LITERATURE CITED

(1) Berman, N.S., Larkam, C.W., McKetta, J.J., J. CHEM. ENG. DATA 9, 218 (1964).
(2) Berman, N.S., McKetta, J.J., *J. Phys. Chem.* **66**, 1444 (1962).
(3) Beynon, E.T., "Thermodynamic Properties of 2-Methyl-2-propanol and 2-Methyl-2-butanol," University Microfilms, Ann Arbor, Mich., 1965.
(4) deVries, T., Collins, B.T., *J. Am. Chem. Soc.* **63**, 1343 (1941).
(5) Ens, A., Murray, F., *Can. J. Chem.* **35**, 170 (1957).
(6) Hales, J.L., Cox, J.D., Lees, E.B., *Trans. Faraday Soc.* **59**, 1544 (1963).
(7) Howard, R.J., "Molecular Association in Supersaturated Vapors of Alcohols," University Microfilms, Ann Arbor, Mich., 1965.
(8) Jatkar, S.K.K., *J. Indian Inst. Sci.* **22A**, 39 (1939).
(9) Lydersen, A.L., Rönne, H.G., *Chem. Eng. Progr. Symp. Ser.* **64** (88), 95 (1968).
(10) Mathews, J.F., McKetta, J.J., *J. Phys. Chem.* **65**, 758 (1961).
(11) Schmidt, E., "VDI-Wasserdampftafeln," 6 ste Auflage, p. 145, Springer Verlag, Berlin, 1963.
(12) Sinke, G.S., deVries, T., *J. Am. Chem. Soc.* **75**, 1815 (1953).
(13) Stribolt, K., Lydersen, A.L., *Chem. Ing. Tech.* **39**, 96 (1967).
(14) Weltner, W., Pitzer, K.S., *J. Am. Chem. Soc.* **73**, 2606 (1951).
(15) Yuan, S.C., Mok, Y.I., *Hydrocarbon Process.* **47** (3), 133 (1968).
(16) *Ibid.*, **47** (7), 153 (1968).

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Effect of Impurities on Density and Viscosity of Simulated Wet-Process Phosphoric Acid

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Each of the common metallic impurities—Al, Fe, K, Ca, and Mg—increased the density and viscosity at 25° C. of simulated wet-process phosphoric acids containing 50, 75, and 104.4% H_3PO_4. Common anionic impurities—Cl, F, SO_4, and SiO_2—had little effect on either viscosity or density. When two or more impurities were present, their effects were roughly additive, but no general relationship of the effects of the different impurities could be established.

THE BEGINNINGS of the manufacture of wet-process phosphoric acid from phosphate rock and sulfuric acid are difficult to date precisely, but the method attained its prominence in 1917 to 1932 (*18*). Only in the last few years, however, the impurities in the wet-process acid have increased sufficiently to interfere seriously with the processing of the acid into fertilizers (*1, 5*). The increase in the amounts of these impurities, largely iron and aluminum, dissolved from the rock in the acidulation step results from the use of lower-grade rock in the manufacture of the acid because of the depletion of the reserves of high-grade rock. The impurities increase the viscosity of the acid as long as they remain in solution; as the acid is concentrated they precipitate as sludges that interfere with the mechanical handling of the acid. The sludge compounds, largely complex iron and aluminum phosphates, have been identified and characterized by Lehr *et al.* (*9*).

Dahlgren (*4*) studied the effects of the common impurities on the density and viscosity of acids containing 30, 43, and 54% P_2O_5 (41, 59, and 75% H_3PO_4). Burkert and Nickerson (*2*) studied the effects of iron, aluminum, magnesium, and sulfate on the properties of acids in the range 65 to 78% P_2O_5 (90 to 108% H_3PO_4) in an attempt to determine the amounts of impurities that could be tolerated in phosphoric acids that were to be concentrated to superphosphoric acid (usually 70 to 75% P_2O_5, or 97 to 104% H_3PO_4).

Results are reported here of a study of the effects of the common impurities on the density and viscosity at 25° C. of acids containing 36.2, 54.3, and 75.6% P_2O_5 (50, 75, and 104.4% H_3PO_4). Some of the mixtures were prepared to be initially supersaturated with respect to the impurities; the salts that precipitated were identified and the compositions of the acids were determined when precipitation was complete and the acids presumably were saturated with the impurities.

MATERIALS AND METHODS

To control the initial amounts and proportions of the impurities, the study was made with simulated wet-process acids. Acids containing 50 and 75% H_3PO_4 were prepared from reagent 85% H_3PO_4, and acid containing 104.4% H_3PO_4 was prepared from a superphosphoric acid produced in the TVA stainless steel demonstration plant. In the superphosphoric acid, 55.7% of the phosphorus was present as orthophosphate and 44.3% as condensed phosphates or polyphosphates.

In the simulated acids containing 50 or 75% H_3PO_4, almost all the cations were added as nearly saturated solutions of their phosphates in acid of the desired concentration. Solutions of the iron and aluminum phosphates were prepared by dissolving the pure metals in the phosphoric acid; the iron solutions were oxidized with hydrogen peroxide except when the ferrous salt was desired. Solutions of other phosphates and of the anion impurities, which were usually added as acids, were prepared from reagent chemicals.

