
ARTICLES

Ionic Effects on the Hydrolysis of Polyphosphates in Liquid Fertilizers

A. William Frazier* and Ewell F. Dillard

The catalytic effects of iron, aluminum, ammonium, potassium, and fluoride on the hydrolysis of polyphosphates above pyrophosphate in liquid and suspension fertilizers were determined. A relationship describing the concentration of these polyphosphate species with time as a function of the iron, aluminum, ammonium, and fluoride concentrations was developed. The catalytic effect of iron and aluminum is partially offset by a small quantity of fluorine; however, fluoride in excess of this amount is extremely detrimental to the polyphosphate values of the fertilizers. These hydrolysis effects are necessary to predict the storage life of liquid fertilizers prior to the onset of precipitation. In this same study, an extremely rapid interaction between NH_4HF_2 and ammonium polyphosphates, including pyrophosphate, was detected. The reaction produced two compounds, $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{PO}_3\text{F}$ (anhydrous), which were characterized chemically and optically.

The hydrolysis of polyphosphates in high-analysis liquid fertilizers prepared from wet-process phosphoric acid is a serious problem to the fertilizer industry. The extent to which dissolved impurities affect hydrolysis rates is poorly understood and of growing concern with today's lower quality phosphate raw materials.

Most cations are reported to catalyze the rate of hydrolysis, but their effect may be altered by the presence of anions that may combine to form stable complexes (Van Wazer, 1958). Ammonia is the predominant cation in liquid polyphosphate fertilizers, but its effect on the rate of hydrolysis of polyphosphates has not been quantified, except for one published account indicating its catalytic effect to be insignificant (Farr et al., 1972).

Similarly, Willard et al. (1975) reported a half-life for dilute ammonium triphosphate solution (1.3% N) at pH 6.0 and 25 °C to be 500 days for the triphosphate species. However, early in the present investigation a half-life of 160 days was observed for the polyphosphate fraction above pyrophosphate (mostly triphosphate) in liquid grades (11% N; 37% P_2O_5) prepared from clean electric-furnace phosphoric acid. Thus, the effect of ammonia appeared highly significant and required more quantitative evaluation.

The significance of catalytic hydrolysis due to dissolved metal impurities from wet-process phosphoric acid also had been recognized during the study of high-poly liquid fertilizers prepared by the pipe-reactor process from polyphosphoric acid using wet-process phosphoric acid (Meline et al., 1972). These products initially contained 35-51% of the phosphate as polyphosphate having a chain length greater than two (pyrophosphate), and their storage life free of postprecipitation varied greatly. Storage life appeared to correlate with the loss of polyphosphate above pyrophosphate. However, it was not directly related to the total quantity of polyphosphate in the initial fertilizer products. Likewise, the fluoride level was low and did not

directly affect the storage properties of these high-poly liquids.

Considering all these parameters, it was difficult to quantify how the hydrolysis of polyphosphate above pyrophosphate was affecting storage life. One additional factor was observed to be the increased level of pyrophosphate that formed as the higher polyphosphates hydrolyzed, which acted to offset an overall decrease in polyphosphate content. This component increased to 70% of the total phosphate in some samples and hastened precipitation of insoluble pyrophosphate salts due to the mass action effect and the imbalance in the ratio pyrophosphate to fluoride (Frazier et al., 1972). At the initial low pyrophosphate levels in these products, the normal levels of fluoride impurity were sufficient to maintain a clear liquid fertilizer free of precipitation because of metal complexing by fluoride ions. However, the rapid hydrolysis rate of the polyphosphate above pyrophosphate to increase the pyrophosphate concentration eventually negated the fluoride effect and initiated precipitation that rapidly decreased storage life. These observations and supporting chemical analyses demonstrated a varying hydrolysis rate for the higher polyphosphates. The half-life of the polyphosphates above pyrophosphates in these high-poly liquids ranged from 25 to 60 days. These values are significantly low when compared to the value of 155 days obtained for pure 11-37-0 fertilizers produced from high-purity electric-furnace phosphoric acid. Thus, it was obvious that the metallic impurities were very effective catalysts in the hydrolysis of polyphosphates above pyrophosphates.

