Structure of Aluminum Hydroxide Gel I: Initial Precipitate

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Abstract □ The initial aluminum hydroxide gel precipitate resulting from the reaction of aluminum chloride or aluminum sulfate with ammonium hydroxide is shown by potentiometric titration, chemical analysis, and the ratio of bound hydroxide to aluminum to fit a polymer model described previously. The formation of polynuclear hydroxyaluminum particles is treated as a stepwise process involving a deprotonation–dehydration mechanism, which results in the formation of six-membered rings; these rings may further coalesce by the same mechanism. The aluminum hydroxide gel precipitated from aluminum chloride can be represented by the formula $Al(OH)_{2.55}(Cl)_{0.45}$ and probably exists as a polymer of 10 fused six-membered rings. The aluminum hydroxide gel precipitated from aluminum sulfate can be represented by the formula $Al(OH)_{2.30}(SO_4)_{0.35}$. This species probably exists as a polymer of three fused six-membered rings.

Keyphrases □Aluminum hydroxide gel—polymer structure of initial precipitate from reaction of aluminum chloride or sulfate with ammonium hydroxide □ Gels—aluminum hydroxide, polymer structure of initial precipitate from reaction of aluminum chloride or sulfate with ammonium hydroxide □ Polymer structure—aluminum hydroxide gel, initial precipitate from reaction of aluminum chloride or sulfate with ammonium hydroxide □ Antacids—aluminum hydroxide gel, polymer structure of initial precipitate from reaction of aluminum chloride or sulfate with ammonium hydroxide

Aluminum hydroxide gel is an effective antacid, although many aspects of its structure and acid reactivity are not well understood. Aluminum hydroxide gel is often represented by the formula $Al(OH)_3$. This representation is somewhat misleading, since the crystalline polymorphs of aluminum hydroxide, gibbsite, bayerite, and nordstrandite, are resistant to attack even by concentrated acid. In addition, acid-reactive aluminum hydroxide gels, useful as pharmaceutical antacids, contain anions associated with the gel structure (1–9).

The purposes of this investigation were to study the initial precipitate resulting from the reaction of solutions of aluminum chloride or aluminum sulfate with dilute ammonium hydroxide to a final pH of 7.0 and to propose a structure as the basis for explaining the antacid properties of aluminum hydroxide gel and the changes in antacid properties that occur upon aging. The proposed structure is based on potentiometric titration, chemical analysis, and reaction with sodium fluoride to determine the molar ratio of bound hydroxide to aluminum in the aluminum hydroxide gel.

EXPERIMENTAL

Materials—All chemicals used were either reagent or analytical grade.

Potentiometric Titrations—The ratio of hydroxyl to aluminum in the initial precipitate was determined by potentiometric titration of 0.294 M $AlCl_3 \cdot 6H_2O$ and 0.145 M $Al_2(SO_4)_3 \cdot 16H_2O$ with standard 1.0 N NaOH and 13% strong ammonia solution. The pH was measured[1] after the addition of each 5 ml of base, allowing the system to equilibrate until the pH was stable for 30 sec. The graphical method of Matijević et al. (10) was used to calculate the hydroxyl to aluminum ratio.

Sodium hydroxide was used as the titrant because it is a strong base and, therefore, gives an accurate value of the hydroxyl to aluminum ratio. Ammonium hydroxide was used because it is a common reactant in the precipitation of aluminum hydroxide gel.

Aluminum Hydroxide Gel Preparation—To make 1 liter of chloride-containing gel, 71.8 g of aluminum chloride hexahydrate was dissolved in 835 ml of distilled water. To make 1 liter of sulfate-containing gel, 92.6 g of aluminum sulfate hexadecahydrate was dissolved in 835 ml of distilled water. Ammonium hydroxide solution was then added at a rate of 120 ml/min.

The gel system was stirred[2] throughout the precipitation, and a combination electrode[3] was placed in the system for continuous monitoring of the pH. When the pH reached 4.5–5, there was a sharp increase in viscosity and a sharp rise in the rate of pH increase with further addition of base. At this point, base was added dropwise until pH 7.00 was reached. The system was maintained at this pH, with continuous stirring, for 30 min.