In the simulated acids containing 50 or 75% H_3PO_4, the $H_2O:H_3PO_4$ ratio was maintained at its value in the initial acid. The phosphate added with a cation impurity was assumed to be present in the final mixture as H_3PO_4 and to require the proper amount of water to maintain the desired concentration. The cation impurities and the anhydrous acid impurities were ignored in calculating the concentration of the phosphoric acid. When all the impurities had been added, the $H_2O:H_3PO_4$ ratio was

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[1] Deceased.

adjusted to the desired value by addition of water or reagent 85% H_3PO_4.

In the simulated acids containing 104.4% H_3PO_4, however, adjustment of the acid concentration was infeasible, and the impurities were added as anhydrous phosphates (as of iron and aluminum), as metals (such as magnesium), or as anhydrous salts (K_2SO_4, KCl, KF). Concentrated sulfuric acid, even after being heated to fumes, contained enough free water to dilute the acid significantly.

In initial studies with each acid concentration the number of added impurities was kept low. Acids containing several impurities were prepared later, but none of the mixtures approached commercial wet-process phosphoric acids in complexity. Potassium, the impurity most likely to cause precipitation, usually was added last; when calcium was present, sulfate was added last. In a number of solutions that were prepared only for measurements of viscosity and density, care was taken to add the impurities in combinations and amounts that would not cause precipitation of a solid phase.

The viscosity and density of each simulated acid were measured immediately after its preparation. Each acid then was stored at room temperature (about 25° C.) in a stoppered glass or polyethylene bottle and shaken by hand two or more times per week until precipitation appeared to be complete. The mixture then was filtered by suction on a Büchner funnel and the precipitate was washed rapidly with small portions of ethyl formate and then with acetone and the washed precipitates were allowed to dry in air.

In a brief study of the rate of precipitation, each acid mixture in the series was filtered whenever a suitable amount of precipitate was formed. These precipitates were washed and dried, as were those from the equilibrated mixtures.

Viscosity and density were measured at 25° C. The densities were determined in 25-ml. pycnometers. The viscosities of the acids containing 50 and 75% H_3PO_4 were measured with Cannon-Fenske viscometers calibrated with National Bureau of Standards oils; the viscosities of acids containing 104.4% H_3PO_4 were measured with a Model LVT Brookfield viscometer.

In the chemical analyses, potassium, sodium, calcium, magnesium, and manganese were determined by atomic absorption spectrophotometry (*11*) and chlorine by silver nitrate titration (*16*). All other determinations and tests were made by the methods used by Lehr *et al.* (*9*).

RESULTS AND DISCUSSION

The amounts and compositions of the precipitates and the density and viscosity of the simulated acids were affected by both the impurities and the interactions among the impurities.

Acids Containing 50% H_3PO_4 (36.2% P_2O_5). Results of representative tests with acid mixtures containing 50% H_3PO_4 are shown in Tables I and II; results of all the tests are available from ASIS National Auxiliary Publications Service.

In mixtures in which iron, aluminum, and potassium were the only impurities, the precipitates that formed were either $(Fe, Al)_3KH_{14}(PO_4)_8\cdot 4H_2O$ or $(Fe, Al)_3KH_8(PO_4)_6\cdot 6H_2O$; mixtures of these two salts were never observed. The results indicated that $(Fe, Al)_3KH_8(PO_4)_6\cdot 6H_2O$ was formed when the initial mole ratio K:(Fe + Al) was less than 0.16 and that $(Fe, Al)_3KH_{14}(PO_4)_8\cdot 4H_2O$ was formed when the initial acid contained relatively more potassium. High aluminum and low iron tended to favor precipitation of $(Fe, Al)_3KH_8(PO_4)_6\cdot 6H_2O$, and low aluminum and high iron favored precipitation of $(Fe, Al)_3KH_{14}(PO_4)_8\cdot 4H_2O$. The end members of the series $(Fe, Al)_3KH_{14}(PO_4)_8\cdot 4H_2O$ were precipitated when either iron or aluminum alone was present; the aluminum end member precipitated slowly as very fine crystals that were difficult to wash. When both iron and aluminum were present, the iron precipitated more

Table I. Simulated Wet-Process Phosphoric Acids, 50% H_3PO_4, at 25° C.