EXPERIMENTAL SECTION

For quantification of this effect, a series of laboratory experiments was designed. For one test, a high-polyphosphate 11-37-0 fertilizer prepared by the pipe-reactor process (Meline et al., 1972) was aliquoted and treated with iron and aluminum phosphate to increase the original Al_2O_3 and Fe_2O_3 content by 1 and 2%. These samples were adjusted to pH 6.0, maintained at 25 °C, and sampled after 30, 60, and 90 days for chromatographic analysis. The results are shown in Table I where sample 6 is the original

Division of Chemical Development, National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama 35660.

Table I. Chemical Analysis and Half-Life Values of 11-37-0 Liquid Fertilizers (WPA)

sample	wt %			polyphosphate P ₂ O ₅ , % of total ^a						half-life, av value, days ^b
	Fe ₂ O ₃	Al ₂ O ₃	F	30 days		60 days		90 days		
				pyro	other	pyro	other	pyro	other	
(1) as produced + 1% Fe ₂ O ₃	1.76	0.58	0.1	45	24	53	13	57	5	29
(2) as produced + 2% Fe ₂ O ₃	2.76	0.58	0.1	52	16	59	5	62	0	18
(3) as produced + 1% Al ₂ O ₃	0.76	1.58	0.1	43	24	52	12	54	9	31
(4) as produced + 2% Al ₂ O ₃	0.76	2.58	0.1	49	15	55	7	59	0	19
(5) as produced + 1% Fe ₂ O ₃ + 1% Al ₂ O ₃	1.76	1.58	0.1	49	16	57	6	59	3	19
(6) as produced, blank	0.76	0.58	0.1	39	35	46	25	49	18	60

^a Difference = orthophosphate [i.e., 100 - (pyro + other) = ortho]; zero time composition = 19% ortho, 31% pyro, and 50% other. ^b H.L. = 0.301t/log (C₀/C_t) (t = time in days, C₀ = initial concentration, and C_t = concentration after time t).

Table II. Phosphate Species Distribution for 11-37-0 from Electric-Furnace Acid

time, days	P ₂ O ₅ as % of total P ₂ O ₅			
	ortho	pyro	tripoly	higher
0	22.6	41.7	22.2	13.5
21	24.8	42.3	22.3	10.6
42	26.8	43.8	22.6	6.8

fertilizer as produced. The hydrolysis rate is expressed as the time in days required for half the polyphosphate above pyrophosphate to hydrolyze to ortho- and pyrophosphate. The bulk of this polyphosphate is tripolyphosphate, and the longer chain polyphosphates hydrolyze as a unit at the same rate as tripolyphosphate so that the total quantity will hydrolyze as a single unit similar to tripolyphosphate. This condition is shown in Table II where a detailed comparison of the chromatographic data for the high-purity, electric-furnace 11-37-0 shows that pyrophosphate increases, while tripolyphosphate remains constant and higher species decrease. This indicates that higher species are hydrolyzing to tripolyphosphate about as fast as tripolyphosphate is hydrolyzing to ortho- and pyrophosphate. The tripolyphosphate content essentially remains the same during the test period. For this reason the hydrolysis rates for all polyphosphates above pyrophosphates in liquid fertilizers can be compared to the fundamental values collected for tripolyphosphate, especially since the major part of this fraction is tripolyphosphate.

This hydrolysis is a first-order reaction (Williard et al., 1975) and can be expressed by the equation

$$\ln (C_0/C_t) = Kt \text{ or } 2.303 \log (C_0/C_t) = Kt \quad (1)$$

which reduces to

$$K = \frac{2.303 \log (C_0/C_t)}{t} \quad (2)$$

so that when *t* is the half-life value

$$K = \frac{2.303 \log 2}{t_{0.5}} = 0.6933/t_{0.5} \quad (3)$$

and combining eq 2 and 3 gives

$$\frac{0.6933}{t_{0.5}} = \frac{2.303 \log (C_0/C_t)}{t} \quad (4)$$

which reduces to

$$t_{0.5} = \text{half-life} = \frac{0.6933t}{2.303 \log (C_0/C_t)} = \frac{0.301t}{\log (C_0/C_t)} \quad (5)$$

This half-life equation is a fundamental rate relationship based only on the initial concentration, C₀, and the final concentration, C_t, after time, *t*, and represents the time

required for half the initial concentration of a component to be consumed by a chemical or physical action.

