Structure of Aluminum Hydroxide Gel II: Aging Mechanism

STEVEN L. NAIL *, JOE L. WHITE ‡, and STANLEY L. HEM *ˣ

Abstract □ The aging of aluminum hydroxide gel prepared by the reaction of aluminum chloride and ammonium hydroxide was studied by measurement of pH, acid-consuming capacity, hydroxide to aluminum ratio, chloride activity, and X-ray line broadening. The results were consistent with a polymer model involving particle growth by a deprotonation–dehydration mechanism. Anions inhibit this reaction by binding to the positively charged edges of the hydroxyaluminum polymers.

Keyphrases □ Aluminum hydroxide gel—aging mechanism studied, effect of anions □ Gels—aluminum hydroxide, aging mechanism studied, effect of anions □ Aging mechanism—aluminum hydroxide gel, effect of anions □ Antacids—aluminum hydroxide gel, aging mechanism studied

A polymer model based on a six-membered ring was found to describe the properties of an aluminum hydroxide gel precipitated by the reaction of aluminum chloride or aluminum sulfate solutions with sodium hydroxide or ammonium hydroxide to a final pH of 7.0 (1). The purpose of this investigation was to determine whether this polymer model can be applied to explain the loss of acid reactivity observed as the gel ages.

A series of aluminum hydroxide gels was prepared from aluminum chloride and ammonium hydroxide at a final pH of 7.0. The washing process was controlled to produce gels with different chloride concentrations. The aging process was then monitored by determination of the pH of the gel, acid-consuming capacity, hydroxide to aluminum molar ratio, and chloride activity in the gel. Crystallite size of the (hkl) dimensions of two different gels was measured by X-ray line broadening.

EXPERIMENTAL

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

Aluminum Hydroxide Gel Preparation—Gels were prepared by the addition of 13% (v/v) strong ammonia solution to 0.29 M $AlCl_3 \cdot 6H_2O$ at a rate of 120 ml/min to a final pH of 7.0. Since this study involved the effect of washing on the aging characteristics of the gel, a large batch was precipitated (1) and subsequently divided into 1-liter portions to eliminate the effects of batch-to-batch variation. Each portion was washed individually with 1, 3, or 5 liters of distilled water, as previously described (1), and adjusted to 1 liter with distilled water.

The gels were stored in tightly capped 1-liter glass bottles.

Another gel was prepared in an identical manner except that aluminum sulfate replaced the aluminum chloride. To make 1 liter of gel, 92.6 g of aluminum sulfate hexadecahydrate was dissolved in 835 ml of distilled water.

Analytical Procedures—The equivalent aluminum oxide content was determined by the ethylenediaminetetraacetic acid titration (2). The prepared gels contained between 1.40 and 1.50% equivalent aluminum oxide.

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

The molar ratio of bound hydroxide to aluminum was determined by reaction of a 1-g sample of gel with sodium fluoride solution (1). As the gel aged, several heat-and-titrate steps were required to drive the reaction to completion. The reported values are the averages of four determinations. The standard deviation ranged from 0.15 to 1.6%.

The pH of each gel was measured at approximately 5-day intervals. The pH meter[1] was calibrated prior to each measurement.

The acid-consuming capacity of each gel was determined as a function of age by a modification of the USP test (4). Samples were back-titrated to an end-point of pH 3.5 rather than using bromophenol blue TS as given in the USP.

The chloride activity of each gel was measured periodically by means of a chloride-selective electrode[2] and a pH meter[1] adjusted for millivolt measurement. Solutions of 1.0, 0.75, 0.50, 0.25, 0.10, and 0.05 N NaCl were standardized by the Volhard titration (3). The activity of these samples was calculated (5), and a calibration curve of millivolts versus the log of the chloride activity was prepared. The potential of the aluminum hydroxide gel samples was then measured, and the chloride activity was calculated from the calibration curve.

The total chloride content of each gel was determined by the Volhard titration periodically during aging to assure that changes in chloride activity were not due to changes in chloride concentration.