Soln. No.	Age, Days	Composition, Moles/Liter					Mole Ratio $R_2O_3:P_2O_5$	Density, G./Ml.	Viscosity, Cp.
		P	Fe	Al	K	Other			
4	0	6.912	0.750	. . .	0.167	. . .	0.109	1.4008	8.27
	116	5.971	0.258	. . .	0.013	. . .	0.043	1.3131	4.70
5	0	6.978	0.508	0.517	0.169	. . .	0.147	1.4132	10.60
	116	6.280	0.138	0.436	0.007	. . .	0.091	1.3398	6.13
6	0	7.001	0.381	0.768	0.166	. . .	0.164	1.4193	12.00
	116	6.365	0.108	0.792	0.014	. . .	0.141	1.3542	7.12
14	0	6.792	0.494	0.505	0.174	. . .	0.147	1.4313	10.80
	111	6.237	0.223	0.573	0.085	. . .	0.128	1.3823	7.55
23	0	6.942	0.506	0.516	0.189	0.177 S	0.147	1.4193	10.65
	114	6.309	0.205	0.442	0.030	0.186 S	0.103	1.3587	6.71
26	0	6.957	0.507	0.504	0.095	0.176 S	0.145	1.4178	10.56
	114	6.556	0.317	0.522	0.013	0.189 S	0.128	1.3831	8.14
28	0	6.882	0.752	. . .	0.398	. . .	0.109	1.4050	8.44
	114	5.618	0.087	. . .	0.185	. . .	0.015	1.2889	4.04
29	0	6.711	0.734	. . .	0.394	0.519 S	0.109	1.4232	8.66
	116	5.518	0.116	. . .	0.188	0.583 S	0.021	1.3183	4.38
57	0	6.968	0.505	0.396	. . .	2.281 F	0.129	1.4285	. . .
	167	7.347	0.526	0.132	. . .	1.072 F	0.090	1.4105	. . .
60	0	7.199	0.726	. . .	0.194	2.170 F	0.101	1.4234	. . .
	167	7.143	0.710	. . .	0.115	1.977 F	0.099	1.4158	. . .
61	0	7.096	0.500	0.476	0.200	2.278 F	0.138	1.4320	. . .
	167	6.828	0.236	0.112	0.084	0.951 F	0.051	1.3658	. . .
65	0	7.275	0.477	0.483	0.181	. . .	0.132	1.4244	11.13
	163	6.628	0.149	0.439	0.062	. . .	0.089	1.3611	7.01
67	0	7.113	. . .	1.449	0.190	. . .	0.204	1.4351	17.18
	163	7.114	. . .	1.491	0.209	. . .	0.210	1.4350	17.13
73	0	7.060	0.466	0.455	0.178	1.095 Cl	0.130	1.4231	9.69
	161	6.410	0.135	0.468	0.075	1.141 Cl	0.094	1.3637	6.40
75	0	6.902	. . .	1.387	0.179	1.084 Cl	0.201	1.4317	14.09
	161	6.911	. . .	1.493	0.205	1.104 Cl	0.216	1.4321	14.10

Table II. Precipitates from Phosphoric Acids, 50% H_3PO_4

From Soln. No.	Composition, Wt. %					Compound
	P	Fe	Al	K	F	
4	24.84	15.9	...	3.74	...	$Fe_3KH_{14}(PO_4)_8 \cdot 4H_2O$
29	23.49	15.5	...	3.50	...	$Fe_3KH_{14}(PO_4)_8 \cdot 4H_2O$
28	23.52	14.9	...	3.47	...	$Fe_3KH_{14}(PO_4)_8 \cdot 4H_2O$
73	23.71	13.76	0.82	4.39	...	$(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$
14	23.65	14.2	1.39	3.75	...	$(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$
26	23.36	13.6	1.68	3.79	...	$(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$
65	22.99	12.54	1.95	4.37	...	$(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$
5	21.59	13.3	3.03	4.48	...	$(Fe, Al)_3KH_8(PO_4)_6 \cdot 6H_2O$
23	21.75	12.6	3.13	4.33	...	$(Fe, Al)_3KH_8(PO_4)_6 \cdot 6H_2O$
6	21.78	10.7	4.41	4.44	...	$(Fe, Al)_3KH_8(PO_4)_6 \cdot 6H_2O$
67	22.38	...	9.45	5.06	...	$Al_3KH_8(PO_4)_6 \cdot 6H_2O$
60	16.46	14.30	...	21.67	11.2	2 phases, unidentified
61	15.57	8.90	6.28	3.44	13.4	2 phases, unidentified
57	2.49	0.68	17.49	...	35.5	90% $AlF_3 \cdot 3.5H_2O$

readily than the aluminum, and the precipitate contained relatively more iron and less aluminum than the initial acid mixture (*9*).

When added to acid mixtures that also contained potassium, ferrous iron oxidized slowly to ferric iron and then precipitated in the complex phosphates. Only traces of ferrous iron were observed in the precipitates.

Sulfate, added as H_2SO_4, both retarded and decreased the precipitation of the complex iron and aluminum phosphates (*17*).

No precipitates formed in acid mixtures that contained ferric iron, aluminum, and 2.75% Cl (added as HCl); addition of potassium to these mixtures precipitated $(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$. The chloride did not appear in the precipitate, but it decreased the amount of the precipitate and tended to decrease the ratio Al:Fe in the precipitate.

