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PHOSPHORIC ACID IMPURITIES

Precipitated Impurities in Wet-Process Phosphoric Acid

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The sludges in raw wet-process phosphoric acid consist mostly of calcium sulfate and sodium fluosilicate; those in merchant-grade acid are mostly $(\text{Fe, Al})_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4 \text{H}_2\text{O}$, whose precipitation depends upon the amount of potassium dissolved during the manufacture of the acid; and those in superphosphoric acid are mostly iron and aluminum tripolyphosphates and metaphosphates. Addition of potassium salts to merchant-grade acid precipitates iron and, to a smaller extent, aluminum, but removal of the precipitate entails considerable loss of phosphate. The optical properties and x-ray patterns of the sludge components are presented.

THE sludges that precipitate in wet-process acid are composed of crystalline salts of the impurities that dissolve when phosphate rock is treated with sulfuric acid. Iron, aluminum, potassium, fluorine, and silica were the most important constituents of sludges recovered from acids from various sources. In addition to calcium sulfate, the principal constituents of these sludges were complex iron and aluminum phosphates, some of which contain potassium as an essential constituent, and sodium fluosilicate. The filtration and sedimentation characteristics of the sludges are governed by the rate of crystal growth of the principal sludge phase rather than by the chemical nature of the precipitating solids.

Solubilities in the aqueous systems of orthophosphoric acid and aluminum (5), ferric (2, 7, 11), and ferrous iron (8) are reported, and several iron and aluminum polyphosphates have been described (24). Some of the compounds described in these studies occur as components of sludges, but their characterizations were incomplete.

Precipitates from three concentrations of acid were examined: raw wet-process phosphoric acid, 12 to 14% P (28 to 32% P_2O_5); merchant-grade acid, 22 to 24% P (50 to 54% P_2O_5); and superphosphoric acid, 31% P (70% P_2O_5). The acids were obtained from several commercial and experimental sources and the details of their production usually

were not available. Many of the acids received for examination had been partially clarified, so that the relations between the amounts of the residual sludges and the total amounts formed in production of the acids are not known, but the precipitated compounds were generally the same in all acids.

The precipitates were examined petrographically and by x-ray. Many of the compounds were new, and, when possible, these were synthesized in crystal form suitable for determination of their chemical composition (Table I), optical properties (Table II), and x-ray diffraction patterns (Table III). In the chemical analyses, iron was determined by titration with dichromate (12), aluminum colorimetrically with 8-quinolinol (18), potassium by atomic absorption spectrophotometry (1), phosphorus gravimetrically with quinolinium (17), magnesium (9) and zinc (6) by EDTA titration, silicon gravimetrically with quinolinium (4), fluorine by distillation and titration (22), and sulfur gravimetrically as barium sulfate (13). Total water (of constitution and hydration) was determined by difference, and condensed phosphates were detected by infrared spectroscopy and determined quantitatively by ascending paper chromatography (23).

Raw Wet-Process Acid

The precipitates in raw wet-process phosphoric acid (12 to 14% P, 28 to 32%

P_2O_5) are largely sodium fluosilicate (usually with minor substitution of potassium for sodium) and calcium sulfate (anhydrous, hemihydrated, and dihydrated), with small amounts of calcium fluoride.

The compound with the empirical formula $\text{Ca}_2\text{SO}_4\text{SiF}_6\text{AlF}_6\text{OH} \cdot 12\text{H}_2\text{O}$ was detected in several raw acids, but never in merchant-grade acid. This compound, described in a patent on the clarification of phosphoric acid (14), is an isometric salt with an octahedral habit and a refractive index that make it indistinguishable from calcium fluoride, but it may be identified by x-ray or microchemical tests.

Merchant-Grade Acid

The solid phases in the sludges in most of the commercial merchant-grade acids (22 to 24% P, 50 to 54% P_2O_5) are mainly acidic iron and aluminum orthophosphates that contain potassium. Of these, the major portion is a mixture of members of the isomorphous series $(\text{Fe, Al})_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$. Secondary phases are calcium sulfate, calcium fluoride, and mixed crystals of sodium and potassium fluosilicates. These secondary phases usually constitute a small fraction of the sludge; their amounts vary with the fluorine content and history of the acid—precipitation of the secondary phases usually accelerates after most of the iron and aluminum has precipitated.

