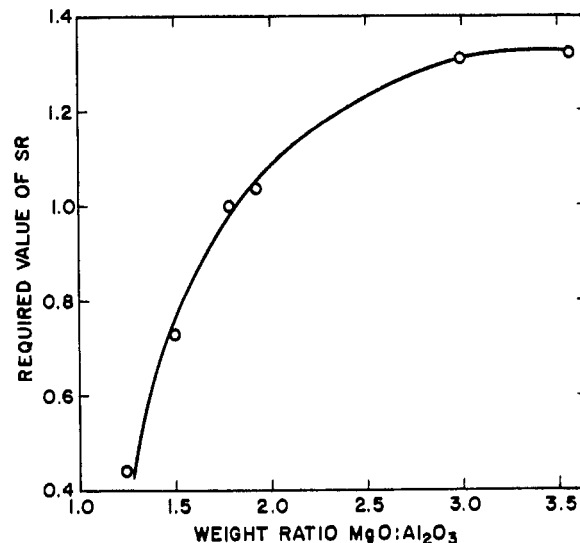


Figure 2. Effect of high magnesium content on required value of sequestration ratio. (50% of P₂O₅ present as pyrophosphate; Al₂O₃ content ranged at random from 0.27 to 1.45%)

tations that are to be prevented are those of the complex pyrophosphates of the impurities.

The pH of liquid ammonium polyphosphate fertilizer solutions usually ranges only from 5.5 to 6.0 and, as shown by entries 25 to 27 in Table VII, the proper value of SR does not change significantly with variation in pH over this range, and changes only slightly when the pH is raised from 6.0 to 6.5.

As shown by entries 28 and 29, fluoride and fluosilicate are equally effective in sequestering the impurities. Scrubber solutions, such as those produced in preventing escape of fluorine into the atmosphere from phosphate plants (Barber and Farr, 1970) are satisfactory sources of fluorine.

In addition to the separate effects of magnesium and aluminum on the proper value of SR, the ratio MgO:Al₂O₃ has a

considerable effect. As shown by the samples of the commercial fertilizer solutions in Table VII, the weight ratio MgO:Al₂O₃ usually ranges from about 0.4 to 1.4, and an SR of about 0.4 is sufficient to sequester the impurities. Entries 30 to 35, however, are those of solutions prepared from reagent chemicals in which the weight ratio MgO:Al₂O₃ was raised as high as 3.56, which required an SR of 1.32 for sequestration of the impurities. These results, which are shown graphically in Figure 2, represent conditions that probably would never be encountered in commercial solutions.

Table VIII. Behavior of Simulated 10-34-0 Solutions on Storage at 40° C for 4 Weeks

No.	Pyro-, % of total P ₂ O ₅ ^a	Compn, % ₀ of initial solution				SR ^b	Solid phase ^c
		F	MgO	Al ₂ O ₃	Fe ₂ O ₃		
51	10	0.3	0.7	0.4	0.5	0.16	Clear liquid
52	33	0.0	0.7	0.4	0.5	0.00	MgN ₂
53	33	0.1	0.7	0.4	0.5	0.05	MgN ₂ + MgAl + minor gel
54	33	0.3	0.0	0.4	0.5	0.26	Clear liquid
55	33	0.3	0.7	0.0	0.5	0.35	Moderate gel
56	33	0.3	0.7	0.4	0.0	0.18	Moderate gel + MgN ₂
57	33	0.3	0.7	0.4	0.5	0.16	Strong gel, no ppt
58	33	0.3	0.7	0.8	0.5	0.10	MgAl + MgN ₂
59	33	0.6	0.7	0.4	0.5	0.32	Very minor MgN ₂
60	33	0.6	0.7	0.8	0.5	0.21	Minor MgN ₂
61	50	0.3	0.7	0.4	0.5	0.16	MgN ₂ + amorphous grains

^a Rest of P₂O₅ present as orthophosphate. ^b $SR = F / (MgO + 2.5 Al_2O_3 + 0.33 Fe_2O_3)$, where formulas denote concentration, in weight units, of components. ^c MgN₂ = Mg(NH₄)₂P₂O₇·4H₂O; MgN₆ = Mg(NH₄)₃(P₂O₇)₂·6H₂O; MgAl = MgAl(NH₄)₃(P₂O₇)₂·6H₂O I (insoluble dimorph).