An examination of the data in Table I shows a significant change in half-life due to iron and aluminum in liquid polyphosphate fertilizers. However, more fundamental data were needed to define the limits of this effect. Likewise, an additional study was needed to include fluorine since this element is a strong complexing agent for iron and aluminum in liquid fertilizers (Frazier et al., 1972).

A basic factorial study was designed to quantify these effects. An 11-37-0 liquid fertilizer prepared from electric-furnace superphosphoric acid was chosen for its high degree of purity and high level of polyphosphate having chain lengths greater than pyrophosphate. The test solutions prepared for this study were adjusted at several levels of Fe₂O₃ between 0 and 1.29%, Al₂O₃ between 0 and 2.5%, and fluorine between 0 and 1.86% by using freshly precipitated FePO₄·nH₂O, AlPO₄·nH₂O, and NH₄HF₂ as reagents. The solutions were adjusted to pH 6.0 and equilibrated at 25 °C for the time periods shown in Table III. The chemical analysis and chromatographic results are shown for each time period, and the hydrolysis rates are calculated by two methods for comparison. The chromatographic data were not given a least-squares treatment when the polyphosphate value above pyrophosphate was less than 4% of the total phosphate because of the poor correlation obtained between the catalytic effect and the chromatographic values below this level. The impurity and chromatographic data in Table III were used to derive the following empirical formula relating the hydrolysis rates (H.L.) to impurity levels in concentrated liquid fertilizers.

$$\log \text{H.L.} = 2.19 - 0.313(\text{wt \% Fe}_2\text{O}_3 + \text{wt \% Al}_2\text{O}_3) + 0.119[\text{wt \% F}(2 \text{ wt \% Al}_2\text{O}_3 + \text{wt \% Fe}_2\text{O}_3)]^{1/2} \quad (6)$$

This equation is satisfactory for saturated liquid fertilizers at 10-12% nitrogen; however, a comparison of our half-life value in the pure system of 155 days (Table III) or 165 days (Table II) to the reported (Williard et al., 1975) value of 547 days for tripolyphosphate indicated that ammonia also was a significant catalyst. The reported value of 547 days was obtained at 1.3% N. For quantification of the nitrogen effect, which also reflects the total ionic strength, a series of reported values (Williard et al., 1975; Farr et al., 1967) was compared with our values of 155 and 165 days, which were calculated from the data reported for the product in Tables II and III. These data are given in Table IV along with the data obtained from a series of diluted samples containing potassium tripolyphosphate. Both sets of results are plotted in Figure 1 to show that the half-life varies inversely in a logarithmic nature with the nitrogen and potassium content. Extrapolating these data to zero nitrogen and potassium gives a half-life value of 933 days.

Table III. Chemical Analysis of 11-37-0 Liquid Fertilizers with Fe, Al, and F Amendments

test no.	Fe ₂ O ₃	Al ₂ O ₃	F	chromatograms, pyro and poly > pyro ^a								half-life, days ^b	
				21 days		42 days		60 days		90 days		A	B
				pyro	other	pyro	other	pyro	other	pyro	other		
3156	0.68	1.28	0.00	46	24	49	16	53	10	56	6	34	38
3157	0.68	1.20	1.10	42	29	44	23	47	19	51	13	62	66
3158	0.66	0.59	0.69	41	31	43	26	45	21	48	16	75	86
3159	0.66	2.42	0.00	50	13	53	7	57	2	58	1	17	17
3160	0.67	2.44	1.09	45	20	50	14	53	9	56	5	32	32
3161	0.61	2.42	1.75	40	25	46	18	48	15	51	10	50	41
3162	1.23	1.18	0.00	46	21	52	12	55	8	56	5	31	27
3163	1.29	1.31	1.14	43	26	46	20	51	13	54	9	44	42
3164	1.19	0.73	0.81	42	27	45	21	48	17	51	12	57	58
3165	1.20	2.40	0.00	52	11	57	3	58	2	58	1	12	12
3166	1.26	2.50	1.09	45	20	51	12	54	7	56	4	26	22
3167	1.20	2.41	1.86	44	21	48	14	52	10	54	6	35	29
3168	0.00	0.00	0.00	42	33	44	29	44	28	45	24	155	155