Table I. Composition of Precipitated Compounds

Compound	Composition, %					Moles/Mole P				
	Fe	Al	M ^a	P	H ₂ O ^b	Fe	Al	M ^a	H ₂ O ^b	
Fe ₃ KH ₁₄ (PO ₄) ₈ ·4H ₂ O	16.0	...	3.74	23.5	18.7	0.376	...	0.126	1.37	
Stoichiometric	15.90	...	3.70	23.53	18.6	0.333	...	0.125	1.37	
Al ₃ KH ₁₄ (PO ₄) ₈ ·4H ₂ O	...	8.4	3.74	25.4	21.4	...	0.380	0.117	1.45	
Stoichiometric	...	8.36	4.04	25.67	20.5	...	0.333	0.125	1.37	
Fe(H ₂ PO ₄) ₂ ·2H ₂ O	19.8	21.2	25.9	0.52	2.11	
Stoichiometric	19.60	21.70	25.2	0.50	2.00	
FeH ₃ (PO ₄) ₂ ·4H ₂ O	17.6	19.2	31.0	0.508	2.83	
Stoichiometric	17.43	19.30	30.9	0.500	2.75	
FeH ₉ (PO ₄) ₄	12.7	26.5	21.1	0.266	1.37	
Stoichiometric	12.60	27.86	18.2	0.250	1.13	
AlH ₃ (PO ₄) ₂ ·3H ₂ O	...	9.9	...	22.6	29.6	...	0.503	...	2.25	
Stoichiometric	...	9.85	...	22.62	30.1	...	0.500	...	2.25	
AlH ₃ (PO ₄) ₂ ·2H ₂ O	...	11.3	...	23.7	23.4	...	0.505	...	1.70	
Stoichiometric	...	10.59	...	24.23	24.6	...	0.500	...	1.75	
AlH ₃ (PO ₄) ₂ ·H ₂ O	...	11.3	...	26.0	19.2	...	0.498	...	1.28	
Stoichiometric	...	11.33	...	26.07	18.9	...	0.500	...	1.25	
Al(H ₂ PO ₄) ₃	...	8.3	...	28.6	18.9	...	0.334	...	1.14	
Stoichiometric	...	8.47	...	29.25	17.0	...	0.333	...	1.00	
FeH ₂ P ₃ O ₁₀	17.7	29.6	6.8	0.331	0.40	
Stoichiometric	17.99	29.91	5.8	0.333	0.33	
Al _{0.7} Fe _{0.3} H ₂ P ₃ O ₁₀	6.2	6.4	...	32.0	5.9	0.107	0.230	...	0.32	
Stoichiometric	6.38	6.09	...	31.95	6.2	0.111	0.222	...	0.33	
AlH ₂ P ₃ O ₁₀	...	9.5	...	32.7	7.1	...	0.332	...	0.38	
Stoichiometric	...	9.58	...	32.96	6.4	...	0.333	...	0.33	
AlH ₂ P ₃ O ₁₀ ·2H ₂ O	...	8.2	...	29.0	18.4	...	0.323	...	1.08	
Stoichiometric	...	8.52	...	29.25	16.9	...	0.333	...	1.00	
Fe _{0.46} Al _{0.53} (PO ₃) ₃	9.0	5.0	...	33.2	1.6	0.151	0.174	...	0.08	
Stoichiometric	9.31	5.19	...	33.57	0.0	0.153	0.177	...	0.00	
FeH ₂ P ₂ O ₇	23.8	26.6	8.4	0.495	0.54	
Stoichiometric	24.08	26.72	7.7	0.500	0.50	
MgH ₂ P ₂ O ₇	12.3	30.5	8.9	0.520	0.50	
Stoichiometric	12.18	30.95	9.0	0.500	0.50	
ZnH ₂ P ₂ O ₇	24.8	26.4	10.2	0.505	0.71	
Stoichiometric	25.71	27.07	7.5	0.500	0.50	

Compound	Composition, %					Mole/Mole F					
	Ca	Al	Si	F	S	H ₂ O ^b	Ca	Al	Si	S	H ₂ O ^b
Ca ₄ SO ₄ ·AlF ₃ SiF ₆ OH·-											
12H ₂ O	20.2	3.54	4.91	31.0	3.84	28.9	0.309	0.080	0.108	0.074	0.98
Stoichiometric	20.73	3.50	3.63	29.53	4.15	30.3	0.333	0.083	0.083	0.083	1.00

^a Metal other than Fe or Al.

^b Determined by difference when other constituents calculated as oxides.

A few sludges were observed that had abnormally high fluorine contents—20 to 40% F; these sludges were mixtures of (Fe,Al)₃KH₁₄(PO₄)₈·4H₂O and a complex isometric fluoride with a composition similar to that of ralstonite, NaMgAl₃F₁₂(OH)₆·3H₂O, and with the x-ray pattern reported for this mineral (ASTM 8-67). Ralstonite can vary widely in its proportions of sodium, magnesium, aluminum, and hydroxyl water without alteration of its isometric crystal form (16), and only slight shifts in the x-ray d-spacings. Its occurrence in a sludge indicates that the acid in which it forms is abnormally high in magnesium and aluminum as well as fluorine.

The major sludge phase, (Fe,Al)₃-KH₁₄(PO₄)₈·4H₂O, begins to precipitate when the concentration of the acid reaches a phosphorus content of 15% (35% P₂O₅) and to redissolve when the concentration is increased above 26% P (60% P₂O₅). It is most insoluble in

acid of merchant-grade concentration, and its solubility at any concentration increases with rising temperature.

Since potassium is a minor but essential constituent of this compound, a small amount of potassium in the phosphate ore has a marked effect on the formation of sludge. For example, each 0.1% of soluble potassium in an acid-grade phosphate rock that contains the usual amounts of iron and aluminum results eventually in the precipitation of about 80 pounds of the compound in the sludge in each ton of merchant-grade acid produced from the rock. Precipitation of this compound proceeds until the concentration of potassium in the acid is decreased to about 0.01%. Considerable iron and aluminum (2 to 3% R₂O₃) usually remain in solution after the supply of dissolved potassium is exhausted, and more of these metals can be precipitated by adding a soluble potassium salt to the acid.

The solubility of (Fe,Al)₃KH₁₄(PO₄)₈·4H₂O decreases as its iron content increases. The sodium analog of this compound (3) is hygroscopic and rather soluble; it was not detected in any of the sludges in wet-process acids. Although (Fe,Al)₃KH₁₄(PO₄)₈·4H₂O is relatively insoluble in water, it dissolves incongruently in dilute phosphoric acid with dissolution of potassium and precipitation of colloidal (Fe,Al)PO₄·nH₂O. It thus would be feasible technically, but perhaps not economically, to filter the sludge from the acid, wash the sludge with water, and add the potassium in the dilute acid washings to fresh acid to increase the precipitation of iron and aluminum.