When the weight ratio MgO:Al₂O₃ is less than 0.2, however, and the Al₂O₃ content is more than 1%, the required value of *SR* increases somewhat above the usual value. This condition is rarely encountered in commercial fertilizer solutions, but it can be produced when spent pickling liquor from the treatment of aluminum articles is used as a source of phosphate. Ammonium polyphosphate liquids prepared from electric-furnace high (about 80%) polyphosphate 12-40-0 suspension and ammoniated pickling liquor usually are low grade, such as 8-25-0, and contain about 1.5% Al₂O₃. In the absence of fluorine the aluminum eventually precipitates as a voluminous mass of very small needle crystals of Al(NH₄)₂P₂O₇·OH·3H₂O that thicken the liquid to a stiff paste. Fluorine in an amount to provide an *SR* of about 0.65 is required to liquefy such a mixture when 33% of the P₂O₅ is present as polyphosphate, but less fluorine may have been sufficient to prevent precipitation.

The difference in the coefficients for iron and aluminum in the expression of *SR* indicates that other components of the solution are complexing the ferric iron much more than the aluminum, and pyrophosphate apparently has the greatest effect. In the absence of fluorine, Al(NH₄)₂P₂O₇·OH·3H₂O precipitates from solutions containing about 1% Al₂O₃, from which it is concluded that pyrophosphate when present to the extent of more than 30% of the total P₂O₅ is not an effective sequestant for aluminum in the absence of fluorine.

The effect of iron on the proper value of *SR* is relatively slight, but it suggests that the effects of other cations, such as micronutrient metals, perhaps should be considered also. The effects of other cations can be estimated from published stability constants (Ringbom, 1963), but these effects would eventually have to be determined experimentally.

Attempts to prepare simulated 10-34-0 solutions in which 50% of the P₂O₅ was present as pyrophosphate and in which one of the complex ferric ammonium pyrophosphates would precipitate showed that a concentration of about 4% Fe₂O₃ was required for the formation of any precipitate of a ferric iron salt in the pH range 6.0 to 8.5. It is then apparent that much larger amounts of ferric iron than are normally present in 10-34-0 solutions can be tolerated without forming sludges in short storage periods. On prolonged storage, however, small amounts of Fe(NH₄)₃HPO₄P₂O₇·H₂O (Frazier *et al.*, 1966) may precipitate, presumably when hydrolysis has lowered the mole ratio P₂O₅:Fe below 2.

FORMATION OF GEL

A somewhat different problem is encountered in commercial solutions, such as those with grades 10-34-0, 7-21-7, or

8-25-0, in which 20 to 40% of the P₂O₅ is present as polyphosphate, the weight ratio MgO:Al₂O₃ is greater than 1.0, and the fluorine content is between 0.1 and 0.3% F. Under these conditions the stable solid phase is a gel-forming material that converts both liquid and suspension fertilizers into semisolid nonpourable masses. As shown by sample 57 in Table VIII, this condition is readily duplicated with reagent chemicals as a 10-34-0 solution in which 33% of the P₂O₅ is present as pyrophosphate and 67% as orthophosphate and that contains 0.7% MgO, 0.4% Al₂O₃, 0.5% Fe₂O₃, and 0.3% F. This mixture forms a tough, clear gel in 2 days at 40° C or in 3 to 4 weeks at room temperature (about 25° C). Several mixtures with similar compositions were prepared and stored at 40° C for 4 weeks. The results are shown in Table VIII.

The range of compositions in which this gel forms is very small, and the gel can be prevented by either a small decrease in the fluorine content or small increase in the Al₂O₃ content; either change destroys the aluminum-fluorine complex required for gel formation. This behavior markedly complicates the phase-diagram relations of the system, since each of the many aluminum-fluorine complexes could be considered a separate component of the system. Addition of Al₂O₃ to lower the weight ratio MgO:Al₂O₃ to 1.0 or below will prevent formation of the gel, and this procedure is suitable for suspension fertilizers but not for fertilizer solutions, since Mg(NH₄)₂P₂O₇·4H₂O or MgAl(NH₄)₃(P₂O₇)₂·6H₂O I would then be precipitated.