In acid mixtures containing iron, aluminum, and fluorine (added as HF) the pattern of precipitation was complex. In the absence of potassium, little or no ferric iron was precipitated, but the iron affected the precipitation of the aluminum. In the presence of ferric iron the aluminum precipitated readily as $AlF_3 \cdot 3.5H_2O$; in the absence of iron it precipitated as a fluorophosphate. Ferrous iron in acid mixtures that contained aluminum and fluorine but no potassium precipitated with the aluminum as $AlF_3 \cdot FeF_2 \cdot 7H_2O$.

Addition of potassium to an acid mixture that contained iron and fluorine precipitated $FeK_2H_3(PO_4)_2F_2$. When the mixtures contained aluminum also, the precipitates were mixtures of two or more phases, one of which was sometimes $AlF_3 \cdot 3.5H_2O$. The other phases could not be identified.

Acids Containing 75% H_3PO_4 (54.3% P_2O_5). Results of tests with acid mixtures containing 75% H_3PO_4 are shown in Tables III and IV.

Table III. Simulated Wet-Process Phosphoric Acids, 75% H_3PO_4, at 25° C.

Soln. No.	Age, Days	Composition, Moles/Liter							Mole Ratio R_2O_3:P_2O_5	Density, G./Ml.	Viscosity, Cp.
		P	Fe	Al	K	S	F	Si			
103	0	12.098	0.149	0.274	0.090	0.200	...	...	0.035	1.6124	29.58
	116	11.955	0.057	0.261	0.037	0.210	...	...	0.027	1.5972	25.64
104	0	12.370	0.457	0.858	0.094	0.204	...	...	0.106	1.6814	80.53
	116	12.123	0.272	0.869	0.000	0.216	...	...	0.094	1.6520	56.59
107	0	12.075	0.149	0.287	0.173	0.195	...	...	0.036	1.6152	30.79
	117	11.869	0.040	0.254	0.106	0.209	...	...	0.025	1.5956	25.40
108	0	12.360	0.460	0.933	0.180	0.200	...	...	0.113	1.6838	83.85
	118	11.824	0.139	0.782	0.000	0.224	...	...	0.078	1.6261	42.03
111	0	11.841	0.149	0.276	0.091	0.597	...	...	0.036	1.6242	29.94
	116	11.777	0.078	0.292	0.041	0.616	...	...	0.031	1.6097	26.75
112	0	12.104	0.462	0.902	0.095	0.624	...	...	0.113	1.6909	82.47
	116	11.857	0.265	0.912	0.000	0.658	...	...	0.099	1.6616	57.86
115	0	11.829	0.149	0.276	0.158	0.601	...	...	0.036	1.6236	30.65
	118	11.739	0.051	0.265	0.114	0.625	...	...	0.027	1.6077	26.31
116	0	12.092	0.462	0.862	0.164	0.619	...	...	0.109	1.6931	85.66
	118	11.573	0.129	0.820	0.000	0.670	...	...	0.082	1.6363	43.14
140	0	12.158	0.407	0.866	0.078	0.196	0.769	0.131	0.105	1.6767	...
	91	11.973	0.241	0.754	0.000	0.194	0.758	0.098	0.083	1.6501	50.05
142	0	11.899	0.142	0.306	0.167	0.210	0.802	0.138	0.038	1.6205	...
	91	11.922	0.098	0.267	0.029	0.200	0.454	0.036	0.031	1.6080	27.55
144	0	11.637	0.147	0.305	0.073	0.606	0.805	0.139	0.039	1.6283	...
	91	11.726	0.146	0.299	0.024	0.621	0.478	0.139	0.038	1.6253	29.69
147	0	11.916	0.282	...	0.080	0.212	0.816	0.138[a]	0.024	1.6185	...
	90	11.813	0.119	...	0.010	0.150	0.626	0.092[b]	0.010	1.5905	21.44
163	0	11.975	0.291	...	0.132[c]	0.199	0.803	0.138	0.024	1.6158	...
	90	12.047	0.280	...	0.003[c]	0.203	0.332	0.023	0.023	1.6084	25.07
164	0	12.324	0.418	0.821	0.153[c]	0.197	0.754	0.132	0.101	1.6846	...
	90	12.436	0.409	0.834	0.018[c]	0.199	0.334	0.000	0.100	1.6765	68.91
170	0	12.137	0.401	0.793	0.288[c]	0.559	0.732	0.126	0.098	1.6917	...
	90	12.226	0.398	0.741	0.102[c]	0.557	0.168	0.000	0.093	1.6828	69.59

[a] Contained 0.084 mole Ca/liter. [b] Contained 0.005 mole Ca/liter. [c] Na content.