The refractive indices of this compound decrease linearly with increasing substitution of aluminum for iron and can be used to show the composition of a sample. The x-ray diffraction patterns of the end members are nearly identical,

Table II. Morphological and Optical Properties of Precipitated Compounds

Compound	Crystal System, Class, and Habit	Refractive Indices	Optical Properties ^a
Fe ₃ KH ₁₄ (PO ₄) ₃ ·4H ₂ O	Orthorhombic, <i>mmm</i> . Hexagonal shaped tablets, sometimes elongated along <i>z</i>	$\alpha = 1.556$ $\beta = 1.600$ $\gamma = 1.606$	Biaxial (-), $2V = 30^\circ (38^\circ)$. OAP and $X \perp$ tabular plane. $\beta = 90^\circ$, $d. = 2.44$
Al ₃ KH ₁₄ (PO ₄) ₃ ·4H ₂ O	Orthorhombic, <i>mmm</i> . Hexagonal shaped tablets	$\alpha = 1.500$ $\beta = 1.528$ $\gamma = 1.531$	Biaxial (-), $2V = 30^\circ (36^\circ)$. OAP and $X \perp$ tabular plane. $\beta = 90^\circ$, $d. = 2.35$
Fe(H ₂ PO ₄) ₂ ·2H ₂ O	Monoclinic, <i>2/m</i> . Rod crystals elongated along <i>c</i> , modified by {110} and {101} and small {011}	$\alpha = 1.527$ $\beta = 1.558$ $\gamma = 1.587$	Biaxial (-), $2V = (83^\circ)$. OAP = (010). $Y = b$. $X \wedge c = 26^\circ$ in acute β . $\beta = 102^\circ$, $d. = 2.46$
FeH ₃ (PO ₄) ₂ ·4H ₂ O	Monoclinic, <i>2/m</i> . Prisms having prominent {110} and {111} with other modifications	$\alpha = 1.565$ $\beta = 1.615$ $\gamma = 1.617$	Biaxial (-), $2V = 22^\circ (22^\circ)$. OAP = (010). $Y = b$. $X \wedge c = 25^\circ$ in obtuse β . $\beta = 100^\circ$, $d. = 2.29$
FeH ₃ (PO ₄) ₄	Monoclinic, <i>2/m</i> . Prisms tabular on (100) modified by (011), (011), (011), and (011)	$\alpha = 1.566$ $\beta = 1.568$ $\gamma = 1.606$	Biaxial (+), $2V = 25^\circ (26^\circ)$. OAP = (010). $Y = b$. $X \wedge c = 30^\circ$ in acute β . $\beta = 103^\circ$, $d. = 2.43$
AlH ₃ (PO ₄) ₂ ·3H ₂ O	Hexagonal, probably rhombohedral, 3, 2. Truncated rhombic plates	$\epsilon \sim 1.543$ $\omega \sim 1.523$	Uniaxial (+). $E \perp$ plane of tabularity. $d. = 2.26$
AlH ₃ (PO ₄) ₂ ·2H ₂ O	Orthorhombic, <i>mmm</i> . Rod to needle crystals	$\alpha = 1.507$ $\beta = 1.520$ $\gamma = 1.530$	Biaxial (-), $2V = (82^\circ)$. OAP and $Z \parallel$ length. $d. = 2.32$
AlH ₃ (PO ₄) ₂ ·H ₂ O	Monoclinic, <i>2/m</i> . Blade crystals tabular on (100)	$\alpha = 1.548$ $\beta = 1.549$ $\gamma = 1.562$	Biaxial (+), $2V = (31^\circ)$. OAP \perp (010). $X = b$, $Z \wedge c \sim 13^\circ$. $d. = 2.53$
Al(H ₂ PO ₄) ₃	Hexagonal, <i>6/mmm</i> . Needles	$\epsilon \sim 1.506$ $\omega \sim 1.462$	Uniaxial (+), $E \parallel$ length. $d. = 2.19$
FeH ₂ P ₃ O ₁₀ , form II	Monoclinic, <i>2/m</i> . Prisms tabular on (001) modified by {110}	$\alpha = 1.624$ $\beta = 1.633$ $\gamma = 1.638$	Biaxial (-), $2V = 70^\circ (73^\circ)$. OAP \perp (010). $X \wedge a = 38^\circ$ in acute β . $Z = b$. $d. = 2.80$
(Al _{0.7} Fe _{0.3})H ₂ P ₃ O ₁₀ , form II	Monoclinic, <i>2/m</i> . (001) tablets modified by {110}	$\alpha = 1.575$ $\beta = 1.582$ $\gamma = 1.586$	Biaxial (-), $2V = (74^\circ)$. OAP = (010). $Y = b$, $Z \wedge a \sim 3^\circ$ in obtuse β . $\beta = 112^\circ$, $d. = 2.74$
AlH ₂ P ₃ O ₁₀ , form II	Monoclinic, <i>2/m</i> . Prisms tabular on (001) modified by {110} and small (101)	$\alpha = 1.546$ $\beta = 1.551$ $\gamma = 1.570$	Biaxial (+), $2V = (55^\circ)$. OAP = (010). $Z \wedge a \sim 30^\circ$ in acute β . $Y = b$. $\beta = 112^\circ$. $d. = 2.78$
AlH ₂ P ₃ O ₁₀ ·2H ₂ O	Orthorhombic, <i>mmm</i> . Plates tabular on the <i>X-Z</i> plane and elongated along <i>Z</i>	$\alpha = 1.506$ $\beta = 1.520$ $\gamma = 1.531$	Biaxial (-), $2V = (84^\circ)$. OAP = tabular plane. $d. = 2.59$
Fe _{0.46} Al _{0.53} (PO ₃) ₃	Monoclinic, <i>2/m</i> . Prisms tabular on (010)	$\alpha = 1.630$ $\beta = 1.634$ $\gamma = 1.650$	Biaxial (+), $2V = 50^\circ (54^\circ)$. OAP = (010). $Z \wedge c \sim 36^\circ$. $d. = 3.09$
(Fe,Al)(PO ₃) ₃	Cubic, trapezohedrons	$n_D = 1.545$ to 1.600 ^b	
FeH ₂ P ₂ O ₇	Monoclinic, rod crystals with prominent {110} terminated by {011}	$\alpha = 1.559$ $\beta = 1.579$ $\gamma = 1.589$	Biaxial (-), $2V = 70^\circ (70^\circ)$. OAP = (010). $Y = b$, $Z \wedge c \sim 3^\circ$ in acute β . $\beta = 97^\circ$, $d. = 2.87$
MgH ₂ P ₂ O ₇	Monoclinic, <i>2/m</i> . Rod crystals with prominent {110} terminated by {011}	$\alpha = 1.513$ $\beta = 1.532$ $\gamma = 1.545$	Biaxial (-), $2V = 75^\circ (78^\circ)$. OAP = (010). $Y = b$, $Z \wedge c \sim 9^\circ$ in acute β . $\beta = 98^\circ$. $d. = 2.58$
ZnH ₂ P ₂ O ₇	Monoclinic, <i>2/m</i> . Rods with prominent {110} terminated by (111), (111), (111), and (111)	$\alpha = 1.555$ $\beta = 1.579$ $\gamma = 1.588$	Biaxial (-), $2V = 70^\circ (67^\circ)$. OAP \perp (010). $Z \wedge c \sim 4^\circ$ in obtuse β . $X = b$. $\beta = 108^\circ$. $d. = 3.04$
Ca ₄ SO ₄ ·AlF ₆ SiF ₆ OH·12H ₂ O	Cubic, octahedral	$n_D = 1.435$	