While being stirred continuously, the gels were washed with various amounts of deionized water by draining through a canvas bag. After washing, the volume of each gel was adjusted to 1 liter with distilled water.

Analytical Procedures—The equivalent aluminum oxide content was determined by the ethylenediaminetetraacetic acid titration (11).

The total chloride content was determined by the Volhard titration (12) after 3 g of gel was dissolved in 15 ml of 6 N nitric acid.

A procedure similar to that reported by Hsu and Bates (13) was used to determine the molar ratio of bound hydroxide to aluminum in the aluminum hydroxide gel samples. The procedure is as follows:

1. Place 50 ml of 0.5 N NaF in a 100-ml beaker. Add 2 drops of phenolphthalein indicator and measure the pH of the solution. If necessary, adjust the pH to about 7.4 with 0.10 N HCl.

2. Using a syringe, accurately weigh about 1.0 g of gel and add it to the sodium fluoride solution. Agitate thoroughly. Prepare a 50-ml aliquot of sodium fluoride solution as a blank.

3. Immerse the pH electrode in the sample and titrate to the original pH of the sodium fluoride solution (about 7.4) with standard 0.10 N HCl.

4. Cover the beaker containing the sample with aluminum foil or plastic wrap and place on a steam bath for 1 hr.

5. Allow the sample to cool and again titrate to the original pH. Repeat this heat-and-titrate operation until no more than 1 drop of 0.10 N HCl is required. The phenolphthalein serves as a visual indicator of the extent of reaction taking place with each heat-and-titrate step.

6. Record the total milliequivalents of acid used and subtract from this value the number of milliequivalents consumed by the blank. The net milliequivalents of acid consumed equals the milliequivalents of hydroxide liberated from the sample.

7. Calculate the molar ratio of bound hydroxide to aluminum from the milliequivalents of hydroxide liberated and the millimoles of aluminum present in the sample.

RESULTS AND DISCUSSION

Potentiometric Titrations—A plot of pH *versus* milliliters of base added is shown in Fig. 1 for the titration of 0.29 M $AlCl_3 \cdot 6H_2O$ with 1.0 N NaOH. The hydroxide to aluminum molar ratio is also shown on the x-axis. A very small increase in pH with addition of base was
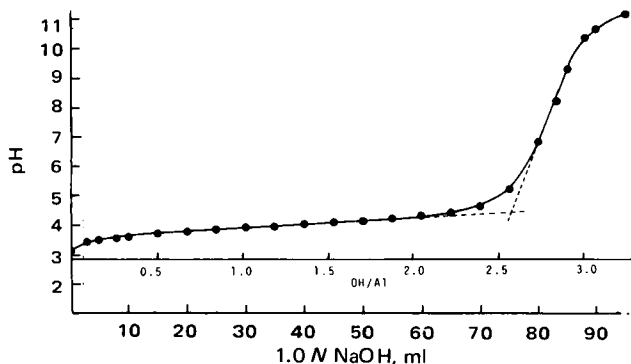

Figure 1—*Potentiometric titration of 0.29 M AlCl₃ with 1.0 N NaOH.*

observed for hydroxide to aluminum ratios in the 0–2 range. This finding indicates that the added hydroxide ions were immediately bound by aluminum ions. Little change in the appearance or viscosity of the precipitate occurred during this phase of the titration. At a ratio of about 2.5, there was a sharp increase in pH. At this point, the viscosity also sharply increased and the system changed in appearance from a dilute suspension to a gel.

Sodium hydroxide added beyond the break point of the curve caused a rapid increase in pH, which indicates that the hydroxide ions were not included in the hydroxyaluminum structure but were in solution. The ratio of hydroxyl to aluminum in the initial precipitate was taken as the point where added sodium hydroxide caused a sharp increase in pH (10), reflecting the appearance of hydroxide ions in solution. Hydroxide ions added prior to this point had little effect on pH, because they were bound by aluminum and were not free to affect the pH. As seen in Fig. 1, the hydroxyl to aluminum ratio in the initial precipitate formed from the reaction of aluminum chloride and sodium hydroxide was 2.55. A duplicate titration gave a value of 2.49.