Table IV. Precipitates from Phosphoric Acids, 75% H_3PO_4

From Soln. No.	Composition, Wt.% P	Fe	Al	K	Si	F	Compound
147	19.05	13.01	...	3.59	0.8	3.9[a]	$Fe_3KH_{14}(PO_4)_8 \cdot 4H_2O$ 83, $CaSiF_6$ 6, $CaSO_4 \cdot 0.5H_2O$ 11%
112	23.76	11.69	1.69	3.49	...	...	$(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$
111	23.99	12.30	1.85	3.80	...	...	$(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$
142	15.46	8.14	1.27	14.15	4.5	17.8	$(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$ 65, K_2SiF_6 35%
140	23.25	12.02	2.06	3.48	1.0	0.1	$(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$ 95, K_2SiF_6 0.3, $SiO_2 \cdot xH_2O$ 4%
115	23.96	11.45	2.13	3.77	...	...	$(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$
104	24.06	11.47	2.22	3.65	...	...	$(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$
103	24.09	11.57	2.29	3.74	...	...	$(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$
116	23.84	9.96	2.56	3.57	...	...	$(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$
107	24.07	10.07	2.61	3.62	...	...	$(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$
108	23.84	9.07	2.76	3.30	...	...	$(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$
144	2.65	0.09	0.23	30.65	11.0	47.4	$(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$ 11, K_2SiF_6 89%
170	5.00	0.71	1.22	18.90[b]	13.0	38.3[c]	$(Fe, Al)NaH_5(PO_4)_3 \cdot H_2O$ 20, Na_2SiF_6 67, $SiO_2 \cdot xH_2O$ 13%
164	7.12	0.73	1.52	13.50[b]	12.0	34.6[d]	$(Fe, Al)NaH_5(PO_4)_3 \cdot H_2O$ 28, Na_2SiF_6 54, $SiO_2 \cdot xH_2O$ 19%
163	1.83	0.14	...	24.20[b]	13.6	60.3	Na_2SiF_6

[a] Contained 2.4% S, 4.06% Ca also. [b] Na content. [c] Contained 0.6% S also. [d] Contained 0.2% S also.

When ferric iron, aluminum, potassium, and sulfate were the only impurities, the only precipitate formed was $(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$. As in acid mixtures containing 50% H_3PO_4, the iron precipitated preferentially and the precipitate contained a higher Fe:Al ratio than that in the initial acid mixture. Sulfate did not appear in the precipitate, but it tended to increase the Fe:Al ratio in the precipitate. In the absence of potassium no precipitate was formed.

Addition of 0.95% Cl as HCl had no appreciable effect on the amount or composition of the precipitated $(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$. Addition of 0.95% F as HF decreased the amount of precipitate and increased its Fe:Al ratio, but only traces of fluorine were found in the precipitate.

Addition of 0.9% F as H_2SiF_6, however, changed the pattern of precipitation. The iron and aluminum again precipitated as $(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$, but K_2SiF_6 appeared as a second phase in the precipitate from solutions that contained relatively little iron, and the amount of K_2SiF_6 in the precipitate was proportional to the K:Fe ratio in the initial acid mixture. Silica gel, $SiO_2 \cdot xH_2O$, precipitated from two mixtures that were initially high in both iron and aluminum. In a study of the rate of precipitation from two acids with initial compositions similar to those in which silica gel precipitated, K_2SiF_6 and $SiO_2 \cdot xH_2O$ were formed in the initial stages of precipitation. The results showed that a higher concentration of potassium is required for precipitation of K_2SiF_6 than of $(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$.

Addition of 0.2% of Ca, Mg, or Mn to a mixture containing ferric iron, aluminum, potassium, and sulfate changed the composition of the precipitates slightly but did not alter significantly the pattern of precipitation. The calcium usually precipitated as $CaSO_4 \cdot 0.5H_2O$. In one mixture, however, one fourth of the calcium was precipitated as $CaSiF_6$; no K_2SiF_6 formed in this mixture, but similar mixtures that contained no calcium precipitated K_2SiF_6. Part of the small amounts of magnesium and manganese precipitated from the mixtures to which they were added, presumably as the fluosilicates. These compounds were not detected petrographically, but their presence was deduced from the chemical analyses of the precipitates.

Substitution of sodium for potassium, as in mixtures 163, 164, and 170, precipitated Na_2SiF_6 as the major phase when the mixture contained enough silica and fluorine; the precipitate contained smaller amounts of $(Fe, Al)NaH_5(PO_4)_3 \cdot H_2O$. In the absence of silica and fluorine, this complex phosphate precipitated as the major phase with small amounts of $(Fe, Al)_3NaH_{14}(PO_4)_8 \cdot 4H_2O$ which is much more soluble than its potassium analog. The ready precipitation of Na_2SiF_6 explains the proposals for the use of fluosilicate for the removal of alkali metals (*8*, *14*) and of sodium salts for the removal of silicon and fluorine (*7*, *15*) from wet-process phosphoric acid.

Table V. Solutions for Rate-of-Precipitation Tests

Soln. No.	Composition, % H_3PO_4	P	Fe	Al	K	S
133	72.4	22.88	3.02	0.00	0.40	0.00
134	72.8	23.00	1.50	1.53	0.40	0.00
135	72.6	22.96	1.01	2.02	0.40	0.00
136	69.8	22.05	3.03	0.00	0.40	1.20
137	70.0	22.11	1.52	1.53	0.40	1.20
138	70.1	22.15	1.01	2.01	0.40	1.19

Sodium was less effective than potassium in precipitating iron and aluminum as complex phosphates. In the presence of fluosilicic acid, sodium precipitated aluminum more readily than iron; in the absence of fluosilicic acid, sodium precipitated iron more readily. All the precipitates of the sodium salts were very finely divided and difficult to wash, and much of the unidentified material in these precipitates was adsorbed mother liquor.