^a Calculated values for $2V$ in parentheses. All values for densities calculated. ^b $n_D = 1.545$ in aluminum end member, increasing with substitution of iron; in usual salt in wet-process phosphoric acid, $n_D \sim 1.59$.

but small regular shifts occur in some of the reflections.

The compound (Fe,Al)₃KH₁₄(PO₄)₃·4H₂O forms pseudohexagonal plates when it precipitates slowly, as it usually does in cold merchant-grade acid in storage; when precipitated rapidly it forms rosette clusters of fragile scalar crystallites. Elevated temperature, a high degree of supersaturation, high ratios of iron to aluminum, and the presence of other impurities accelerate its precipita-

tion; when aluminum is high and iron is low the salt supersaturates and precipitates slowly. The ratio of iron to aluminum is always higher in the precipitate than in the acid, as shown in Table IV, and the rate of precipitation usually decreases as precipitation proceeds and the ratio of iron to aluminum in solution decreases. Although it does not enter into the composition of the precipitate, fluorine accelerates the precipitation, perhaps by complexing aluminum, which increases

the ratio of iron to aluminum and permits precipitation of a less-soluble, higher-iron form.

Another salt that appears in the sludge in merchant-grade acid is AlH₃(PO₄)₂·nH₂O; the dihydrate is found as a minor phase in acids unusually high in aluminum. Attempts to synthesize the dihydrate in simulated acids were unsuccessful; the trihydrate was obtained from room temperature to about 150°, and monohydrate at 150° or above.

Several salts were characterized that were not found in commercial wet-process acids but were prepared under conditions that may be encountered in the production of the acids. The salt $\text{FeH}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ precipitated from an acid containing 17% P, 1.4% Ca, and 1.4% Fe (40% P_2O_5 , 2% CaO , 2% Fe_2O_3). The hygroscopic salt $\text{FeH}_3(\text{PO}_4)_4$ precipitated abundantly when an acid containing 24% P and 3.5% Fe (54% P_2O_5 , 5% Fe_2O_3) was concentrated at 150° C. to 28% P (65% P_2O_5); the acid then contained 1.0% Fe (1.4% Fe_2O_3). The acid salt $\text{Al}(\text{H}_2\text{PO}_4)_3$ formed as a voluminous precipitate from a hot acid containing 25% P and 2.6% Al (58% P_2O_5 , 5% Al_2O_3). The acid ferrous phosphate $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ precipitates slowly from an acid containing 22% P and 3.5% Fe(II) (50% P_2O_5 , 4.5% FeO) as coarse pale green crystals which slowly discolor and finally decompose and dissolve in the acid as the result of autoxidation. When this reaction occurs in acids that contain potassium, pseudomorphs of $\text{Fe}_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$ precipitate as the oxidation of ferrous iron proceeds. Wet-process acids usually contain little ferrous iron, but iron may be dissolved in the ferrous state when the acid is handled in iron or steel equipment.

Superphosphoric Acids

When wet-process phosphoric acid is concentrated beyond a phosphorus content of 28% (65% P_2O_5), pyro-, tripoly-, and more highly condensed phosphoric acids appear and their concentrations increase with increase in concentration of the acid. Precipitates of iron and aluminum orthophosphates usually redissolve as the acid is concentrated, and salts of the condensed phosphoric acids begin to precipitate. Formation of these salts in superphosphoric acid can best be minimized by using clarified merchant-grade acid or by using high-grade phosphate rock in the preparation of the acid (19). The solids that form in superphosphoric acid prepared from unclarified merchant-grade acid, or in wet-process acids high in dissolved iron and aluminum, are difficult to settle because the precipitates are usually fine-grained crystallites and the acids are viscous.