test no.	Fe ₂ O ₃	Al ₂ O ₃	F	chromatograms, pyro and poly > pyro ^a						half-life, days ^b	
				16 days		45 days		93 days		A	B
				pyro	other	pyro	other	pyro	other		
3210	0.91	0.00	0.82	44	30	49	21	52	14	68 ^c	102 ^c
3211	0.08	0.63	0.00	42	32	44	26	48	18	93	93
3212	0.00	0.42	0.42	41	33	43	28	46	22	131	134
3213	1.09	0.60	0.00	42	29	48	20	52	12	59	46
3214	1.10	0.40	0.41	41	31	45	23	50	15	73	67
3215	1.10	<0.02	0.61	43	29	47	21	51	14	69 ^c	88 ^c
3216	0.96	0.55	0.00	43	30	48	20	52	11	54	52
3217	0.93	0.32	0.39	41	32	45	24	49	16	78	78

^a Difference = ortho [i.e., 100 - (P₂O₅ - P + other - P) = ortho - P]; zero time composition = 23% ortho - P, 42% pyro - P, and 36% other - P. ^b A = calculated by eq 3; B = calculated by eq 6. ^c Equation is insufficient when wt % F ≥ 1.5 wt % Al₂O₃ + 0.5 wt % Fe₂O₃ (excess F completely disrupts the hydrolysis properties).

Table IV. Chemical Analysis Showing the Hydrolysis of Polyphosphate above Pyrophosphate in Ammonium and Potassium Phosphate Solutions at pH 6.0 and 25 °C

wt %	K	N	total P ₂ O ₅	chromatograph, P ₂ O ₅ as % of total P ₂ O ₅ , of poly-above pyrophosphate		half-life [0.301 t/log (C ₀ /C _t)]
				initially	after 59 days	
21.0			29.7	25.0	11.4	52
10.6			15.0	39.0	30.3	162
5.3			7.6	41.4	36.6	332
2.9			4.0	38.0	35.6	497
		11.0	37.0	Table II	Table II	165
		9.72	32.7	a	a	215
		3.2	10.8	b	b	547

^a Farr et al. (1967). ^b Williard et al. (1975).

Thus, the hydrolysis rate for polyphosphate above pyrophosphate in ammonium polyphosphate liquid solutions at 25 °C and pH 6.0 can be calculated accordingly:

$$\log \text{H.L.} = 2.97 - 0.071 \text{ wt \% N} \quad (7)$$

Assuming that the catalytic effect of the impurities is the same in dilute fertilizer solutions, the two equations, eq 6 and 7, can be combined to give

$$\log \text{H.L.} = 2.97 - 0.071 \text{ wt \% N} - 0.313(\text{wt \% Fe}_2\text{O}_3 + \text{wt \% Al}_2\text{O}_3) + 0.119[\text{wt \% F}(2 \text{ wt \% Al}_2\text{O}_3 + \text{wt \% Fe}_2\text{O}_3)]^{1/2} \quad (8)$$

This equation was tested on the typical liquid fertilizers from Table I and the comparisons are shown in Table V.