X-Ray Line-Broadening Measurements—The line widths of the (002) and (110) reflections were measured using a technique described by Klug and Alexander (6). Samples were prepared by the McCreery technique (7). The 4.27-Å peak of novaculite was used to determine the amount of broadening due to instrumental factors. Since instrumental broadening is a function of the diffraction angle, this peak was chosen because it lies close to the sample peaks of interest: 4.82 and 4.35 Å. The following conditions were used in recording the diffractogram: Cu K_α radiation, 40 kV, 20 mamp, 500 Hz sensitivity, and 0.2°/min scan speed.

RESULTS AND DISCUSSION

The aging of three portions of a gel, washed with 1, 3, or 5 liters of distilled water, was compared. The milliequivalents of chloride per millimole of aluminum in these gels were 0.80 (Gel I, wash volume of 1 liter), 0.37 (Gel II, wash volume of 3 liters), and 0.35 (Gel III, wash volume of 5 liters).

pH Measurement and Acid-Consuming Capacity—Plots of gel pH and the log of the acid-consuming capacity versus aging time for each of the three gels are shown in Figs. 1–3. By plotting the two parameters together, the relationship between the decrease in pH and a loss of acid reactivity is apparent.

The decrease in pH of the gel with age is consistent with a deprotonation–dehydration condensation polymerization reaction between adjacent hydroxyaluminum particles (8). This type of reaction results in the two particles being joined by one or more double hydroxide bridges. The formation of each double hydroxide bridge results in the release of two protons and two water molecules.

The pH versus time curves in Figs. 1–3 can be divided into four different parts. A relatively rapid decrease was seen during the first 1–10 days. A linear decrease was then seen until the gel pH reached about 5, at which time the pH decreased at a considerably faster rate. When the pH reached a value of 3.8–3.9, it remained nearly constant.

The initial decrease in pH was consistent with the incorporation of unbound hydroxide ions into the gel structure as double hydroxide bridges. During the first 20 days, the pH of Gel I (Fig. 1) decreased more rapidly than the other gels, probably because it had more "free" hydroxyl groups as evidenced by the highest initial pH. After the first 20 days, the rate of decrease in pH of this gel was slower than Gels II and III.

The reason for the break in the pH versus time curve at about pH 5 is not well understood; however, the physical appearance of the gel changed at a time corresponding to this break. Prior to this inflection point, the gel appeared as a milky dispersion which partially settled

Figure 1—*Change in pH and acid-consuming capacity of Gel I during aging at 25°. Key: O, acid-consuming capacity; and ●, pH.*

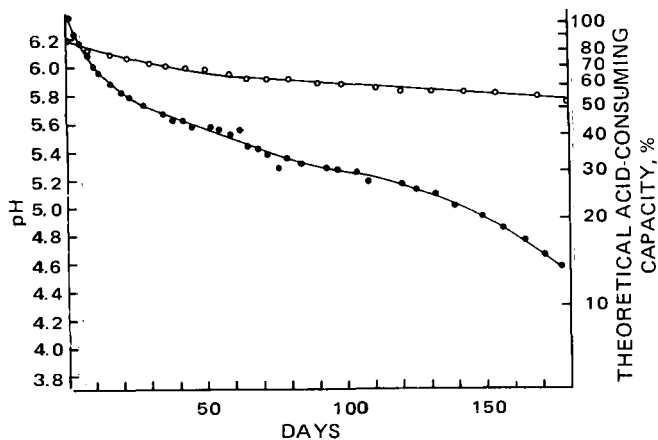**Figure 3**—*Change in pH and acid-consuming capacity of Gel III during aging at 25°. Key: O, acid-consuming capacity; and ●, pH.*

when allowed to stand overnight. However, when a time was reached that apparently corresponded to the inflection point of the pH *versus* time curve, the gel became more translucent. No sediment was observed even when the gel was allowed to stand for prolonged periods; *i.e.*, the gel appeared to be completely dispersed.

The rate of interparticular condensation (and, therefore, the rate of decrease in pH of the gel) would be expected to be determined by the fraction of the total number of collisions due to Brownian motion between the particles that are of sufficient energy for a reaction to occur. This fraction would be affected by the interaction of van der Waals forces of attraction and electrical double-layer repulsion between the charged colloidal particles. Figure 4 is a typical potential energy curve showing the sum of the attractive and repulsive forces between particles.

