Determination of Soluble Species and Precipitates of Aluminum Phosphate

Tanhum Goldshmid[a]; Alan J. Rubin[a]

[a] WATER RESOURCES CENTER, COLLEGE OF ENGINEERING THE OHIO STATE UNIVERSTTY, COLUMBUS, OHIO

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TANHUM GOLDSHMID and ALAN J. RUBIN*

WATER RESOURCES CENTER
COLLEGE OF ENGINEERING
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO 43210

Abstract

The interaction between aluminum(III) and orthophosphate salts was studied. The investigation involved the direct measurement of phosphate remaining in solution after precipitation with different applied concentrations of aluminum(III) at varying pH, the establishment of the pH limits of precipitation as determined from light-scattering measurements taken at varying P to Al ratios, and alkametric potentiometric titrations with subsequent computer analysis using the program SCOGS. Several soluble species and their formation constants were determined. Solid phases identified included $AlPO_4(s)$, $Al_3(OH)_3(PO_4)_2(s)$, and $Na_3Al_5H_6(PO_4)_8(s)$.

INTRODUCTION

Aluminum salts are used extensively for the clarification of raw water for drinking purposes and in physical-chemical wastewater treatment processes for suspended solids removal and phosphate precipitation. Because the chemical interactions between aluminum and phosphate have not been fully described, particularly with respect to the solubility of the condensed phase in metastable solutions, it has been difficult to develop a rational model of phosphate precipitation using aluminum salts. Furthermore, since the ability of aluminum to coagulate suspended solids and to precipitate phosphate are interrelated, it is evident that the

*To whom correspondence should be addressed.

aluminum phosphate system must be understood in order to achieve higher efficiencies and a better control of wastewater treatment processes.

In contrast to the relatively simple and well-defined aqueous reactions of the orthophosphate ion, those of aluminum(III) are more complicated since they involve both mononuclear and polynuclear ionic species as well as insoluble phases. The free, unhydrolyzed metal ion, Al^{3+}, which exists only at very low pH, is highly hydrated, octahedrally coordinating six water molecules. As the pH increases, the hydrated aluminum ion hydrolyzes, yielding soluble and insoluble hydroxy-aluminum products. Some of these are well characterized while the stoichiometry of others is more speculative, being based on somewhat circumstantial evidence.

The interaction between aluminum(III) and phosphate in acid solutions has been studied by many investigators (e.g., *1-5*). In general, the complexes have been reported to have the stoichiometry $Al(H_2PO_4)_x^{(3-x)+}$ in which x ranges between 1 and 3 depending on the ratio of the applied concentrations of aluminum and phosphate (*1*). In addition, these complexes dissociate to yield phosphato-aluminum complexes of the type $AlH_y(PO_4)_x^{(3+y-3x)+}$ in which y ranges from 1 to $2x$ depending on pH.

A large number of aluminum phosphate solid phases have been identified, the majority by x-ray diffraction of natural samples. However, only a few of those solid phases have been reproduced experimentally. Among these have been variscite, $Al(OH)_2H_2PO_4(s)$, and sterrettite, $(Al(OH)_2)_3HPO_4H_2PO_4(s)$, identified by Cole and Jackson (*5*). Variscite is essentially the hydrated form of the teritary salt, $AlPO_4(s)$. The existence of a family of minerals in nature, known as the taranakites, $M_3Al_5H_6(PO_4)_8 \cdot 18H_2O(s)$, where M is any monovalent ion including ammonium analogs, has been shown in the laboratory (*8*).

The objective of this research was to examine the interaction between aluminum(III) and phosphate over a wide range of concentrations and pH to develop a rational model for the system in metastable solution. The solubility of aluminum-phosphate precipitates was studied as a function of the aluminum, phosphate, and hydrogen ion concentrations to define the equilibrium reactions between soluble species and insoluble phases. Also identified were the soluble and insoluble products of the reactions between aluminum(III) and phosphate, and their concentration distribution over a wide range of P and Al concentrations and pH was determined. The study was limited to pure systems of well-defined solutions. No dispersed solid phases were present other than those precipitated through the interaction between aluminum and phosphate or as a result of changing the pH.

EXPERIMENTAL

Preparation of Solutions

Stock nitric acid solutions were prepared by diluting the concentrated reagent acid and were standardized titrametrically against tris(hydroxymethyl)aminomethane. End points were detected potentiometrically as were all the other determinations unless otherwise stated. Stock base solutions were prepared from sodium or potassium hydroxide pellets and were standardized by titration with the standard acid. Aluminum nitrate stock solutions were prepared in concentrations greater than 0.1 M to prevent hydrolysis and subsequent aging. Diluted working solutions of the metal salt were prepared as needed just prior to each experiment. The concentrations of the aluminum(III) solutions were determined by alkalimetric titrations, or colorimetrically using calgamite as the chromogenic reagent in an extraction procedure (9). The method was found to be virtually unaffected by the presence of phosphate. Reproducible results were obtained even when the phosphate concentration was a thousand times greater than that of the metal. The extraction process was carried out in 250-mL separatory funnels instead of vials as proposed in the original method. This modification allowed the determination of soluble aluminum in very dilute solutions by taking larger volumes for the analysis. The absorbance of the uncomplexed calgamite reagent increases with its concentration and with decreasing wavelength. Readings were taken at 602.5 nm instead of at 550 nm as originally reported to minimize the absorbance of the uncomplexed dye.

Phosphate solutions were standardized by alkalimetric titrations or colorimetrically using the modified ascorbic acid-molybdate method (10). The molar absorbtivity of the colored complex was calculated to be 29,800 at 890 nm. Sodium nitrate solutions were prepared by dissolving accurately weighed quantities of the dried reagent grade salt. Determination of the sodium ion content of the solutions was by atomic absorption spectrophotometry.

Solubility Studies

Stock solutions containing known concentrations of aluminum nitrate and sodium dihydrogen phosphate were split into 100-mL aliquots and stored in 4-oz polyethylene bottles. The pH's of the solutions were

systematically varied with sodium hydroxide solution, and the samples were shaken for 24 h in a mechanical shaker at room temperature. The solutions were vacuum filtered through 0.2 μm microporous membrane filters, and the filtrates were examined for the absence of precipitate by comparing their light-scattering intensities to that of distilled-deionized and membrane-filtered water. The samples were refiltered if precipitate was detected. The filtrates were then anlyzed for aluminum or phosphate, as required, and their pH's measured. Figure 1 shows a typical plot of residual soluble phosphate concentration against pH. The results displayed were obtained from solutions containing applied concentrations of aluminum nitrate and sodium dihydrogen phosphate of 1.0×10^{-3} M.