The titration curve of a 0.29 M AlCl₃·6H₂O with 13% strong ammonia solution had an initial region in which the pH was nearly constant, indicating that the added hydroxide ions were bound by aluminum ions. A point was reached where the added hydroxide was not incorporated into the hydroxyaluminum structure, as evidenced by a rapid increase in pH. The rapid rise in pH began at pH 4.5, corresponding to the pH at the break point for the aluminum chloride–sodium hydroxide system. In addition, this gel increased in viscosity and changed in appearance at this point. These observations suggest that the initial aluminum hydroxide gel precipitated with ammonium hydroxide is equivalent to that precipitated with sodium hydroxide.

The potentiometric titration of 0.145 M Al₂(SO₄)₃·16H₂O with 1.0 N NaOH was similar to the titration shown in Fig. 1. In this case, the hydroxyl to aluminum ratio of the initial precipitate was 2.30.

Titration of a similar aluminum sulfate solution with 13% strong ammonia solution gave the same titration curve as was obtained for aluminum sulfate–sodium hydroxide.

The fact that the titration curves for aluminum chloride and aluminum sulfate gave different inflection points must be attributed to the different aluminum salt anion present. The hydroxyl to aluminum ratio taken from the titration curve of the aluminum chloride system suggests the formation of a hydroxyaluminum complex of approximate composition Al(OH)₂.₅₀₋₂.₅₅Cl₀.₅₀₋₀.₄₅. The titration curve of the sulfate system suggests a composition of approximately Al(OH)₂.₃₀(SO₄)₀.₃₅. These formulas represent average values, because the slow attainment of equilibria in these systems prevents the precise determination of the hydroxyl to aluminum ratio (14). In addition, there is evidence that hydrolyzed aluminum species are polynuclear (10, 14, 15).

Reaction with Fluoride—When aluminum hydroxide gels are treated with sodium fluoride solution, the fluoride ion displaces hydroxide ions from the gel structure (13, 16). The hydroxide ions released into solution are then titrated, which allows calculation of the hydroxide to aluminum ratio.

Duplicate determinations of the hydroxide to aluminum ratio of seven different chloride-containing gels precipitated at pH 7.0 gave an average value of 2.55 ± 0.03 (*SD*). The results of both the potentiometric titration experiment and hydroxide to aluminum ratio determinations by reaction with fluoride led to the postulation of an
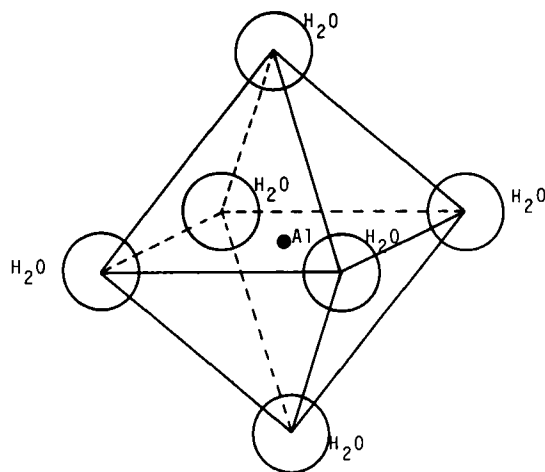

Figure 2—*Hydrolyzed aluminum ion Al(OH₂)₆⁺³. (Reprinted, with permission, from Ref. 15.)*

empirical formula for the fresh precipitate of Al(OH)₂.₅₅Cl₀.₄₅. This ratio of hydroxide to aluminum is a numerical average. The fresh precipitate is probably a highly random structure (17, 18) containing polynuclear hydroxyaluminum species with a wide range of values of bound hydroxide to aluminum.

Duplicate determinations of the hydroxide to aluminum ratio of a gel precipitated from aluminum sulfate–ammonium hydroxide gave a value of 2.38, which is in reasonable agreement with the value of 2.30 obtained from the titration curve.