The results in Tables III-V show that ammonia, iron, and aluminum are effective catalysts for the hydrolysis of polyphosphates above pyrophosphates and that fluorine will compensate for this effect to a limited degree. Results

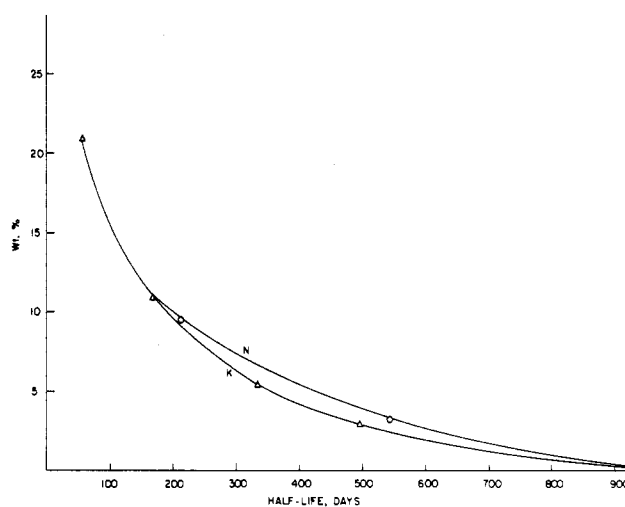


Figure 1. Half-life of poly > pyro, days at 25 °C, pH 6.0.

Table V. Hydrolysis Rates for High-Polyphosphate Liquids

sample value	half-life of polyphosphates above pyrophosphates in days					
	1	2	3	4	5	6
chemical ^a	29	18	31	19	19	60
formula ^b	33	17	34	18	17	66

^a Equation 5. ^b Equation 8.

of tests 3210 and 3215 (Table III) show that fluorine in excess of that required for complexing the iron and aluminum is a strong catalyst. The other data in Table III indicate that the effect becomes significant when wt % F ≥ 1.5 wt % Al₂O₃ + 0.5 wt % Fe₂O₃. Fluid fertilizers prepared from merchant-grade phosphoric acids will not contain this level of fluorine unless unusual process factors

Table VI. Chemical Analysis for $(\text{NH}_4)_2\text{PO}_3\text{F}$ and $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$

sample	analysis, wt %			H_2O diff.	mol/mol of P_2O_5		
	$(\text{NH}_4)_2\text{O}$	P_2O_5	F		$(\text{NH}_4)_2\text{O}$	F	H_2O
$(\text{NH}_4)_2\text{PO}_3\text{F}$	38.0	52.0	12.4	2.8	2.00	1.78	0.43
theoretical	38.81	52.99	14.18	0.0	2.00	2.00	0.00
$(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$	34.1	46.5	11.9	12.5	2.01	1.91	2.12
theoretical	34.21	46.71	12.50	11.84	2.00	2.00	2.00

Table VII. Optical Data for Ammonium Fluorophosphates

compound	crystal system	refractive indexes	optical properties ^a
$(\text{NH}_4)_2\text{PO}_3\text{F}$	orthorhombic, <i>mmm</i> ; bipyramids slightly elongated along <i>c</i> and exhibiting {110}, {101}, and (100)	$\alpha = 1.454$ $\beta = 1.481$ $\gamma = 1.487$	biaxial (-), $2V_{\text{calcd}} = 45^\circ$; OAP = (001) and $b = Z$; density = 1.64 g/cm ³
$(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$	monoclinic, <i>2/m</i> ; rod crystals elongated along <i>c</i> and exhibiting prominent {110} terminated by (001)	$\alpha = 1.446$ $\beta = 1.451$ $\gamma = 1.456$	biaxial (-), $2V_{\text{calcd}} = 89^\circ$; OAP \perp 010 and $Y \angle c = 7^\circ$ in acute β ; $\beta = 98.7^\circ$; density (calcd) = 1.53 g/cm ³

^a Density calculated from the Gladstone-Dale equation and $2V$ determined by Johannsen's equation (Farr et al., 1967; Larsen and Berman, 1934).