The precipitates were washed 5 times with 5 mL distilled water and were dried in a dissector over calcium sulfate (Drierite) to constant weight. Samples of approximately 50 mg were accurately weighed and dissolved with 2 mL of 1 M nitric acid in 50-mL volumetric flasks on a hot plate. The solutions were cooled and diluted to the mark with distilled water, and aliquots were taken for aluminum and phosphate analysis. Aluminum phosphate precipitate was also prepared by the procedure for taranakite described by Taylor and Gurney (8). Dried and ground 500-mg
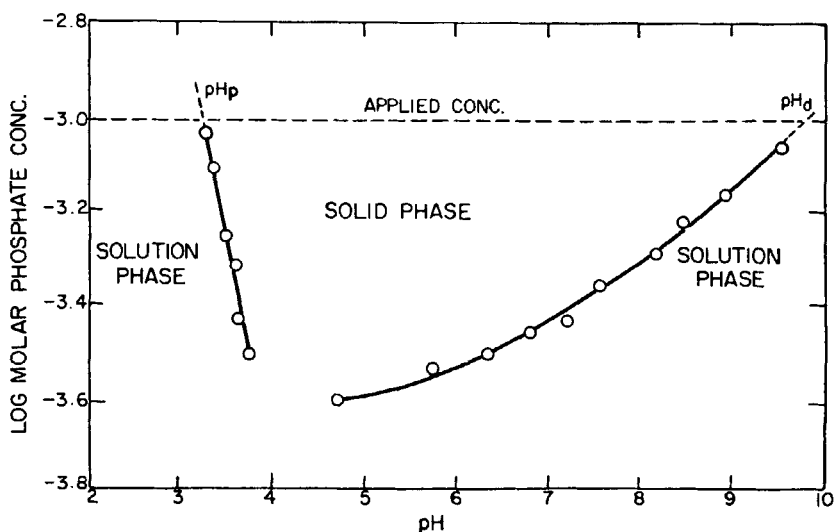
FIG. 1. Soluble phosphate concentration–pH curve for 1×10^{-3} M aluminum nitrate and 1×10^{-3} M sodium dihydrogen phosphate solutions.

samples were equilibrated with 100-mL solutions of varying alumi-num(III) phosphate, sodium, and hydrogen ion concentrations. These components were determined in the supernatants weekly until two successive measurements were identical.

Ligh-Scattering Studies

Light scattering was used to detect the formation of solid phase upon adding aluminum(III) to phosphate. Scattering intensities were measured with unfiltered light at 90° to the incident light with a nephelometer. The measurements are expressed as relative scattering units on a 0 to 100 scale. The solutions were placed in round 19 × 105 mm cuvettes which were previously matched to within 0.5 relative scattering units with distilled water. The nephelometer was calibrated wtih turbidity standards of relative scattering values ranging between 0 and 81. A series of samples, each containing the same concentrations of aluminum nitrate, sodium dihydrogen phosphate, and sodium nitrate, were prepared for each experiment. The pH was systematically varied with sodium hydroxide or nitric acid as needed, and the solutions were brought to a
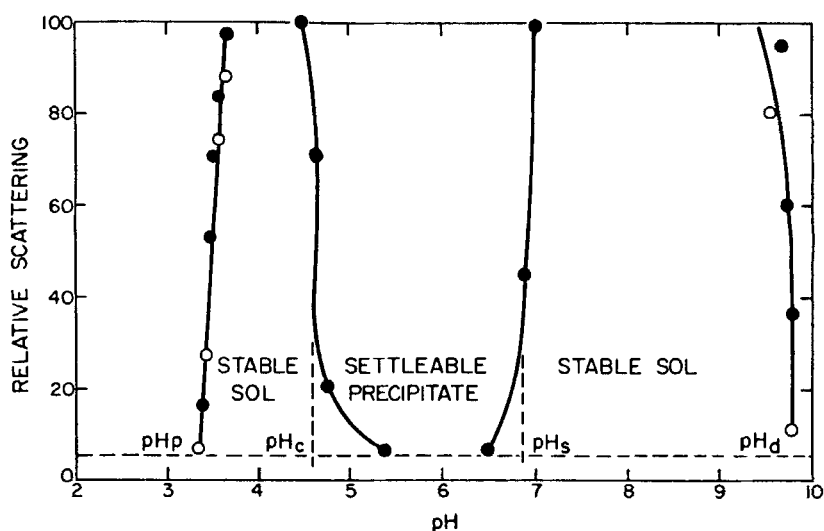

FIG. 2. Relative scattering–pH curve for 1×10^{-3} M aluminum nitrate and 1×10^{-3} M dihydrogen phosphate solutions. (O) 1-h data. (●) 24-h data.

constant volume of 10 mL with distilled water. The cuvettes were stoppered, vigorously mixed for 30 s, and left undisturbed for 60 min before being measured for pH and scattering intensity. The same measurements were repeated after incubation for 24 h but without further agitation. A typical relative scattering–pH curve for equal applied concentration of 1×10^{-3} M aluminum nitrate and sodium dihydrogen phosphate is shown in Fig. 2. The results were used to obtain the limiting pH of precipitation (denoted as pH_p) and dissolution (pH_d) which define the boundary of precipitation or the conditions under which the applied concentrations of the reactants are in equilibrium with the precipitate. This was accomplished by extrapolating the steepest segment of the curve back to the initial scattering value.

EXPERIMENTAL RESULTS

Excess Aluminum in Acid Solutions

The solubility limits, pH_p, for aluminum phosphate precipitates in acid solutions were determined by light scattering. The results were obtained at several applied phosphate concentrations over the range of 1×10^{-5} to $1 \times 10^{-2} M$, each in the presence of three applied metal concentrations of 1×10^{-2}, 1×10^{-3}, and $5 \times 10^{-4} M$. The results are summarized in Table 1 and plotted in Fig. 3 in terms of the logarithm of applied phosphate concentration against pH. Each of the data points marked by a square above pH 3 represents the average of three critical pH values. As indicated by Table 1, these pH values were almost identical, although each was determined in the presence of a differently applied aluminum(III) concentration.