Results of a study of the rate of precipitation of impurities from simulated wet-process phosphoric acid containing 75% H_3PO_4 are shown in Tables V and VI. The kinetics of the precipitation were essentially those described by Chepelevetskiĭ and Kryukova (*3*). Precipitation was initially very slow during nucleation and early crystal growth, but it accelerated markedly with crystal growth and concomitant increase in the surface area of the solid phase; when the solid phase became heavy enough to settle out, or was filtered off, precipitation again was slow, as in the initial stage, and a new cycle of nucleation and crystal growth began. Stirring or agitation kept the solid phase

Table VI. Precipitation from 75% H_3PO_4 Solutions
[Based on 600 grams initial solution; all precipitates were $(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$]

Age, Days	Precipitate Removed from Indicated Solution, Grams			Age, Days	Precipitate Removed from Indicated Solution, Grams		
	133	134	135		136	137	138
3	16.0	14.0	6.6	1	17.0	30.3	32.0
6	11.0	7.0	6.7	4	10.0	46.1	36.0
13	28.5	7.0	6.6	11	13.5	0.0	0.0
35	10.3	11.9	12.9	32	16.2	0.0	0.0
41	0.0	20.8	22.4	39	5.6	0.0	0.0
Total	65.8	60.7	55.2		62.3	76.4	68.0

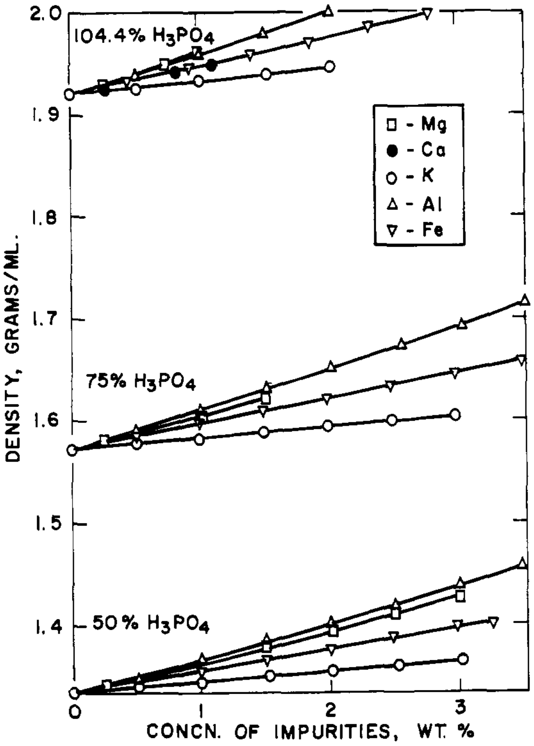

Figure 1. Density of simulated wet-process phosphoric acids

suspended and increased the rate of precipitation markedly without changing the sequence of precipitation or the composition of the solid phase. Stirring also accelerated nucleation in a clear acid, and this effect explains the formation of large amounts of sludge in clarified wet-process acid that is moved or agitated, as during shipment in a tank car.

All the precipitates in this series were $(Fe, Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$. Sulfate had no effect on the composition of the precipitate but retarded the precipitation slightly from the acid mixture that contained iron but no aluminum, and accelerated and increased the precipitation markedly in the two mixtures that contained both iron and aluminum.

In studies of precipitation from similar solutions that were stirred continuously, nucleation and crystal growth were highly erratic. The precipitates from the stirred acid mixtures were very finely divided and difficult to filter and wash, in agreement with the results reported by Hahnert and Kleber (*6*).

Acids Containing 104.4% H_3PO_4 (75.6% P_2O_5). Iron and aluminum, even in the presence of potassium, are more soluble in superphosphoric acid (97% H_3PO_4 or higher) than in merchant-grade acid (75% H_3PO_4), and precipitates of these metals from solution in acid containing 104.4% H_3PO_4 were not observed in this study. Lehr *et al.* (*9*) found that the precipitates in superphosphoric acid were mostly iron and aluminum tripolyphosphates and metaphosphates. These precipitates in superphosphoric acid are