Based on these data, it is not possible to specify the number of aluminum atoms contained in the average polymeric particle. However, a theory that provides a structural picture of the formation of polynuclear hydroxyaluminum complexes by the neutralization of aqueous aluminum salt solutions has evolved in the mineralogy literature. This model, discussed in detail by Hem and Roberson (15), makes possible an estimate of the polymer size based on the hydroxide to aluminum molar ratio.

The formation of polynuclear hydroxyaluminum complexes in dilute solution was treated by Hem and Roberson (15) as a stepwise process involving a deprotonation–dehydration mechanism. In aqueous aluminum salt solutions below pH 4, aluminum exists primarily as the trivalent cation with six water molecules in octahedral coordination, Al(H₂O)₆⁺³ (Fig. 2). The coordinated water molecules are oriented with the oxygen toward the aluminum ion. The high charge of the aluminum ion tends to weaken the oxygen—hydrogen bond of the coordinated water, which facilitates the removal of a proton and accounts for the initial low pH of aluminum salt solutions.

The first step in the conversion of hydrated aluminum ions to polymerized species involves deprotonation of one of the coordinated water molecules of the aluminum cation (Scheme I).

$$Al(OH_2)_6{}^{+3} \rightleftharpoons Al(OH)(OH_2)_5{}^{+2} + H^+$$
Scheme I
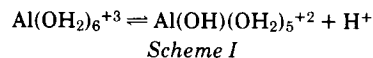
Two deprotonated octahedra can then join to form a dimer (Scheme II).

$$2Al(OH)(OH_2)_5{}^{+2} \rightleftharpoons Al_2(OH)_2(OH_2)_8{}^{+4} + 2H_2O$$
Scheme II
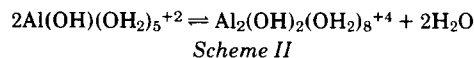
This unit contains the characteristic double hydroxide bridge between aluminum ions (Fig. 3).

Dimers then can join to form either a chain structure or a ring structure by the same deprotonation–dehydration mechanism. The general formula for a chain structure would be: $Al_m(OH)_{2m-2}(OH_2)_{2m+4}^{+(m+2)}$. The upper limit of the hydroxide to aluminum ratio for a chain structure is 2. This structure is not consistent with the experimental values of 2.55 and 2.38, nor would it allow the formation of bayerite, gibbsite, or nordstrandite, all having hydroxide to aluminum ratios of 3.0.