The precipitation boundary so determined consisted of four linear segments. Three segments were found within the lower end of the pH range examined, indicating that the values of the critical pH of precipitation are dependent on the applied concentrations of both aluminum(III) and phosphate. As the pH increased, the segments converged into a straight line where the pH_p were independent of the applied concentration of the metal. The slopes and intercepts of the various segments were calculated by least squares. The slope and intercept of the common boundary of precipitation were -1.86 and 3.37, respectively, whereas those calculated for the segment that corresponds to applied aluminum(III) concentration of 1×10^{-2} M and within the concentrations range of phosphate of 1×10^{-2} and $1 \times 10^{-3} M$ were -1.36

TABLE 1

Summary of Critical pH of Precipitation Values as a Function of the Applied Concentrations of Aluminum Nitrate and Sodium Dihydrogen Phosphate

| Concentration, log $[NaH_2PO_4]$ | Concentration, log $[Al(NO_3)_3]$ | | | Average pH_p |
| | pH_p | | | |
	-2.00	-3.00	-3.30	
-5.00	4.37	4.39	4.40	4.39
-4.70	4.23	4.24	4.24	4.24
-4.52	4.17	4.17	4.15	4.16
-4.30	4.06	4.06	4.03	4.06
-4.00	3.90	3.87	3.85	3.87
-3.70	3.66	3.71	3.69	3.69
-3.52	3.53	3.60	3.57	3.57
-3.30	3.47	3.45	3.45	3.46
-2.70	3.12	3.16	3.36	3.30
-2.70	3.12	3.16	3.36	3.14^a
-2.52	2.95	3.14	3.37	
-2.30	2.74	3.14	3.37	
-2.00	2.52	3.21	3.38	

^{a}An average of two critical pH values.

and 0.40, respectively. The remaining pair of segments was nearly vertical to the pH axis, indicating that the critical pH points were independent of the applied phosphate concentration.

The absolute value of the slope of the boundary of precipitation decreased with pH and with increased applied phosphate concentration. If the slope is indicative of the charge of the ionic species in equilibrium with the precipitate, then there must be at least two phosphato-aluminum species in equilibrium with the precipitate because of the two calculated slopes of the precipitation boundaries. The first is dominant in the very low pH region whereas the second complex is formed within the upper end of the examined pH range of this boundary.

The boundary of precipitation of aluminum phosphate solid phases was also studied by measuring the concentration of soluble phosphate remaining after 24 h of mixing and upon separating the precipitate from the solution. The results are shown in Table 2. The slope, intercept, and standard deviation of the regression line were calculated to be -2.01, 3.64, and 0.08, respectively. In general, there is a good agreement between the parameters of the regression line and those of the common segment of the boundary of precipitation shown in Fig. 3, although the data points
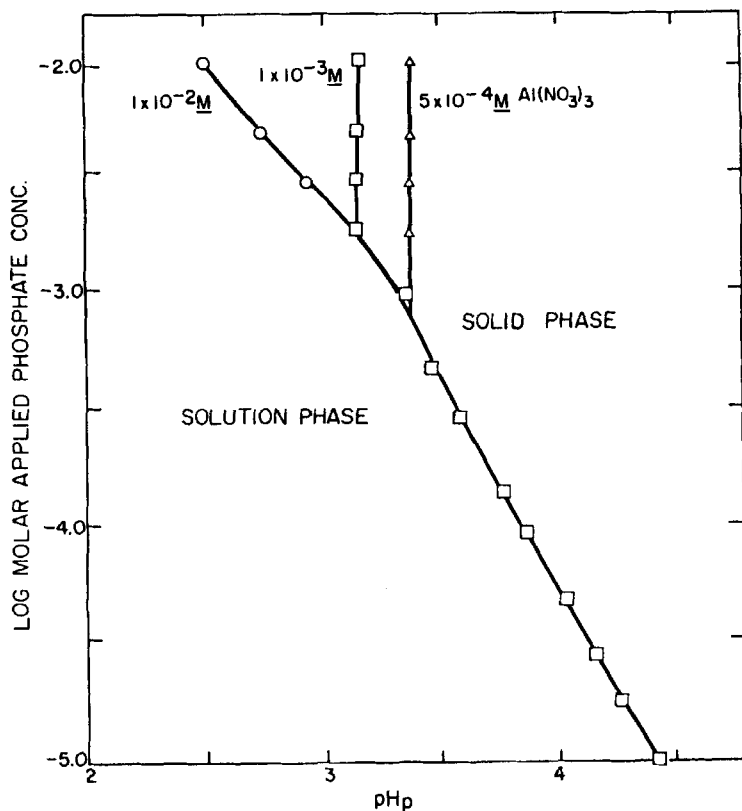
FIG. 3. Solubility limits of aluminum phosphate precipitate as a function of pH and applied phosphate concentration at three applied aluminum nitrate concentrations.

were obtained by different analytical approaches. The smaller values calculated for the slope of the common boundary of precipitation are due apparently to the shift of the critical pH points of precipitation, corresponding to the lower end of the phosphate concentration range, toward a higher pH range. The amount of precipitate formed at the true boundary of precipitation was apparently insufficient to be detected by the nephelometer. Consequently, the lower end of the precipitation boundary was shifted toward a higher pH range where more precipitate was formed.
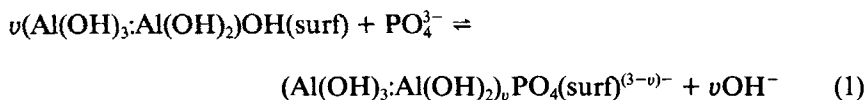
TABLE 2

Solubility of Phosphate in Acid Solutions as a Function of pH and Applied Concentration of Aluminum Nitrate

Applied aluminum concentration							
$2 \times 10^{-3}\,M$		$3 \times 10^{-3}\,M$		$5 \times 10^{-3}\,M$		$1 \times 10^{-2}\,M$	
$-\log [P]_s$	pH	$-\log [P]_s$	pH	$-\log [P]_s$	pH	$-\log [P]_s$	pH
3.02	3.31	3.02	3.34	3.14	3.45	3.80	3.81
3.06	3.35	3.11	3.40	3.38	3.57	4.53	4.20
3.14	3.39	3.23	3.48	3.72	3.74	4.89	4.31
3.23	3.44	3.41	3.56	4.03	3.95	4.85	4.39
3.34	3.49	3.63	3.64	4.31	4.25		
3.49	3.58	3.90	3.80	4.34	4.35		
3.59	3.62	4.16	3.93	4.42	4.38		
3.85	3.74	4.38	4.04				
		4.62	4.14				
		4.95	4.22				
		5.29	4.35				

Excess Aluminum in Alkaline Range

The concentrations of soluble phosphate in high pH solutions containing excess aluminum(III) remaining after precipitation and subsequent filtration through a membrane filter were determined colorimetrically. Typical results obtained after 24 h of mixing are shown in Fig. 1. The solubility of phosphate in the alkaline range increased with pH and decreased with increased applied aluminum(III) concentration.