The behavior of the gels might be explained by flocculation of the fresh gel due to the secondary minimum, M. The character of this type of flocculation is unique in that it is completely reversible and equilibrium distances between particles are of the order of several times the thickness of the double layer (9). Because of the potential energy barrier between particles, the rate of the deprotonation–dehydration reaction between particles would be expected to be relatively slow. However, each collision that does result in a reaction also results in a lower surface potential due to the neutralization of a positively charged edge aluminum ion. As this process continues and the surface potential approaches zero, the potential energy maximum, S, and secondary minimum, M, disappear (Fig. 4). The removal of the potential energy barrier, S, should increase the rate of the deprotonation–dehydration reaction, while removal of the secondary minimum, M, should result in deflocculation or dispersion of the system. Both of these phenomena, dispersion and an increased rate of change of pH, are observed experimentally at nearly the same time during aging.

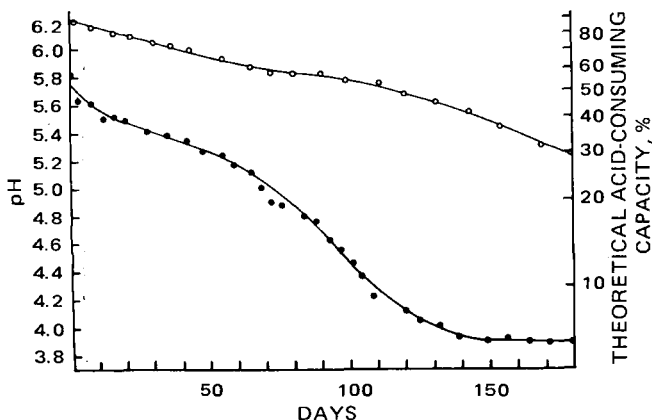Figures 1–3 show that the mechanism responsible for the decrease
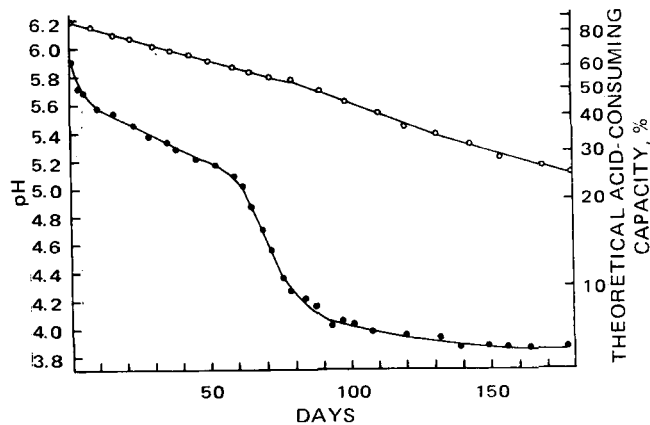
in the pH of the gel with time also causes a decrease in acid-consuming capacity. Polymerization would result in a system in which the hydroxyaluminum particles are larger and more highly ordered; therefore, they should be less susceptible to attack by acid. Therefore, the relationship between acid-consuming capacity and pH decrease is strong evidence for the proposed deprotonation–dehydration reaction.

Based on this mechanism, it would be expected that once the pH reaches a constant value, the acid-consuming capacity should do the same. Figures 2 and 3 clearly indicate that this is not the case. There is, however, a mechanism by which the system could become more resistant to acid which involves no change in pH. According to Hsu (10), the crystallization of aluminum hydroxide involves the combination of small hydroxyaluminum particles vertically and horizontally. Vertical combination of particles, or stacking, involves hydrogen bonding between layers and would not affect the pH of the system. This explanation is feasible for the fact that acid-consuming capacity continues to decrease after the pH reaches a stable value.

Since the gels represented in Figs. 1–3 were precipitated as one batch, the observed differences in the rate of loss of reactivity must be attributed to differences in the amount of washing. The gels lost reactivity in the order III > II > I. There was an inverse relationship between the chloride concentration and the rate of decrease in pH and loss of acid-consuming capacity. This relationship could be accounted for by inhibition of a deprotonation–dehydration reaction by the chloride ion.