As shown by entry 59 in Table VIII and entries 41 to 47 in Table VII, in the usual range of concentration of impurities in commercial fertilizer solutions, formation of either the gel or a precipitated sludge can be prevented by adding fluorine to provide an *SR* of about 0.4. Addition of aluminum to prevent gel formation would then require an increase in fluorine to provide the *SR* value that would prevent precipitation of a sludge. The gel is very troublesome because it is too thick to permit ready mixing of reagents that would liquefy it and would have prevented its formation if they had been added earlier. Dilution of the initial wet-process acid with water, or addition of other materials such as KCl or furnace-grade 11-37-0 solution, to lower the concentration of MgO to 0.3% and of Al₂O₃ to 0.15% will not prevent the formation of the gel unless the ratio of these metals is kept within the proper limits. It is much easier to prevent the formation of the gel than to liquefy a gel that has formed. As shown in Table VIII, 0.8% Al₂O₃ was sufficient to prevent formation of gel in these mixtures, whereas addition of 2.5% Al₂O₃ was required to liquefy the gel after it had formed. Similar results were obtained for fluorine.

It should be noted that fluorine has the capacity to sequester the impurity cations only in fairly concentrated ammonium phosphate solutions. When well-sequestered solutions are diluted with 2 to 10 times their volumes of water, the iron and aluminum are precipitated as gelatinous $(\text{Al,Fe})\text{PO}_4 \cdot n\text{H}_2\text{O}$. Sequestration in dilute solutions is more difficult than in concentrated solutions because ionization increases with dilution and the concentration of complexes decreases almost to the vanishing point.

CONCLUSIONS

The system formed by ammoniation and concentration of wet-process phosphoric acid is very complex and the regions of stability of the several solid phases can be determined only partially. To provide stable sludge-free ammonium polyphosphate solutions similar to those now produced commercially, at least 10% of the total phosphate should be present as polyphosphate to prevent the formation of iron and aluminum orthophosphate gels or precipitates, and the fluorine content should be sufficient to both sequester the magnesium and assist the pyrophosphate in sequestering the aluminum and so preventing the precipitation of $\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$, $\text{MgAl}(\text{NH}_4)_5(\text{P}_2\text{O}_7)_2\text{F}_2 \cdot 6\text{H}_2\text{O}$ I, and $\text{Al}(\text{NH}_4)_2\text{P}_2\text{O}_7\text{OH} \cdot 3\text{H}_2\text{O}$. The recommended fluorine content is that required to provide a value of *SR*, as determined from eq 1, of 0.50 if 50% of the phosphate is present as polyphosphate, and 0.15 if 10% of the phosphate is present as polyphosphate. Solutions prepared to meet these conditions have remained free of any solid phase for 6 months at room temperature. As hydrolysis of the polyphosphate occurs on longer storage, however, the water-soluble $(\text{NH}_4)_3\text{AlF}_6$ is expected to precipitate. The inverse relation of the two sequestering agents—pyrophosphate and fluorine—is such that 10–34–0 solutions low in polyphosphate

may be effectively sequestered by the fluorine remaining after concentration of the acid. In practice, however, the *SR* values should be about 115% of those listed in Table VII, because too much fluorine causes no significant trouble, whereas a deficiency of fluorine permits the formation of a heavy sludge of $\text{MgAl}(\text{NH}_4)_5(\text{P}_2\text{O}_7)_2\text{F}_2 \cdot 6\text{H}_2\text{O}$ I that is very difficult to redissolve with additions of reasonable amounts of fluorine.

The proper fluorine content of a fertilizer solution is readily determined by seeding portions of the solution with $\text{MgAl}(\text{NH}_4)_5(\text{P}_2\text{O}_7)_2\text{F}_2 \cdot 6\text{H}_2\text{O}$ I, adding different amounts of fluorine to successive portions, and allowing the treated portions to stand at 60° C for 24 hr. At this temperature the formation of sludge is accelerated, and the amount of fluorine that maintains a clear solution in this test will maintain a clear solution for months in normal storage.

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