A ring structure can be formed by joining dimers (Fig. 4). These six-membered rings may then coalesce further by continued polymerization, resulting in a higher ratio of structural hydroxyl to alu-
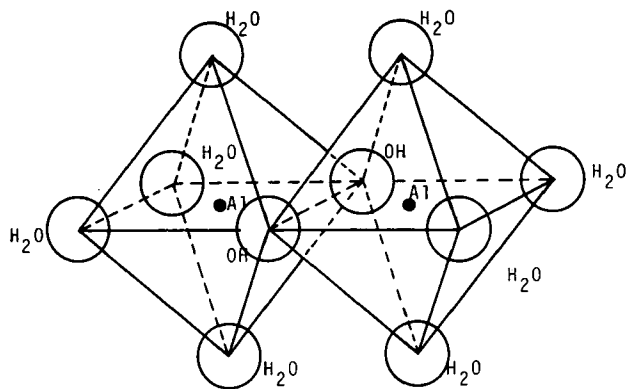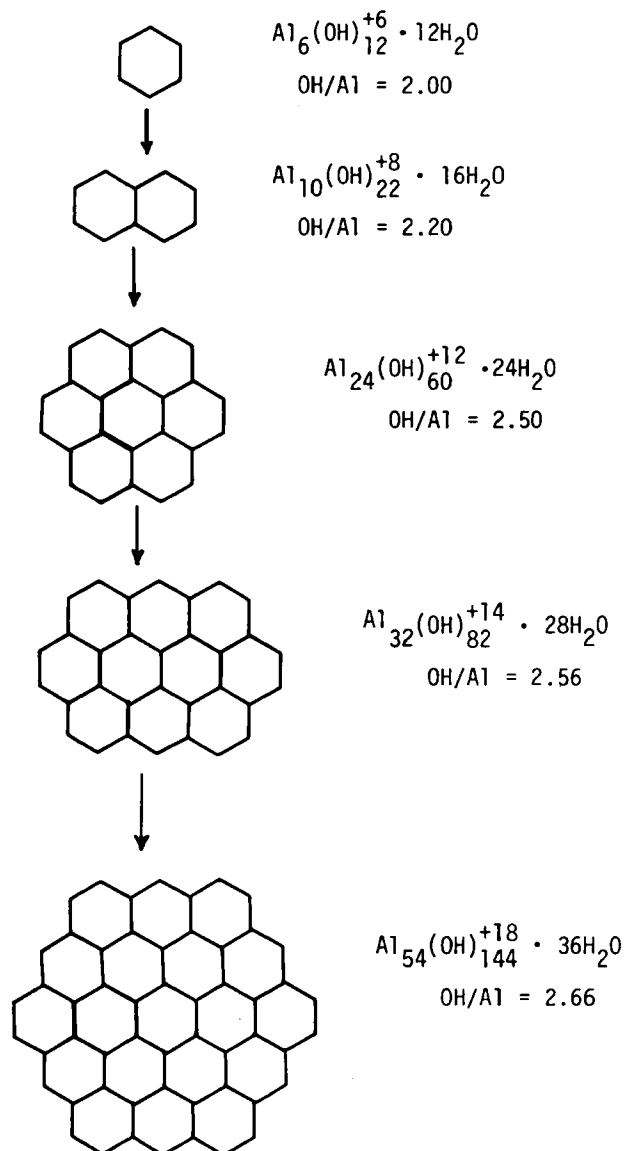
Figure 3—*Dimeric cation $Al_2(OH)_2(OH_2)_8^{+4}$. (Reprinted, with permission, from Ref. 15.)*

minum. The hydroxide to aluminum ratio approaches 3 as the structure increases in size.

The growth of a hydroxyaluminum particle by formation of six-membered rings and multiples thereof is shown in Scheme III. As the number of fused rings in a complex increases, there is a corresponding

$$Al_6(OH)_{12}^{+6} \cdot 12H_2O$$

$$OH/Al = 2.00$$

$$Al_{10}(OH)_{22}^{+8} \cdot 16H_2O$$

$$OH/Al = 2.20$$

$$Al_{24}(OH)_{60}^{+12} \cdot 24H_2O$$

$$OH/Al = 2.50$$

$$Al_{32}(OH)_{82}^{+14} \cdot 28H_2O$$

$$OH/Al = 2.56$$

$$Al_{54}(OH)_{144}^{+18} \cdot 36H_2O$$

$$OH/Al = 2.66$$

Scheme III—Proposed development of crystalline aluminum hydroxide. (Adapted from Ref. 13.)
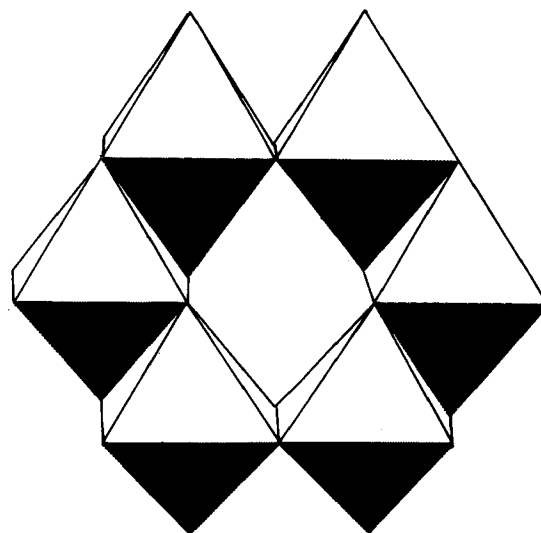
Figure 4—*Ring structure formed by six aluminum hydroxide octahedra. (Reprinted, with permission, from Ref. 15.)*

increase in the ratio of bound hydroxide to aluminum. For a gel precipitated from aluminum chloride and ammonium hydroxide at pH 7.0, this model would suggest that the predominant structure is a polymer of 10 fused rings, $Al_{32}(OH)_{82}^{+14} \cdot 28H_2O$. This species has a bound hydroxide to aluminum ratio of 2.56, which is in close agreement with the experimental data.