In general, trivalent metals—iron and aluminum—are precipitated as tripolyphosphates or metaphosphates, but not as simple pyrophosphates. Divalent metals—calcium, magnesium, zinc, and ferrous iron—precipitate as acid pyrophosphates. Solid fluorides and fluosilicates are not encountered, since concentration of the acid to superphosphoric acid drives off most of the fluorine. The small amount of calcium sulfate dissolved in the feed acid usually precipitates as anhydrite.

Table III. Powder X-Ray Diffraction

<i>d</i> , A.	<i>l</i>	<i>d</i> , A.	<i>l</i>	<i>d</i> , A.	<i>l</i>
$\text{Fe}_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$, 1/2					
9.71	4	3.27	8	2.39	4
8.77	100	3.24	6	2.04	3
4.38	5	3.07	6	1.95	3
3.82	3	3.01	11	1.93	3
3.76	8	2.92	11	1.80	3
3.70	3	2.83	4	1.75	4
$\text{Al}_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$, 1/4					
9.71	2	3.20	4	2.38	2
8.77	100	3.04	6	2.15	1
4.35	7	2.99	11	1.944	2
3.76	4	2.93	14	1.916	1
3.73	8	2.82	2	1.795	2
3.71	11	2.71	1	1.759	1
3.26	6	2.39	2		
$\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, 1/2					
5.85	95	2.94	8	2.08	7
4.70	23	2.82	4	2.07	8
4.50	100	2.77	6	1.958	8
4.10	15	2.66	6	1.851	6
3.81	7	2.58	6	1.786	5
3.64	12	2.50	4	1.744	6
3.42	44	2.35	28	1.710	7
3.34	7	2.29	8	1.666	5
3.18	25	2.25	14	1.637	5
3.02	18	2.18	6	1.541	13
3.00	22	2.13	6		
$\text{FeH}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, 1/2					
7.20	100	3.20	11	2.36	5
5.56	7	2.98	3	2.29	6
5.23	29	2.95	4	2.09	8
4.85	40	2.91	5	2.08	13
4.08	7	2.77	33	2.03	8
3.79	4	2.64	7	1.790	5
3.60	7	2.62	6	1.680	5
3.44	10	2.45	5	1.620	8
3.32	40	2.43	6		
3.25	9	2.41	9		
$\text{FeH}_3(\text{PO}_4)_4$, 1/2^b					
8.86	37	3.06	55	1.835	5
6.13	100	3.02	8	1.728	8
4.71	12	2.92	27	1.710	5
4.03	5	2.40	5	1.694	4
3.74	11	2.34	5	1.570	5
3.64	29	2.32	6		
3.37	11	2.04	25		
$\text{AlH}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, 1/8					
8.73	15	2.60	7	1.845	3
7.12	16	2.44	8	1.778	6
5.81	31	2.38	5	1.753	6
4.52	28	2.36	7	1.709	7
3.95	3	2.25	7	1.697	3
3.82	7	2.16	3	1.661	4
3.55	100	2.11	9	1.636	4
3.18	3	1.942	4	1.596	4
2.92	22	1.932	6	1.537	5
2.90	35	1.910	5		
2.80	13	1.905	6		
$\text{AlH}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, 1					
8.31	100	3.55	25	2.36	14
7.77	39	3.46	50	2.29	4
6.21	28	3.33	16	2.19	5
5.66	6	3.15	65	2.11	6
4.56	5	3.10	32	2.07	5
4.36	4	2.85	9	1.93	19
4.17	8	2.79	19	1.90	8
4.08	19	2.73	13	1.83	8
3.96	75	2.61	12	1.80	5
3.89	25	2.46	3	1.76	3
3.76	24	2.43	3		
$\text{AlH}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, 1/2					
7.33	100	2.94	15	1.852	5
6.32	8	2.88	52	1.841	40
5.73	17	2.56	7	1.808	4
5.55	16	2.53	6	1.794	4