Aging of Gels Containing Sulfate—A gel was precipitated from aluminum sulfate with ammonium hydroxide solution to a final pH of 7.0. As seen in Fig. 5, the acid-consuming capacity and the pH remained nearly constant throughout the aging period studied. It is clear

Figure 2—*Change in pH and acid-consuming capacity of Gel II during aging at 25°. Key: O, acid-consuming capacity; and ●, pH.*
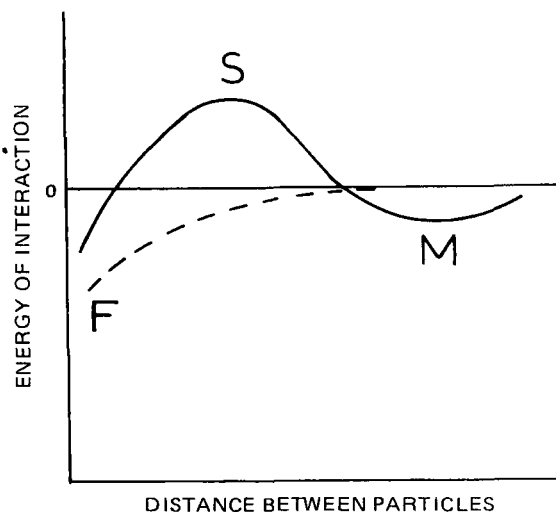

Figure 4—*Potential energy curve showing primary minimum, F, maximum, S, and secondary minimum, M. Key: —, charged surface; and - - -, uncharged surface. (Adapted from Ref. 9.)*
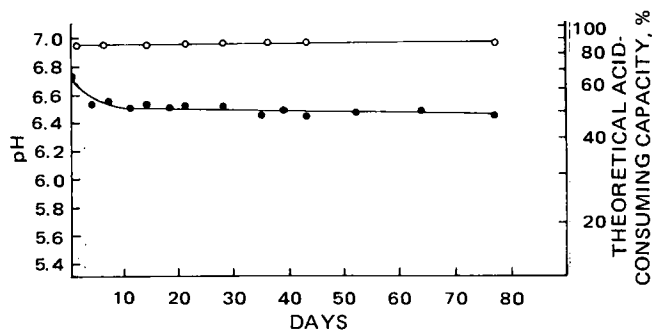
Figure 5—*Change in pH and acid-consuming capacity of sulfate-containing gel during aging at 25°. Key: O, acid-consuming capacity; and ●, pH.*

that the gel containing sulfate was more stable than the corresponding chloride-containing gel.

Hydroxide to Aluminum Ratio—Plots of the molar ratio of bound hydroxide to aluminum for Gels I–III are shown in Fig. 6. The hydroxide to aluminum ratio increased as the gels aged. The change in hydroxide to aluminum ratio was greatest for Gel III, which was most thoroughly washed and therefore had the lowest chloride content. The hydroxide to aluminum ratio was increasing toward 3.0, which is the hydroxide to aluminum ratio that would be predicted by the polymer model as the *ab* dimension approaches infinity. As the hydroxide to aluminum ratio approaches 3, the system should develop the characteristics of a crystalline aluminum hydroxide.

Chloride Activity—The chloride activity, expressed as normality, was determined at several intermediate times during aging for Gels I–III (Fig. 7). The total chloride concentration, as determined by the Volhard titration, and the corresponding activity coefficients expected in aqueous solution are shown in Table I. The fourth column in Table I should represent the maximum value of the chloride activity in the respective gels. If, on the other hand, chloride is being bound by any component of the gel, the measured activity would be expected to be less than the value predicted by Table I.

As seen in Fig. 7, this was exactly what was observed experimentally. In Gels II and III, the chloride activity increased in the order III > II, corresponding to the rates of loss of acid reactivity, decrease in pH, and increase in hydroxide to aluminum ratio. The chloride activity of the gels ultimately reached a constant value which, as shown in Table I, was the activity expected if all chloride in the gels was in solution. These data indicate that chloride ions are being bound in the fresh gel and released gradually as the gel ages. This is consistent with a structural scheme in which anions are bound to the positively charged edge aluminum atoms of the hydroxyaluminum particles. Binding with sufficient strength would prohibit secondary hydrolysis of the edge aluminum, which leads to the formation of a double hydroxide bridge between particles. Although the presence of chloride inhibits this process, the bonding is apparently not strong enough to prevent it entirely.