Since the soluble concentration of phosphate was dependent on the amount of precipitate present, its adsorption onto the solid phase surface is suggested. The mathematical treatment developed by Kurbatov et al. (*11*) in studies of the sorption of cobalt on ferric hydroxide was used to analyze the solubility data. The mathematical model assumes that adsorption can be described quantitatively by the mass action law. Thus, the sorption of phosphate by aluminum hydroxide can be represented by

$$v(Al(OH)_3 \text{:} Al(OH)_2)OH(surf) + PO_4^{3-} \rightleftharpoons$$

$$(Al(OH)_3 \text{:} Al(OH)_2)_v PO_4(surf)^{(3-v)-} + vOH^- \qquad (1)$$

where $(Al(OH)_3:Al(OH)_2)OH(surf)$ and $(Al(OH)_3:Al(OH)_2)_vPO_4(surf)^{(3-v)-}$ are the free and the phosphate-sorbed surfaces, respectively. The mass action expression is given by

$$K_{ad} = \frac{[(Al(OH)_3:Al(OH)_2)_vPO_4(surf)^{(3-v)-}][OH^-]^v}{[(Al(OH)_3:Al(OH)_2)OH(surf)]^v[PO_4^{3-}]} \qquad (2)$$

According to Kurbatov's model, Eq. (2) can be simplified by assuming that the concentration of the phosphate-sorbed surface is equal to the amount of phosphate sorbed, and that the concentration of the free surface is a linear function of the applied aluminum concentration. Introducing these assumptions into Eq. (2), substituting $[P]_s\alpha_3$ for $[PO_4^{3-}]$ and $K_w/[H^+]$ for $[OH^-]$, taking logarithms, and rearranging into a linear form gives

$$\log \frac{\Delta P}{[P]_s\alpha_3} = -v pH + \log \frac{K_{ad}(Q[Al]_t)^v}{K_w^v} \qquad (3)$$

where ΔP is the amount of phosphate sorbed given by $([P]_t - [P]_s)$, the difference between the applied and soluble phosphate concentrations, α_3 is the distribution coefficient for PO_4^{3-}, $[Al]_t$ is the applied aluminum concentration, and Q is a coefficient of linearity. Plots of Eq. (3) are shown in Fig. 4. The slopes and intercepts were calculated by the method of least squares and the results are given in Table 3. These results indicate that the slope of the lines increases with the applied concentration of the metal. This in turn suggests that the activity of the sorbent depends on the amount of phosphate sorbed. If ΔP is very small compared with $Q[Al]_t$, the magnitude of ΔP will not affect the value of the slope since the activity of the sorbent is apparently unchanged by sorption. If, on the other hand, ΔP is not very small with respect to $Q[Al]_t$, a linear relationship is still obtained, but the slope lacks the theoretical significance of indicating the hydroxide ion displacement per equivalent of phosphate sorbed. This assumption was tested by examining the variation of sorbed phosphate according to Eq. (3) for solutions containing applied molar ratios of aluminum(III) to phosphate of 10. The results are shown in Fig. 5 and the statistical parameters in Table 3.

Effects of Excess Phosphate

The solubility of aluminum in solutions containing excess phosphate was studied by measuring the soluble concentration of the metal as a
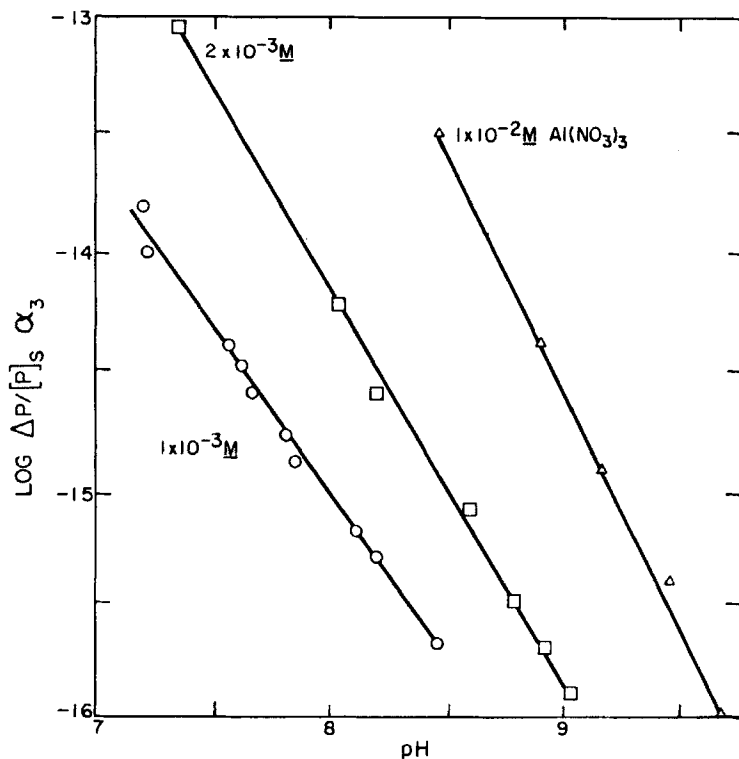
FIG. 4. Plots showing the pH-dependent sorption of phosphate on aluminum hydroxide at three applied aluminum nitrate concentrations. The initial phosphate concentration was 0.001 M.

TABLE 3
Parameters of Adsorption Isotherms of Aluminum
Phosphate in Alkaline Solutions