Patterns of Precipitated Compounds^a

d, A.	l	d, A.	l	d, A.	l
4.59	3	2.51	6	1.772	3
4.28	6	2.45	9	1.715	5
4.06	24	2.42	7	1.691	4
3.90	7	2.37	7	1.658	4
3.67	9	2.34	9	1.646	3
3.61	65	2.30	4	1.631	3
3.49	11	2.27	5	1.601	3
3.42	4	2.15	3	1.590	6
3.33	14	2.11	8	1.580	6
3.27	26	2.07	3	1.544	3
3.16	4	2.05	3	1.535	4
3.08	3	1.986	3		
2.98	9	1.966	3		
Al(H ₂ PO ₄) ₃ , 1/2 ^c					
6.87	100	2.61	17	1.933	4
4.28	6	2.34	2	1.900	3
4.03	40	2.29	5	1.794	3
3.96	13	2.18	3	1.647	2
3.64	5	2.14	2	1.613	3
3.21	10	2.11	2	1.600	2
3.10	10	2.08	2	1.589	2
2.79	2	2.02	4	1.572	3
2.67	7	1.980	7	1.560	2
FeH ₂ P ₃ O ₁₀ , form II, 1/2 ^d					
6.94	29	3.68	10	2.69	9
5.92	6	3.59	6	2.67	14
5.68	9	3.47	18	2.52	4
5.55	27	3.42	24	2.33	8
5.36	18	3.39	100	2.30	4
4.77	11	3.31	10	2.25	4
4.68	12	3.25	4	2.20	4
4.38	16	3.14	3	2.09	4
4.28	3	3.03	4	2.05	3
4.09	4	2.98	16	2.04	3
3.85	8	2.91	3	2.01	3
3.74	8	2.84	6		
(Al _{0.7} Fe _{0.3})H ₂ P ₃ O ₁₀ , form II, 1/2					
6.85	29	3.43	14	2.112	12
5.68	15	3.39	69	2.077	14
5.47	18	3.34	100	2.046	13
5.29	54	3.25	27	1.986	9
4.74	23	3.001	11	1.843	15
4.64	41	2.945	47	1.805	9
4.30	56	2.908	14	1.788	7
4.02	19	2.635	22	1.696	6
3.68	38	2.571	38	1.670	6
3.55	29	2.316	15		
AlH ₂ P ₃ O ₁₀ , form II, 1/2					
7.87	3	2.99	5	1.979	2
6.79	20	2.93	21	1.969	4
6.64	7	2.90	6	1.885	2
5.68	3	2.83	2	1.836	5
5.43	40	2.75	4	1.825	3
5.24	23	2.69	2	1.814	6
4.73	9	2.62	8	1.798	7
4.63	17	2.61	8	1.772	4
4.29	19	2.56	24	1.760	2
4.26	19	2.52	2	1.713	3
3.99	16	2.48	2	1.689	2
3.68	6	2.41	3	1.663	6
3.65	29	2.31	6	1.648	2
3.54	27	2.27	2	1.634	2
3.41	9	2.22	2	1.615	5
3.37	28	2.10	9	1.595	2
3.33	100	2.06	10	1.581	3
3.23	16	2.03	6	1.571	2
AlH ₂ P ₃ O ₁₀ ·2H ₂ O, 1/2					
10.25	5	3.48	9	2.32	7
8.72	3	3.31	26	2.24	2
7.91	100	3.12	13	2.10	2
5.78	8	3.08	17	2.04	2
4.91	37	3.04	7	1.980	2
4.46	26	2.92	5	1.933	3
4.04	3	2.81	28	1.808	5
3.99	4	2.64	7	1.796	5
3.95	5	2.50	11	1.684	2
3.86	5	2.46	4	1.634	3
Fe _{0.46} Al _{0.53} (PO ₃) ₃ , 1/2					
5.38	6	3.03	17	2.05	3

(Continued on page 32)

The most abundant constituents of the precipitates are members of the isodimorphous series, (Al,Fe)H₂P₃O₁₀; the dimorph usually found in superphosphoric acid is d'Yvoire's form II (24). In most precipitates the atomic ratio Al:Fe is about 2. When grown slowly, the crystals have the diamond-shaped monoclinic prismatic habit of the end members. X-ray diffraction patterns of the end members and intermediate compositions are nearly identical. The refractive indices of intermediate compositions decrease regularly as the composition shifts from the iron to the aluminum end member. Nucleation and growth of this phase in superphosphoric acid are promoted by localized overheating and long retention time during the concentration step.

Salts of the composition (Al,Fe)-H₂P₃O₁₀ are insoluble in hot mineral acids, aqua regia, and 30% hydrofluoric acid, but readily soluble in strong caustic. On standing in water or exposed to atmospheric moisture they hydrolyze slowly to iron and aluminum acid orthophosphates; on standing at room temperature in superphosphoric acid they hydrate slowly to (Al,Fe)H₂P₃O₁₀·2H₂O.

When the superphosphoric acid has been locally overheated above the usual temperature of about 280° C., or when the average retention time at the usual temperature is longer than about 15 minutes, iron and aluminum precipitate also as metaphosphates, (Al,Fe)(PO₃)₃. Dimorphic forms of these salts—cubic and monoclinic—have been observed in wet-process superphosphoric acids. Aluminum tends to precipitate as cubic (Al,Fe)-(PO₃)₃ in which the atomic ratio Al:Fe is 4 or more. Iron tends to precipitate as yellow monoclinic (Fe,Al)(PO₃)₃ in which the atomic ratio Al:Fe may approach unity. Both forms of these metaphosphates frequently are present in the same acid.

No simple aluminum or ferric iron pyrophosphates were observed in this study. d'Yvoire (24) reported two iron and aluminum pyrophosphates, but these were precipitated from acid solutions that contained about 20% iron or aluminum oxide. The absence of iron and aluminum pyrophosphates may be attributed to the solubilities of these salts, or to sequestering or complexing of the metals, in superphosphoric acids. The metaphosphates could not be dissolved for chromatographic analysis, but their optical and x-ray properties agree with those reported for the metaphosphates (20, 24).

Simulated superphosphoric acid containing 31% P (70% P₂O₅) can dissolve large amounts of iron and aluminum, but on strong heating or further concentration these metals reprecipitate as tripolyphosphates and metaphosphates. Upon dilution of the unheated acid, iron precipitates as FeH₂(PO₄)₄ or FeH₃-