This picture of the role of the anion is consistent with the fact that gels prepared from aluminum sulfate are more stable than those
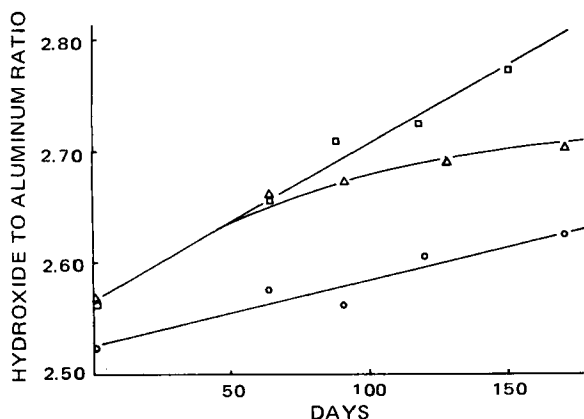

Figure 6—*Change in hydroxide to aluminum ratio during aging at 25°. Key: O, Gel I; △, Gel II; and □, Gel III.*
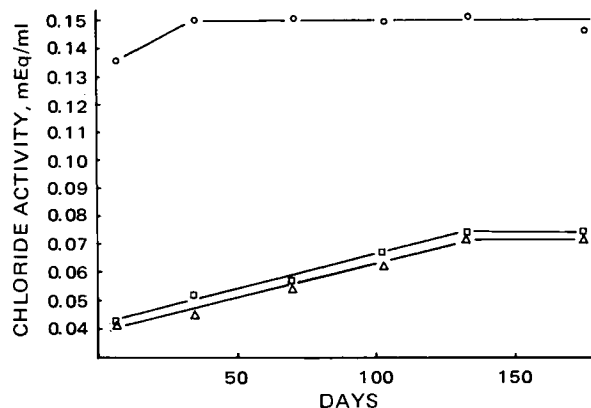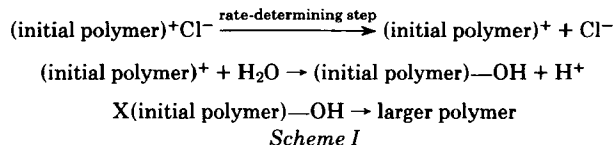

Figure 7—*Change in chloride activity during aging at 25°. Key: O, Gel I; △, Gel II; and □, Gel III.*

prepared from aluminum chloride. The doubly charged sulfate ion would be expected to be more strongly attracted to the positive sites on the hydroxyaluminum particles than the singly charged chloride ion. The small change in pH with age of the sulfate gel (Fig. 5) compared to a chloride gel indicates that interparticular condensation is inhibited to a greater extent in the sulfate gel.

Before the deprotonation–dehydration reaction between particles can occur, the anion must be excluded from the gel structure. Hsu (11) proposed Scheme I for the aging of partially neutralized dilute hydroxyaluminum solutions.

$$\text{(initial polymer)}^+\text{Cl}^- \xrightarrow{\text{rate-determining step}} \text{(initial polymer)}^+ + \text{Cl}^-$$

$$\text{(initial polymer)}^+ + \text{H}_2\text{O} \rightarrow \text{(initial polymer)}\text{—OH} + \text{H}^+$$

$$\text{X(initial polymer)—OH} \rightarrow \text{larger polymer}$$
Scheme I

The first step of this scheme would account for the observed increase in chloride activity with age.

Crystallite Dimensions—It was shown previously (1) that the relative intensities of the 4.82- and 4.35-Å peaks of poorly crystalline aluminum hydroxide gels are reversed in comparison to highly crystalline gibbsite. The more rapid development of the (110) reflection (4.35 Å) is consistent with horizontal alignment of particles resulting from the deprotonation–dehydration reaction.