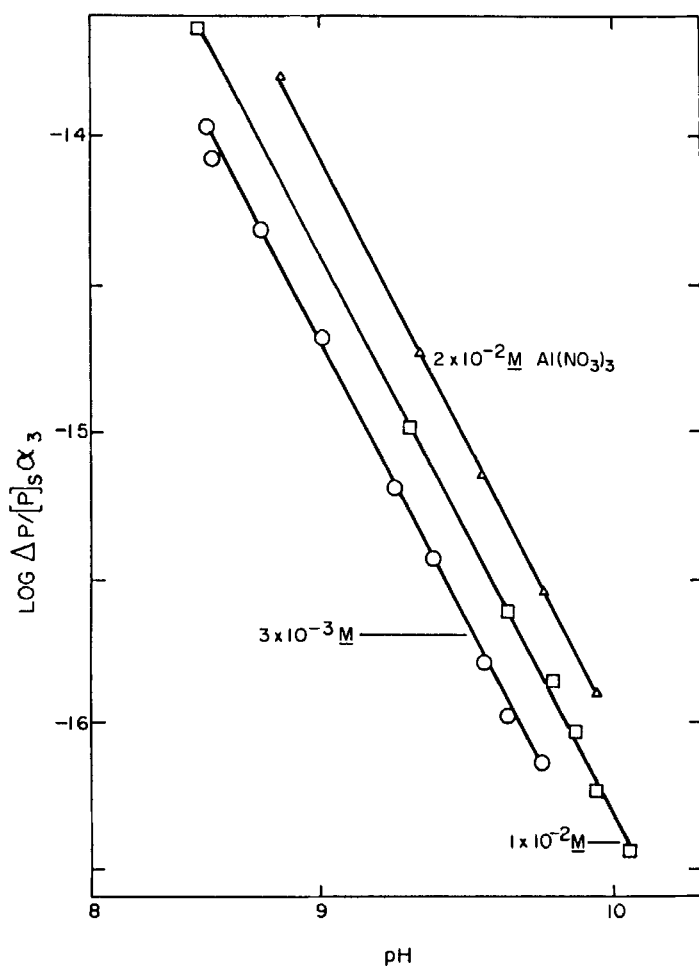| Initial concentrations (M)		Parameters	
$[Al]_t$	$[P]_t$	Slope	Intercept
1×10^{-3}	1×10^{-3}	1.41	-3.77
2×10^{-3}	1×10^{-3}	1.69	-0.66
1×10^{-2}	1×10^{-3}	1.85	2.48
3×10^{-3}	3×10^{-4}	1.92	2.20
2×10^{-2}	2×10^{-3}	1.87	2.69

FIG. 5. Plots showing the PH-dependent sorption of phosphate on aluminum hydroxide at three applied molar ratios of aluminum to phosphate of 10.

function of pH after 24 h of mixing and subsequent separation of the solid phase through membrane filters. The results are shown in Fig. 6. Because of the limited solubility of phosphate in the alkaline range, solutions containing 0.5 and 1 M phosphate were oversaturated above pH 9. In general, the solubility of aluminum was affected significantly by both the phosphate and hydrogen ion concentrations. The solubility of aluminum increased with the applied phosphate concentration except in the basic end of the pH range of precipitation. The solubility curves converged into a single line at the basic end of the pH range of precipitation, suggesting the formation of hydroxy phosphato-aluminum species.

Each of the solubility curves exhibited three pH points of extreme solubility over the examined range of precipitation. Two pH points of solubility minimum were found at approximately 5.0 to 5.5 and 7.5 to 8.0, whereas a solubility maximum was detected at about pH 6.5. This in turn
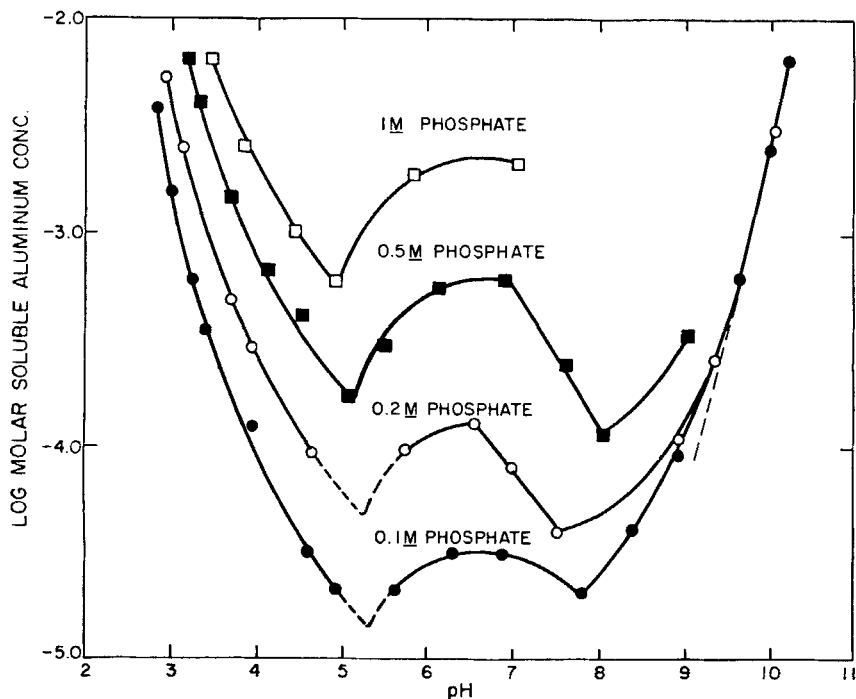
FIG. 6. Effect of excess phosphate on the solubility limits of aluminum at an applied concentration of 0.01 M.

indicates the formation of two distinct solid phases. The first is dominant in the acid side of the precipitation range, being least soluble at around pH 5.5. A second solid phase precipitates in the alkaline range and is least soluble at a pH of approximately 7.5. The pH of solubility maximum represents the transition point where a solid phase transformation occurs.

The precipitates were also analyzed chemically for their aluminum and phosphate contents. The results are plotted in Fig. 7 in terms of the molar ratio of aluminum to phosphate incorporated in the precipitate as a function of the pH of the solutions measured immediately after the separation of the solid phases. The average molar ratios were approximately 0.62 in acid solutions and about 1.0 in the alkaline range. The results tentatively suggest that sodium taranakite, $Na_3Al_5H_6(PO_4)_8(s)$, precipitates in acid solutions and a tertiary salt of aluminum phosphate, $AlPO_4(s)$, in the alkaline range.

The solubility of the precipitate formed in acid solutions was determined by measuring the soluble concentrations of aluminum(III), phosphate, and sodium ions as a function of pH for solutions equilibrated with aluminum phosphate precipitate for approximately 90 days. The precipitate was prepared in accordance with the procedure for the
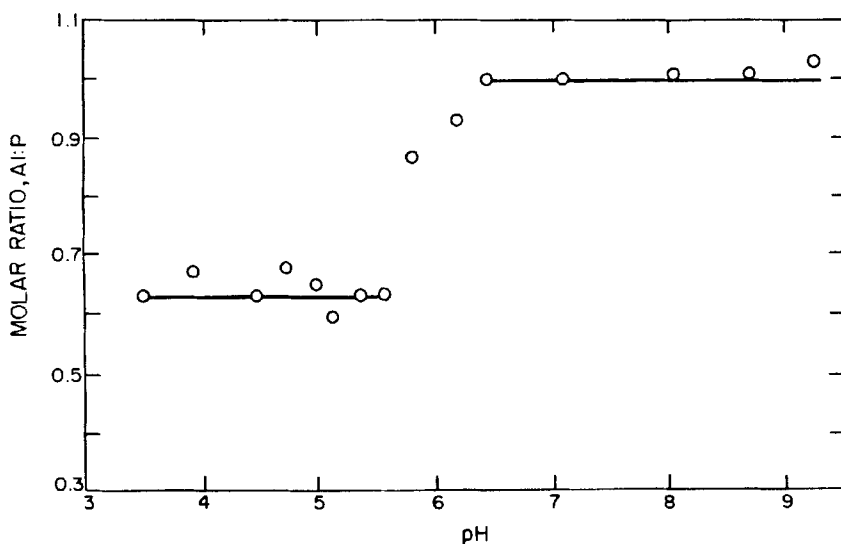

FIG. 7. Variation of the molar ratio of aluminum to phosphate incorporated in the precipitate as a function of pH.