Table III. Continued

<i>d</i> , Å	<i>l</i>	<i>d</i> , Å	<i>l</i>	<i>d</i> , Å	<i>l</i>
5.20	5	2.98	3	2.004	7
4.60	3	2.90	6	1.945	3
4.38	3	2.83	7	1.917	5
4.24	3	2.76	5	1.883	5
3.83	100	2.69	11	1.816	4
3.73	7	2.42	5	1.736	4
3.63	8	2.40	8	1.691	5
3.53	5	2.35	3	1.631	3
3.38	21	2.30	3	1.608	6
3.22	5	2.25	3		
3.14	5	2.20	5		
(Fe,Al)(PO ₃) ₃ , cubic, 1/2					
9.22	15	2.71	22	1.954	5
5.65	25	2.52	10	1.918	5
4.89	13	2.37	19	1.881	13
4.37	100	2.24	14	1.756	7
3.69	48	2.19	7	1.677	8
3.46	58	2.13	5	1.631	9
3.09	24	2.04	3	1.608	13
2.95	30	1.994	5		
FeH ₂ P ₂ O ₇ , 1/2					
7.26	100	3.26	18	2.39	4
6.38	7	3.19	6	2.35	4
5.82	3	3.10	8	2.21	4
4.42	8	3.02	3	2.13	5
4.23	16	2.90	4	2.11	5
3.87	6	2.83	3	2.06	4
3.77	3	2.79	13	2.02	4
3.63	6	2.77	10	1.97	6
3.55	6	2.58	6	1.75	5
3.47	11	2.42	4		
MgH ₂ P ₂ O ₇ , 1/2					
7.49	10	3.06	38	1.910	4
7.16	100	2.85	11	1.860	3
6.38	11	2.78	41	1.817	4
4.83	8	2.72	14	1.787	4
4.63	4	2.56	11	1.753	7
4.33	92	2.47	5	1.737	6
4.21	62	2.39	4	1.718	4
3.87	19	2.37	5	1.689	4
3.74	23	2.31	5	1.656	3
3.53	19	2.21	6	1.634	8
3.43	41	2.13	4	1.610	8
3.21	53	2.10	13	1.567	7
3.19	22	1.989	12		
3.14	8	1.949	11		
ZnH ₂ P ₂ O ₇ , 1/2 ^c					
8.37	10	2.87	4	2.07	2
7.21	100	2.84	5	2.00	4
6.34	6	2.78	17	1.957	6
5.00	2	2.74	5	1.916	2
4.88	2	2.63	2	1.903	2
4.66	2	2.57	7	1.827	2
4.38	6	2.44	4	1.801	2
4.21	21	2.40	3	1.775	2
3.85	7	2.37	2	1.750	3
3.60	5	2.34	2	1.734	4
3.45	8	2.32	3	1.616	4
3.23	17	2.19	4	1.574	3
3.07	8	2.11	5		
Ca ₄ SO ₄ AlF ₆ SiF ₆ OH.12H ₂ O, 1/2					
9.60	100	2.55	16	1.82	11
5.90	33	2.40	2	1.78	2
5.03	17	2.34	6	1.75	3
4.17	13	2.23	13	1.71	3
3.83	7	2.17	19	1.68	3
3.41	6	2.09	1	1.64	2
3.21	20	2.02	2	1.61	3
2.95	3	1.97	3	1.56	2
2.82	9	1.93	4	1.50	3
2.64	10	1.87	1		

^a Patterns obtained with Geiger counter x-ray diffractometer, CuK_α radiation, λ = 1.5405 Å. Numbers following formula denote scanning rate, degrees 2θ/min. Intensities measured as peak heights above background and expressed as per cent of strongest line.

^b Material is hygroscopic; data obtained in air and sample holder repacked every 20° 2θ. Only strongest lines given.

^c Material hygroscopic; pattern obtained from sample protected by 0.5-mil plastic film.

^d Unit cell parameters: a = 12.36, b = 8.64, c = 7.28; β = 112° 56', d. = 2.71; space group is C₂h—P2_{1/a} with z = 4.

Table IV. Composition of Successive Crops of (Fe,Al)₃KH₁₄(PO₄)₈·4H₂O Precipitated from Simulated Wet-Process Phosphoric Acids Prepared from Reagent-Grade Chemicals

Initial acid	Mole Ratio Fe ₂ O ₃ :Al ₂ O ₃ in Salt, (Fe,Al) ₃ KH ₁₄ (PO ₄) ₈ ·4H ₂ O		
	First crop	Second crop	Third crop
No Fluoride in Acid			
1.91	5.25	4.64	0.86
1.29	3.69	2.11	1.67
0.64	1.87	0.91	2.52
0.31	0.58	0.47	0.45
Fluoride Present in Acid			
1.91	7.61	5.85	12.50
1.29	5.05	4.21	5.60
0.64	2.44	2.79	2.75
0.31	2.37	2.14	2.08

(PO₄)₂·4H₂O, and aluminum as Al-(H₂PO₄)₃ or AlH₃(PO₄)₂·nH₂O in which n is 1, 2, or 3. Hence, dissolved or "sequestered" iron and aluminum which may be soluble in superphosphoric acid can be troublesome in subsequent uses of the acid.

A pyrophosphate frequently found in wet-process superphosphoric acid is (Mg,Fe)H₂P₂O₇ in which the atomic ratio Mg:Fe is about 3, but neither magnesium nor ferrous iron contributed significantly to the phosphate precipitates in merchant-grade acid. X-ray diffraction data indicate that zinc also may substitute in the isomorphous series to which this compound belongs. Both ZnH₂P₂O₇ and CaH₂P₂O₇ have been observed as precipitates in superphosphoric acids containing dissolved zinc and calcium. In acids heated no higher than 200° C., zinc precipitated as ZnH₂P₂O₇; at higher temperatures, a hygroscopic zinc salt was obtained whose composition has not been determined.

Discussion

The solid phases that form in wet-process phosphoric acids are composed of crystalline precipitates of three types, each of which is characteristic of a particular concentration range—raw acid (12 to 14% P, 28 to 32% P₂O₅), merchant-grade acid (22 to 24% P, 50 to 54% P₂O₅), or superphosphoric acid (more than 31% P or 70% P₂O₅).