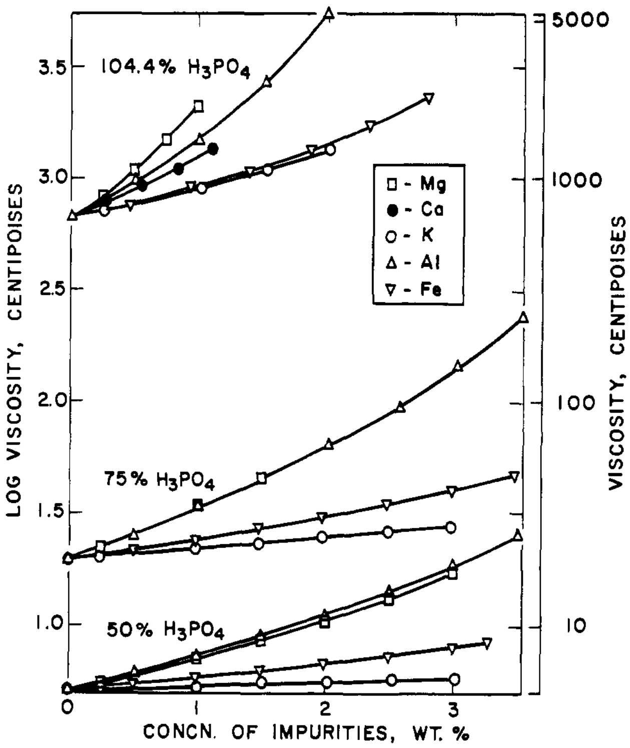

Figure 2. Viscosity of simulated wet-process phosphoric acids

Concentration of impurities on weight per cent basis

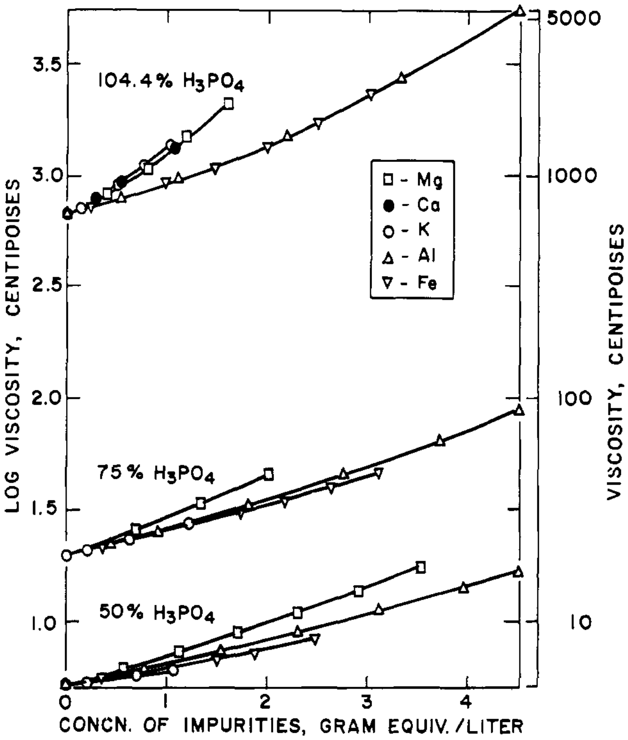

Figure 3. Viscosity of simulated wet-process acids

Concentration of impurities on normality basis

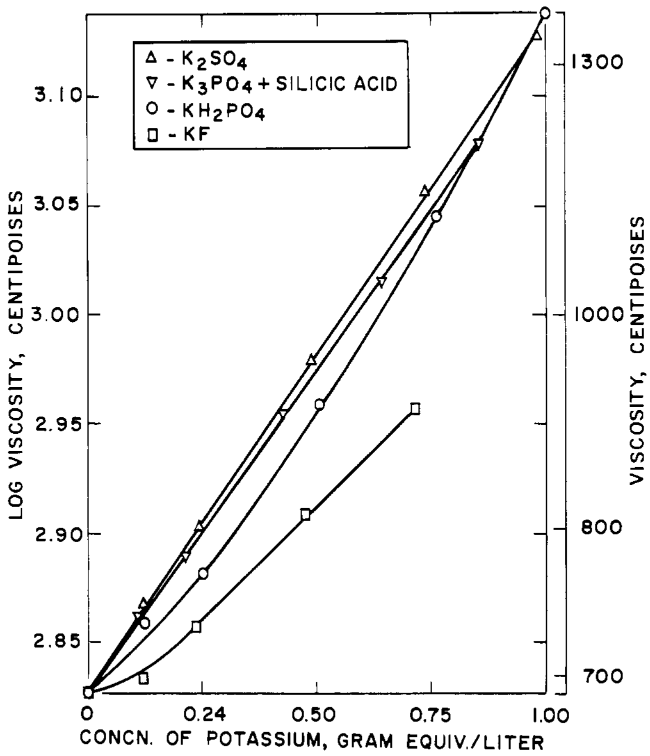

Figure 4. Effect of anions on viscosity of simulated wet-process superphosphoric acid (104.4% H_3PO_4)

generally avoided, however, by clarifying the acid before concentration to the superphosphoric acid range (*12*).

Addition of 0.62% Mg to the superphosphoric acid formed a precipitate of $MgH_2P_2O_7$ contaminated with a small amount of an unidentified iron pyrophosphate. Although more than half of the phosphate in the acid was orthophosphate, no orthophosphate appeared in the precipitate (*9*).