TABLE 4
Equilibrium Concentrations of Soluble Aluminum, Phosphate, and Sodium Ion in Acid
Solutions Containing Aluminum Phosphate Precipitate

$-\log [Al]_s$	$-\log [Na^+]$	$-\log [P]_s$	$-\log [H_2PO_4^-]$	pH	p^*K_s
2.16	3.23	1.07	1.45	2.69	11.39
2.27	2.90	1.40	1.72	2.71	11.56
2.50	3.04	1.38	1.59	2.82	11.85
2.53	3.01	1.25	1.44	2.87	11.85
2.88	2.65	1.42	1.52	3.04	11.71
2.90	2.72	1.38	1.48	3.05	11.95
3.12	2.58	1.55	1.61	3.29	11.72
3.48	2.52	1.31	1.34	3.45	11.73
3.50	2.41	1.58	1.61	3.56	11.76
4.08	2.24	1.61	1.62	4.03	11.88

Average: 11.74 ± 0.51

precipitation of tarankites described by Taylor and Gurney (8). The results are listed in Table 4. Mathematical analysis of the data was based on

$$5AlHPO_4^+ + 3Na^+ + 3H_2PO_4^- \rightleftharpoons Na_3Al_5H_6(PO_4)_8(s) + 5H^+ \qquad (4)$$
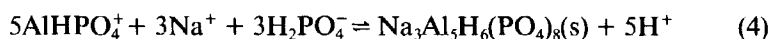
Assuming that the soluble aluminum concentration in the presence of excess phosphate is equal to $[AlHPO_4^+]$, the logarithmic form of the mass action expression of Eq. (4) can be written as

$$\log [Al]_s = -pH - \tfrac{3}{5}[Na^+] + [H_2PO_4^-] + \tfrac{1}{5}p^*K_s \qquad (5)$$

where

$$[H_2PO_4^-] = \frac{([P]_s - [Al]_s)}{(1 + [H^+]/K_1)} \qquad (6)$$

and K_1 is the first dissociation constant of phosphoric acid. A plot of Eq. (5) is shown in Fig. 8. The slope and intercept were calculated to be -0.58 and 2.33, respectively. The calculated slope is in excellent agreement with the predicted value of -0.60.
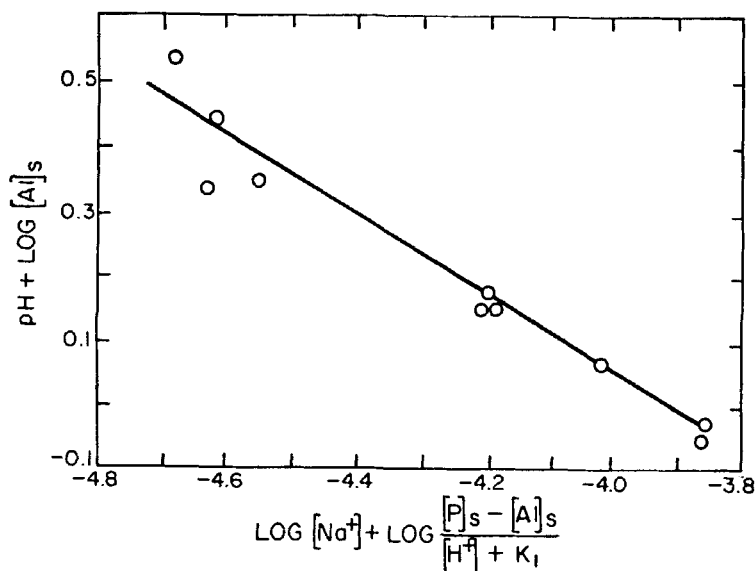
FIG. 8. Solubility isotherm for sodium taranakite.

DISCUSSION AND CONCLUSIONS

The solubility of aluminum phosphate precipitated from acid solutions containing excess aluminum(III) concentrations was examined by two analytical approaches. The results of both methods showed that at low phosphate concentrations the solubility of the precipitate is independent of the applied aluminum concentration. This was indicated by the single solubility line obtained with three different applied aluminum concentrations (Fig. 3) and by the statistical parameters (slope, intercept, and standard deviation) calculated for the regression line of the solubility data shown in Table 2.

Since the slope of both lines was approximately −2, it can be assumed that a predominant soluble aluminum phosphate species with a 2+ charge exists in equilibrium with the precipitate along these lines. Since the pH limits of precipitation of the common boundary were independent of the applied aluminum concentration, the chemical reaction describing the equilibrium between the soluble species and the precipitate can be viewed as a two-component system in which precipitation occurs when the complex is neutralized by two hydroxide ions. Consequently, the stoichiometry of the precipitate is that of the complex plus two hydroxide ions, or some variable of it.

The relationship between the stoichiometries of the precipitate and the soluble complex can also be interpreted by way of elimination. There are two alternatives other than simple neutralization which must be considered. These include the release of aluminum or phosphate ions from the complex upon precipitation or their incorporation into the complex. However, if that is the case, the mass action expression of the precipitation reaction must include a term for the concentration of the species released or added during the reaction. Since the applied aluminum concentrations were constant, the addition or release of aluminum ions should have affected the intercept of the common boundary of precipitation. This should have been indicated by a series of straight lines, each corresponding to a different applied aluminum concentration. Similarly, since the concentration of the phosphate can be expressed as a function of the aluminum concentration, displacement of the former during the precipitation reaction would have also resulted in a series of boundaries of precipitation, each corresponding to a different aluminum concentration.