have been involved (for example, the use of fluoride scrubber liquors for makeup water). Attempts to quantify the catalytic effect of excess fluoride showed that an initially rapid, but decreasing, reaction occurred between the polyphosphates, including pyrophosphate, and fluoride to produce PO_3F^{2-} ions which then very slowly hydrolyzed to orthophosphate and released the fluoride to react with more polyphosphate. The PO_3F^{2-} ion was detected as a faster moving band than orthophosphate during separation of species by paper chromatographic analysis. The polyphosphate-fluoride reaction was essentially complete after 2 months, and the hydrolysis rate of the residual polyphosphates reverted to the basic values as if no fluoride had been added. These exploratory tests showed that about two-thirds of the added fluoride was converted to PO_3F^{2-} when 1.1, 2.0, and 3.8% F were charged to an 11-37-0 liquid fertilizer prepared from electric-furnace superphosphoric acid. The reaction was sufficiently fast that an attempt to saturate a solution with $(\text{NH}_4)_5\text{P}_3\text{O}_{10}$ and NH_4HF_2 or $(\text{NH}_4)_3\text{HP}_2\text{O}_7$ and NH_4HF_2 resulted in an immediate precipitate of $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$. On standing in mother liquor, this salt slowly converted to the anhydrous form, $(\text{NH}_4)_2\text{PO}_3\text{F}$, at 25 °C. The chemical analysis of homogeneous preparations is shown in Table VI and the optical crystallographic data are shown in Table VII. The X-ray powder diffraction data have been reported (Berndt and Sylvester, 1972; Neels and Grunze, 1968; "Powder Diffraction File Alphabetical Index Inorganic Materials", 1979).

Thus, the storage life of polyphosphate liquid fertilizers is directly related to the high level of polyphosphate above pyrophosphate, not because this fraction sequesters the impurities, but because a high content of higher polyphosphates necessarily decreases the quantity of pyrophosphate available to form precipitates with metal impurities, as, for example, the troublesome magnesium component (Frazier et al., 1972). The loss of this higher poly fraction by hydrolysis is related to the concentrations

of ammonia, iron, aluminum, and fluoride, which can now be determined from an empirical equation relating these factors. The saturation composition at which the various magnesium pyrophosphates will precipitate has been reported (Frazier et al., 1972). The data presented here and in the previous publication (Frazier et al., 1972) will allow fertilizer manufacturers to determine the time period for which a liquid polyphosphate fertilizer will remain stable without formation of solids.

The effect of iron and aluminum ions on the hydrolysis of pyrophosphate to orthophosphate is now being investigated, and it appears to be completely different from the results described here for the higher polyphosphates, but the effect of fluoride is similar. Initial results show that iron and aluminum retard the hydrolysis of pyrophosphate, and these data will be presented in a later report.

LITERATURE CITED

- Berndt, A. F.; Sylvester, J. M. *Acta Crystallogr., Sect. B* **1972**, *B28*, 2191-2193.
 Farr, T. D.; Fleming, J. D.; Hatfield, J. D. *J. Chem. Eng. Data* **1967**, *12*, 141-142.
 Farr, T. D.; Williard, J. W.; Hatfield, J. D. *J. Chem. Eng. Data* **1972**, *17*, 313-317.
 Frazier, A. W.; Scheib, R. M.; Thrasher, R. D. *J. Agric. Food Chem.* **1972**, *20*, 138-145.
 Larsen, E. S.; Berman, H. *Geol. Surv. Bull. (U.S.)* **1934**, No. 848.
 Meline, R. S.; Lee, R. G.; Scott, W. C. *Fert. Solutions* **1972**, *16*, 32-45.
 Neels, J.; Grunze, H. *Z. Anorg. Allg. Chem.* **1968**, *360*, 284-292.
 "Powder Diffraction File, Alphabetical Index Inorganic Materials"; International Centre for Diffraction Data: Swarthmore, PA, 1979.
 Van Wazer, J. R. "Phosphorus and Its Compounds"; Interscience: New York, 1958; Vol. 1.
 Williard, J. W.; Farr, T. D.; Hatfield, J. D. *J. Chem. Eng. Data* **1975**, *20*, 276-283.

Received for review November 12, 1980. Revised March 9, 1981.
 Accepted March 17, 1981.