To propose a structure containing 32 aluminum atoms, it must be assumed that all hydroxide groups are present as double hydroxide bridges between aluminum atoms. It is possible that some hydroxide is bound to the polymer by single bonds to edge aluminum. For example, Brosset *et al.* (19) proposed a structure, $Al_6(OH)_{15}^{+3}$, consisting of a six-membered ring with the extra hydroxide groups attached by single bonds to alternate aluminum atoms in the ring. For a given number of aluminum atoms in the complex, the presence of these "nonstructural" hydroxide groups causes larger values of hydroxide to aluminum than those predicted from Scheme III. Therefore, the complex containing 32 aluminum atoms is the maximum size of the polymer that can be postulated from the available data.

It is apparent that the average polymer size resulting from the neutralization of aluminum sulfate solution is smaller than that of the corresponding chloride system. Based on a hydroxide to aluminum ratio of 2.30, a maximum polymer size of three rings containing 13 aluminum atoms is predicted.

Effect of Washing on Initial Precipitate—Several chloride-containing gels were precipitated at pH 7.0 and washed with various amounts of distilled water. Chloride concentrations were determined by the Volhard method (12), and the molar ratio of chloride to aluminum was calculated. These chloride to aluminum ratios varied from 0.78 for gels washed with 1 liter of water/liter of gel to 0.23 for gels washed with 5 liters of water/liter of gel. This range of values is in general agreement with a chloride to aluminum ratio of 0.45, which would be predicted from the hydroxide to aluminum ratio.

A direct relationship was observed between the chloride concentration in the gel after washing and the pH of the gel immediately after washing (Fig. 5). As chloride is removed from the gel by washing, the pH decreases. The chloride ions probably occupy edge position of the hydroxyaluminum particles (13). Removal of chloride by washing results in attraction of water molecules to the positive edge positions. Protons are released due to the polarization of these water molecules, resulting in the observed pH decrease.

Another mechanism contributing to the observed decrease in pH is that any hydroxide added after the inflection point of the titration curve is not bound. It follows that this extra hydroxide should be readily removed from the system by washing. These mechanisms explain the observed relationship between the amount of washing, or chloride content, and the pH after the washing operation.

It also was observed that addition of sodium chloride solution to a gel after washing caused a significant increase in the pH of the gel. A gel was precipitated, washed, and divided into two portions. One portion was diluted to final volume with distilled water, the other with 1 N NaCl. The pH of the gel diluted with water was 6.87, compared
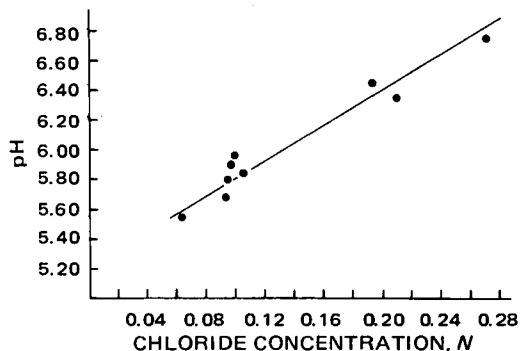
Figure 5—*Gel pH versus chloride concentration for gels precipitated at pH 7.0.*

to 8.28 for the gel diluted with 1 N NaCl. This finding suggests that the chloride ion displaced some hydroxide ion from the gel structure. Although the displacement of structural hydroxide cannot be ruled out, it seems more probable that chloride ions would displace the nonstructural hydroxyl groups from the edge of the hydroxyaluminum particles. The displacement of hydroxide by chloride would result in an increase in pH upon the addition of sodium chloride, as was observed. The direct relationship between chloride concentration in the gel and gel pH shown in Fig. 5 also supports this mechanism.