The nature of the complex which exists in equilibrium with the precipitate was determined from the results of phosphorimetric titrations. It was observed that the pH of aluminum solutions titrated with dihydrogen phosphate decreased with increasing phosphate concentration. This in turn indicates that a phosphato-aluminum complex is formed; otherwise the pH would have increased, since within this pH range the dihydrogen phosphate ion behaves as a base, binding hydrogen ions. Furthermore, this complex must be a basic species since the addition of a base to a chemical system increases the hydroxide ion concentration of the system. Such an increase, when indicated by a decrease in pH, as was observed with the phosphato-aluminum system, can only be explained by the formation of a basic complex which contains bound hydroxide ions.

The approach used to determine the stoichiometry of the basic aluminum-phosphato complex was based on the method of elimination developed by Sillen (12). Essentially, what was done was to assume, from the stoichiometries of basic aluminum phosphates documented in the ASTM x-ray powder data file that the stoichiometry of the basic complex should be limited to $Al_2OH(PO_4)^{2+}$, $Al_3OH(PO_4)_2^{2+}$, or $Al_4OH(PO_4)_3^{2+}$. In general, then, for these complexes

$$(x - 1)AlHPO_4^+ + AlOH^{2+} \rightleftharpoons Al_xOH(PO_4)_{x-1}^{2+} + (x - 1)H^+ \qquad (7)$$
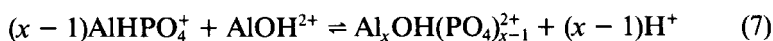
$$K_{x,1,x-1} = \frac{[H^+]^{x-1}[Al_xOH(PO_4)_{x-1}^{2+}]}{[AlHPO_4^+]^{x-1}[AlOH^{2+}]} \qquad (8)$$

Using the phosphorimetric titration data, the concentration of each of these three species was calculated at each point of the titration and a plot of $K_{x,1,x-1}$ against pH was constructed. As shown in Fig. 9, the results indicate that the least variation with pH in the plot is for $Al_3OH(PO_4)_2^{2+}$. Consequently, the precipitation along the common boundary of precipitation (shown in Fig. 3) can be described by

$$Al_3OH(PO_4)_2^{2+} + 2H_2O \rightleftharpoons Al_3(OH)_3(PO_4)_2(s) + 2H^+ \tag{9}$$

the mass action expression being

$$*K_{s3,1,2} = \frac{[H^+]^2}{[Al_3OH(PO_4)_2^{2+}]} = \frac{2[H^+]^2}{[P]_s} \tag{10}$$
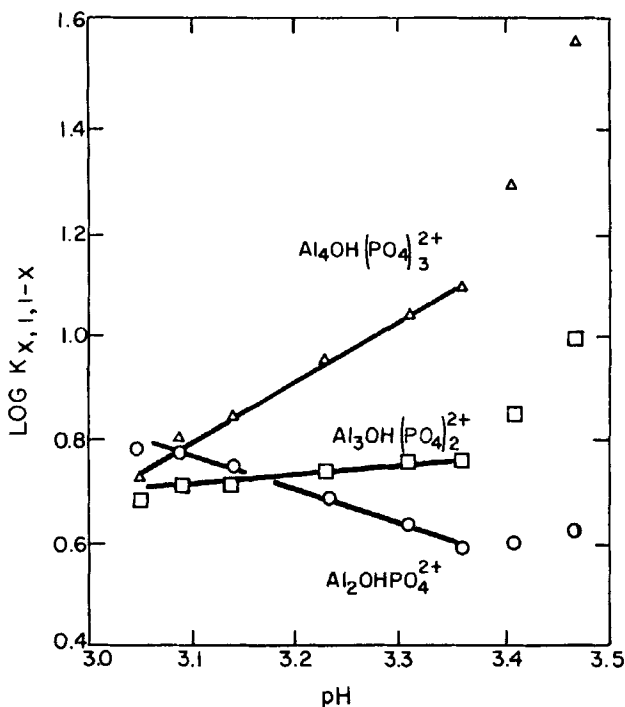

FIG. 9. Effect of pH on the formation constants for the various postulated stoichiometries of the basic complex.

Taking logarithms and rearranging:

$$\log [P]_s = -2pH + p^*K_{s3,1,2} + \log 2 \tag{11}$$

Because of the amorphous nature of the precipitate, it was not possible to confirm the exact composition of the basic solid phase by x-ray diffraction. Nevertheless, the results of this study indicate that the molar ratio of aluminum to phosphate incorporated in the precipitate is 3:2.

The formation of a basic trialuminum phosphate precipitate was also suggested by Cole and Jackson (5). Using electron diffraction, sterrettite, $(Al(OH)_2)_3H_2PO_4HPO_4(s)$, was identified as the principal solid phase precipitating at pH 5.5 from solutions containing an applied molar ratio of aluminum to phosphate of 1:2. This composition can also be written as $Al_3(OH)_3(PO_4)_2 \cdot 3H_2O(s)$, which is the hydrated form of the basic salt identified in this study.

The formation of a basic trialuminum phosphate precipitate can also be interpreted from studies on phosphate precipitation in wastewater treatment processes. Such studies have been performed by several investigators (13, 14). They have demonstrated, and it was also found in this study (Fig. 1), that only about 70% of the applied phosphate concentration can be precipitated from solutions containing an equimolar concentration of aluminum(III). Since an excess aluminum concentration is required to completely precipitate the phosphate, it is apparent that the number of aluminum ions incorporated into the precipitate is greater than that of phosphate. Furthermore, if it is assumed that a basic trialuminum phosphate precipitate is formed, the percent removal of phosphate from solutions containing equimolar concentrations of aluminum should be 66.7, a value in excellent agreement with the experimentally determined percentage of phosphate removal.

The formation constants of $AlHPO_4^+$ and the basic complex were also calculated from the data using the computer program SCOGS (stability constants of generalized species) (15, 16) as follows:

$$\log \beta_{1,1,1} = 19.93 \pm 0.70$$

$$\log \beta_{3,1,2} = 34.94 \pm 0.44$$

where $\beta_{1,1,1}$ and $\beta_{3,1,2}$ are defined by the mass action expressions

$$\beta_{1,1,1} = \frac{[AlHPO_4^+]}{[Al^{3+}][H^+][PO_4^{3-}]} \tag{12}$$

$$\beta_{3,1,2} = \frac{[Al_3OH(PO_4)_2^{2+}][H^+]}{[Al^{3+}]^3[PO_4^{3-}]^2} \qquad (13)$$