The precipitates in raw acid are mostly calcium sulfate, sodium fluosilicate, and occasionally more complex fluosilicates. The amount of calcium sulfate is determined by process conditions and the resultant degree of hydration of the salt. Treatment of the acid with sodium salts would increase the precipitation of fluosilicate and leave less fluorine in the acid (75). On the other hand, addition of fluosilicate would precipitate sodium and potassium as (Na,K)₂SiF₆ and so decrease the formation of sludge when the acid

Table V. Removal of Iron and Aluminum from Commercial Merchant-Grade Acids by Addition of Potassium

Acid	Composition, %							
	Before Treatment				After Treatment			
	Al	Fe	Al ₂ O ₃	Fe ₂ O ₃	Al	Fe	Al ₂ O ₃	Fe ₂ O ₃
A	0.8	1.3	1.5	1.8	0.6	0.19	1.2	0.27
B	0.4	0.6	0.7	0.8	0.4	0.31	0.8	0.44
C	0.9	0.8	1.7	1.2	0.8	0.27	1.5	0.38
D	1.0	0.3	1.8	0.4	1.0	0.16	1.8	0.23
E	0.3	1.0	0.5	1.4	0.5	0.36	1.0	0.52
F	0.6	0.8	1.1	1.1	0.6	0.36	1.2	0.51

was concentrated to merchant grade (70). Neither of these treatments, however, removes any iron or aluminum, the impurities that are most troublesome in subsequent processing of the acid.

Concentration of the acid to merchant grade results in precipitation of (Fe,Al)₃-KH₁₄(PO₄)₈.4H₂O and smaller amounts of other iron and aluminum acid orthophosphates. The predominance of the complex potassium salt in sludge formation in merchant-grade acid shows the controlling effect of potassium on the formation of sludge and indicates that addition of potassium salts to this acid would increase the precipitation of iron and aluminum.

On further concentration to superphosphoric acid, suspended iron and aluminum orthophosphates dissolve, and the metals reprecipitate as highly insoluble tripolyphosphates and metaphosphates. The amount that precipitates depends on the retention time during concentration, localized overheating, and the amount of dissolved metals. Any iron and aluminum that remains dissolved in the superphosphoric acid may form troublesome sludges when the acid is treated with potassium salts or ammonia in its processing into fertilizer; compounds in the isomorphous series (Fe,Al)(NH₄,K)P₂O₇ then are precipitated.

Since the major constituents of the troublesome sludges are iron and aluminum, it is desirable to remove these metals from the acid as early in its production as is convenient. Addition of potassium salts during the concentration to merchant-grade acid appears to be a feasible method of precipitating iron and aluminum.

In a test of this treatment, a simulated acid containing 24% P, 1.7% Fe, and 1.3% Al (55% P₂O₅, 2.5% Fe₂O₃, 2.5% Al₂O₃) was treated with 105% of the amount of potassium sulfate, chloride, or orthophosphate required to form (Fe,Al)₃KH₁₄(PO₄)₈.4H₂O with all the iron and aluminum. Care was taken that seed crystals or foreign nuclei were not present initially, and duplicate mixtures were allowed to stand at room temperature and at 70° C. Temperature affected only the rate and not the extent

of precipitation, and in each mixture 90% of the iron and 30 to 35% of the aluminum were precipitated. Precipitation began in 1.5 hours at room temperature and required 24 hours for completion, whereas precipitation began in 15 minutes at 70° C. and was complete in 3 hours. At either temperature, seeding and agitation would have accelerated the precipitation markedly. The anion of the potassium salt had no significant effect on the precipitation at 70° C., but at room temperature fluoride and sulfate each tend to accelerate the precipitation.

To test the potassium treatment with commercial acids, six merchant-grade acids that contained the usual impurities were allowed to stand until precipitation of sludge had ceased; the potassium content of each acid was then less than 0.01% K. To 100 ml. of each acid there was then added 0.5 gram of potassium as KH₂PO₄, and each acid was mixed thoroughly and allowed to stand for 4 days at room temperature. Each acid was filtered, and the filtrates were analyzed; all the precipitated solids were shown petrographically to be (Fe,Al)₃-KH₁₄(PO₄)₈.4H₂O. As shown in Table V, potassium was effective in precipitating iron but had little effect on the aluminum.

Removal of the sludge, which is mainly (Fe,Al)₃KH₁₄(PO₄)₈.4H₂O, entails loss of phosphorus from the acid. Increasing the amount of sludge by addition of potassium to precipitate more iron and aluminum increases the phosphorus loss significantly and creates a disposal and recovery problem.

This precipitate may be suitable for use as fertilizer without further processing since its phosphorus is soluble in both neutral and alkaline ammonium citrate solution. It can be partially dehydrated at 100° C. to a material containing 26% P (60% P₂O₅) without adversely affecting the citrate solubility of the phosphorus. It can be dehydrated further at 400° C. to a material containing 30% P (69% P₂O₅) which also is soluble in alkaline ammonium citrate.

The salt (Fe,Al)₃KH₁₄(PO₄)₈.4H₂O hydrolyzes in water to release potassium phosphate and phosphoric acid and leave

a residue of colloidal (Fe,Al)PO₄.nH₂O; this colloidal material has been shown to be available to growing plants (27). Results of preliminary greenhouse tests of laboratory preparations of the aluminum and iron end members of (Fe,Al)₂-KH₁₄(PO₄)₈.4H₂O showed them to be equal to concentrated superphosphate as sources of phosphorus for growing plants.

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