It was noted during washing studies that a direct relationship existed between the rate at which water drained from the gel during washing and the pH at which a gel was precipitated. For example, a gel precipitated at pH 5.5 drained quite slowly relative to a gel precipitated at pH 8.5. This observation could be explained by the fact that at pH 5.5, where the hydroxide to aluminum ratio is about 2.5, the positive charge per aluminum atom would be considerably greater than at pH 8.5, where the hydroxide to aluminum ratio is about 2.85 (Fig. 1). The higher charge at low pH means that more water would be polarized, or immobilized, at the lower pH. The higher charge also would result in a more dispersed system, which could produce a lower porosity cake and contribute to a slower draining rate.

SUMMARY

Based on potentiometric titrations and chemical analysis of the precipitate, the freshly precipitated chloride-containing gel can be represented by the empirical formula $Al(OH)_{2.55}Cl_{0.45}$. The empirical formula of the sulfate-containing gel prepared under the same conditions is $Al(OH)_{2.30}(SO_4)_{0.35}$. Polymerization by the formation of six-membered rings and multiples thereof would result in polymeric particles containing a maximum of 32 aluminum atoms per structure in the chloride-containing gel and a maximum of 13 aluminum atoms in the sulfate-containing gel.

The relationship between chloride concentration and gel pH suggests that the chloride ion may be weakly bound to positive sites at the edge of the hydroxyaluminum particles. Washing apparently removes chloride ions from these sites, resulting in an increase in the polarization of water by the edge aluminum ions and a concomitant decrease in pH.

REFERENCES

(1) R. I. Barnhisel and C. I. Rich, *Soil Sci. Soc. Am. Proc.,* **29**, 531(1965).
(2) R. C. Turner and G. J. Ross, *Can. J. Soil Sci.,* **49**, 389 (1969).
(3) R. C. Turner and G. J. Ross, *Can. J. Chem.,* **48**, 723(1970).
(4) S. L. Hem, E. J. Russo, S. M. Bahal, and R. S. Levi, *J. Pharm. Sci.,* **59**, 317(1970).
(5) G. J. Ross and R. C. Turner, *Soil Sci. Soc. Am. Proc.,* **35**, 389(1971).
(6) P. H. Hsu, *Int. Comm. Study Bauxites Aluminum Oxides-Hydroxides, 3rd,* **1973**, 613.
(7) J. L. White and S. L. Hem, *J. Pharm. Sci.,* **64**, 468(1975).
(8) P. H. Hsu, *Soil Sci. Soc. Am. Proc.,* **30**, 173(1966).
(9) P. H. Hsu, *Soil Sci.,* **103**, 101(1967).
(10) E. Matijević, K. G. Mathai, R. H. Ottewill, and M. Kerker, *J. Phys. Chem.,* **65**, 826(1961).
(11) "The United States Pharmacopeia," 18th rev., Mack Publishing Co., Easton, Pa., 1970, p. 26.
(12) I. M. Kolthoff, E. B. Sandell, E. J. Meehan, and S. Bruckenstein, "Quantitative Chemical Analysis," 4th ed., Macmillan, New York, N.Y., 1969, p. 799.
(13) P. H. Hsu and T. F. Bates, *Miner. Mag.,* **33**, 749(1964).
(14) J. Aveston, *J. Chem. Soc.,* **1965**, 4438.
(15) J. D. Hem and C. E. Roberson, "Form and Stability of Aluminum Hydroxide Complexes in Aqueous Solution," U.S. Geological Survey Water-Supply Paper 1827-A, U.S. Government Printing Office, Washington, D.C., 1967.
(16) J. M. Bracewell, A. S. Campbell, and B. D. Mitchell, *Clay Miner.,* **8**, 325(1970).
(17) S. L. Nail, J. L. White, and S. L. Hem, *J. Pharm. Sci.,* **64**, 1166(1975).
(18) *Ibid.,* **65**, 231(1976).
(19) C. Brosset, G. Biedermann, and L. G. Sillén, *Acta Chem. Scand.,* **8**, 1917(1954).