The solubility product of the basic aluminum phosphate salts can be calculated

$$pK_{s0} = p\beta_{3,1,2} + 3pK_2 - p*K_{s3,1,2} \qquad (14)$$

$$= 34.9 + 42 - 3.6 = 73.3$$

where $*K_{s3,1,2}$ is the equilibrium constant defined by Eq. (10). Using this value, the pH of solubility minimum of phosphate can be determined. The experimental results indicated that the pH point of solubility minimum should be within the range of 5 to 7 (Fig. 1). Therefore, the concentrations of phosphoric acid and orthophosphate ion can be ignored. The mass balance equation for phosphate is given by

$$[P]_s = [HPO_4^{2-}] + [H_2PO_4^-] + 2[Al_3OH(PO_4)_2^{2+}] + [AlHPO_4^+] \qquad (15)$$

Since at the pH of the phosphate solubility minimum both the basic aluminum phosphate and the metal hydroxide are equally stable, both solubility product expressions are valid. Expressing each species in terms of the various equilibrium constants and hydrogen ion concentration, differentiating the concentration of phosphate with respect to that of hydrogen ion, equating to zero for the solubility minimum, and rearranging gives

$$10^{23.5}[H^+]^6 + 10^{17.7}[H^+]^3 - 10^{-6.9}[H^+] = 1 \qquad (16)$$

This equation was solved by trial and error to give a minimum pH of phosphate solubility of approximately 6. Below this pH the basic phosphato-aluminum salt is the dominant solid phase; at high pH, aluminum hydroxide is more stable. The concentrations of the various phosphato species and aluminum ion at the pH point of solubility minimum are listed in Table 5. Stumm (17) also calculated the pH of the solubility minimum of phosphate to be approximately 6. His calculation, however, was based on a chemical model which involved the tertiary salt.

One of the reasons that many investigators have been led to propose the tertiary salt as the dominant solid phase is that its solubility product was found to be constant over a broad pH range (17–19). However, most

TABLE 5

Equilibrium Concentrations of Aluminum Ion and the Various Phosphate Species at the pH of Solubility Minimum of Phosphate

Species	Expression	p_{Conc}
$[Al^{3+}]$	$[H^+]^3/*K_{s0}$	7.6
$[PO_4^{3-}]$	$(K_{s0}[H^+]^3/K_w^3[Al^{3+}]_3)^{1/2}$	13.3
$[HPO_4^{2-}]$	$[PO_4^{3-}][H^+]/K_3$	7.0
$[H_2PO_4^-]$	$[HPO_4^{2-}][H^+]/K_2$	5.8
$[AlHPO_4^+]$	$[Al^{3+}][H^+][PO_4^{3-}]\beta_{1,1,1}$	7.0
$[Al_3OH(PO_4)_3^{2+}]$	$[Al^{3+}]^3[PO_4^{3-}]^2\beta_{3,1,2}/[H^+]$	8.5
$[P]_t$		5.8

of their studies were carried out in the presence of aluminum hydroxide precipitate. If it is assumed that the two solid phases are in equilibrium, then the solubility product expression for the basic salt can be written as

$$K_{s0(Al_3(OH)_3(PO_4)_2)} = [Al^{3+}]^2[PO_4^{3-}]^2[Al^{3+}][OH^-]^3$$

$$= [Al^{3+}]^2[PO_4^{3-}]^2K_{s0(Al(OH)_3)} \quad (17)$$

Equation (17) is valid since the solubility product of the metal hydroxide is constant within the pH range of precipitation of aluminum hydroxide. Consequently, the solubility product of the tertiary salt must also be constant:

$$pK_{s0(AlPO_4)} = \frac{pK_{s0(Al_3(OH)_3(PO_4)_2)} - pK_{s0(Al(OH)_3)}}{2}$$

$$= \frac{73.3 - 31.6}{2} = 20.9 \quad (18)$$

The calculated value is well within the range reported in the literature (18–24). Thus, it is evident that the nature and stoichiometry of the precipitate cannot be determined from solubility data alone. Moreover, in several studies where the solubility data were collected outside the pH range of precipitation of the metal hydroxide, the calculated solubility products of the tertiary salt were considerably higher. For example, Makitie (21) calculated a pK_{s0} for the tertiary salt of 18.6 within pH range

4–5 and 23.7 at pH 2.9. In this study, however, the formation of a basic salt was interpreted from solubility data collected outside the pH range of precipitation of aluminum hydroxide and from pH-dependent titration data. Both data sets were obtained within a pH range where aluminum hydroxide precipitate is unstable and therefore not subject to the limitations mentioned previously.

SUMMARY

The interaction between aluminum and phosphate in aqueous solutions can lead to the precipitation of several solid phases, depending on the applied concentrations of aluminum and phosphate and the pH. Figure 10 summarizes the distribution of aluminum phosphate solid phases as a function of pH and the ratio of the applied concentrations of aluminum and phosphate. Four different solid phases precipitate within the range of concentration and pH examined in this study.

In acid solutions containing an excess concentration of aluminum, the most stable solid phase is the basic phosphato-aluminum salt. If the pH is raised beyond the point of solubility minimum of phosphate (pH 6), the basic salt is hydrolyzed to aluminum hydroxide and phosphate is adsorbed to its surface. If, on the other hand, the concentration of phosphate is raised, a taranakite precipitate is formed. The taranakite is
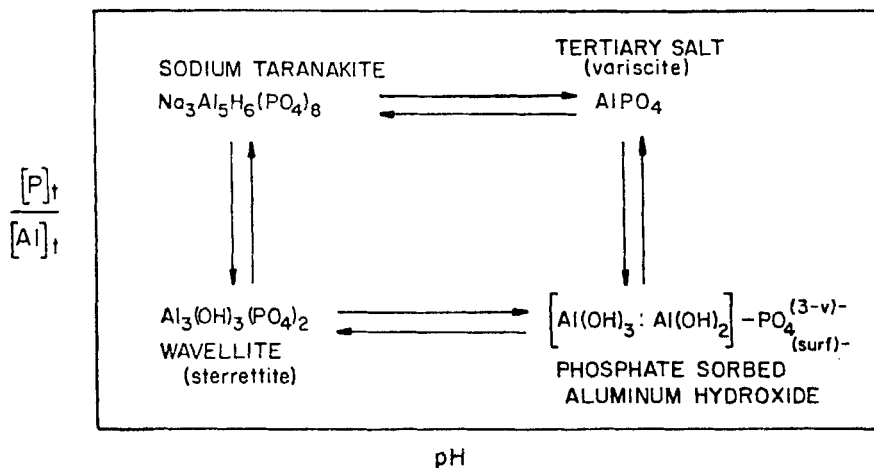

FIG. 10. Distribution diagram of solid phases in the phosphato-aluminum system.

transformed into the tertiary salt when the pH of the system is increased in the presence of a high phosphate concentration.

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