The precipitates in superphosphoric acids were not studied extensively. Most of the common impurity metals are more soluble in superphosphoric acid than in merchant-grade acid. Calcium and magnesium are exceptions (*13*), but calcium usually is removed almost completely as calcium sulfate in the preparation of the wet-process acid. Magnesium remains in solution and precipitates as magnesium phosphates when the acid is concentrated to superphosphoric acid.

Effect of Impurities on Density. As shown in Figure 1, each impurity increased the density of the acid in direct proportion to the concentration of the impurity when the impurity was present alone. The effects of two or more impurities usually were additive when the simulated acids were freshly prepared, but when precipitation had occurred the calculated density was always considerably higher than the measured density. This effect, which may reflect the formation of ionic complexes of the metals with the phosphoric acid (*10*), precluded the development of a mathematical expression of the density in terms of the impurity content of the acid.

Effect of Impurities on Viscosity. Each cationic impurity increased the viscosity of all concentrations of acid, as shown in Figures 2 and 3. The data in these figures were obtained from solutions of single impurities in reagent acids. The effect of each impurity increased with increase in the concentration of acid, as was observed also by Dahlgren (*4*), and this effect was more pronounced for potassium and magnesium than for iron and aluminum.

The effects of the anionic impurities chloride, fluoride, sulfate, and silicate on the viscosity of superphosphoric acid were determined on solutions of KCl, KF, K_2SO_4, or a mixture of silicic acid and K_3PO_4 in the plant superphosphoric acid (104.4% H_3PO_4). The results are summarized in Figure 4.

Chloride was evolved as HCl from the superphosphoric acid so rapidly that its effect on the viscosity could not be determined. However, chloride decreased the viscosity of 50% H_3PO_4 slightly (Table I).

Potassium fluoride increased the viscosity of the superphosphoric acid much less than did the equivalent amount of potassium phosphate, from which it appears that fluoride decreases the viscosity of the acid. Similar comparisons indicate that both sulfate and silicate increase the viscosity of superphosphoric acid, but the effect of either of these impurities appears to be small.

When the simulated acids contained several impurities, the effects of the different impurities on the viscosity appeared to be roughly additive. Attempts to correlate the viscosities with the compositions of these acids were unsuccessful, however, in agreement with the experience of Moelwyn-Hughes (*10*).

LITERATURE CITED

(1) Ando, Jumpei, Lehr, J.R., *J.Agr.Food Chem.* **15**, 741–50 (1967).
(2) Burkert, G.M., Nickerson, J.D., "Polyphosphoric Acids. Viscosity Versus Impurities," 152nd Meeting, ACS, New York, N.Y., September 1966.
(3) Chepelevetskiĭ, M.L., Kryukova, T.A., *Trans. Sci. Inst. Fertilizers Insectofungicides (USSR)* **137**, 102–9 (1937).
(4) Dahlgren, S.-E., *Acta Polytech. Scand., Chem. Met. Ser.* No. 19, 1962.
(5) Frazier, A.W., Lehr, J.R., *J.Agr. Food Chem.* **15**, 348–9 (1967).
(6) Hahnert, H., Kleber, W., *Kolloid-Z.* **162**, 36–46 (1959).
(7) Hodges, W.A., Floyd, J.E., Lange, W.H. (to Swift & Co.), U. S. Patent **2,883,266** (April 21, 1959).
(8) Ittlinger, R. (to International Minerals & Chemical Corp.), *Ibid.*, **3,141,734** (July 21, 1964).
(9) Lehr, J.R., Frazier, A.W., Smith, J. P., *J. Agr. Food Chem.* **14**, 27–33 (1966).
(10) Moelwyn-Hughes, E.A., "Physical Chemistry," pp. 771, 782, Pergamon Press, New York, 1957.
(11) Perkin-Elmer Corp., Norwalk, Conn., "Analytical Methods for Atomic Absorption Spectrophotometry," 1966.
(12) Scott, W.C., Jr., Patterson, G.G., Elder, H.W., *Ind. Eng. Chem.* **53**, 713–16 (1961).
(13) Seidell, A., Linke, W.F., "Solubilities of Inorganic and Metal-Organic Compounds," 4th ed., Vol. **I**, pp. 645–6, Vol. **II**, pp. 520–1, ACS, Washington, D. C., 1965.
(14) Shpunt, S. Ya., Arkhipova, L.N., Leneva, Z.L., Guseva, Z.I., *Khim. Prom.* **41** (9), 674–8 (1965).
(15) Sokolovskii, A.A., Sladkova, V.M., Hofman, I.L., *Trans. Sci. Inst. Fertilizers Insectofungicides (USSR)* **153**, 111–21 (1940).
(16) Swift, E.H., Arcand, G.M., Lutwack, R., Meier, D.J., *Anal. Chem.* **22**, 306–8 (1950).
(17) Viventi, R.V., Hettler, F.G., Jr. (to National Distillers and Chemical Corp.), U. S. Patent **3,119,662** (Jan. 28, 1964).
(18) Weber, W.C., in "Phosphoric Acid, Phosphates, and Phosphatic Fertilizers," W.H. Waggaman, Ed., 2nd ed., pp. 174–209, Reinhold, New York, 1952.

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