Two chloride-containing gels prepared under the same conditions were studied by X-ray diffraction. One had been aged for 1 year, the other for 6 months. The acid-consuming capacities were 9 and 22% of theory, respectively. The pH of both gels was between 3.8 and 3.9. The results for the two gels in terms of crystallite dimensions are D_{002} (Å) = 31.5 at 6 months and 37.3 at 1 year, D_{110} (Å) = 246.0 at 6 months and 238.0 at 1 year.

The dimension of the *ab* plane was nearly the same for the two gels. If crystal growth in the *ab* plane takes place by deprotonation–dehydration between smaller particles, the pH values of the gels would be expected to be nearly the same, which was the case.

The gel aged 1 year had a significantly larger dimension in the *c* direction than the 6-month sample. This finding indicates that stacking of structural units, involving no pH change, was more developed in the older gel. This mechanism could account for the observed difference in acid-consuming capacity.

These findings are consistent with the polymer model discussed previously (1). The initial reaction consists of polymerization of hy-

Table I—Chloride Concentration of Gels and Corresponding Activity Coefficients in Aqueous Solution

Gel	(Cl), N	γ^a	a_{Cl}, N	Final Activity Value (Experimental)
I	0.211	0.67	0.142	0.145
II	0.105	0.77	0.081	0.072
III	0.099	0.77	0.076	0.074

[a] From G. M. Barrow, "Physical Chemistry," 2nd ed., McGraw-Hill, New York, N.Y., 1961, p. 706.

droxyaluminum ions into stable six-membered rings or multiples thereof. According to Hsu and Bates (12), the inclusion of aluminum ions into rings is complete at a hydroxide to aluminum ratio of about 2. Additional base transforms these rings into larger units. Hsu (11) proposed that the difference between the initial precipitation process and the aging process is the source of hydroxide. Hydroxide added during precipitation is taken up rapidly, whereas the spontaneous hydrolysis is slow, especially in the presence of high salt concentrations (11). This secondary hydrolysis results in the formation of larger particles, which are more highly ordered and resistant to attack by acid, and leads ultimately to the formation of gibbsite (13, 14).

SUMMARY

The aging of aluminum hydroxide gels precipitated at pH 7.0 from aluminum chloride solution and strong ammonia solution was studied by determination of the hydroxide to aluminum ratio as a function of the age of the gel, measurement of gel pH and acid-consuming capacity, determination of the chloride activity of the gel, and X-ray line-broadening measurements. The results are consistent with a deprotonation–dehydration polymerization reaction in which positively charged hydroxyaluminum particles are joined at their edges by double hydroxide bridges. This process results in larger particles, which are more highly ordered and resistant to attack by acid. This reaction leads to the eventual formation of microcrystalline gibbsite.

Chloride was found to inhibit the loss of reactivity of aluminum hydroxide gel. The chloride activity increases as the gel ages until it reaches the activity of chloride in aqueous solution. It was concluded that chloride inhibits the loss of reactivity by binding at the positively charged edge of the hydroxyaluminum particles. This inhibits further polymerization of the particles.

A sulfate-containing gel precipitated at pH 7.0 was more stable than a chloride-containing gel precipitated at the same pH. This finding was attributed to stronger binding of the doubly charged sulfate ion by the polymers than the singly charged chloride ion.

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ACKNOWLEDGMENTS AND ADDRESSES

Structure of Aluminum Hydroxide Gel III: Mechanism of Stabilization by Sorbitol

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Abstract □ The effect of sorbitol on the aging of aluminum hydroxide gel, prepared by the reaction of aluminum chloride solution with strong ammonia solution to a final pH of 7.0, was studied by potentiometric titration, acid-consuming capacity, pH, hydroxide to aluminum ratio, chloride activity, X-ray diffraction, and IR spectroscopy. Gels containing sorbitol lost less than 10% of their acid-consuming capacity during a 6-month aging period compared with a loss of more than 60% for an identical gel without sorbitol. The mechanism by which sorbitol stabilizes the gel appears to be inhibition of the secondary polymerization reaction which takes place upon aging. An other polyhydroxy compound, quercetin, also stabilizes aluminum hydroxide gel.

Keyphrases □ Aluminum hydroxide gel—aging mechanism studied, effect of sorbitol □ Gels—aluminum hydroxide, aging mechanism studied, effect of sorbitol □ Aging mechanism—aluminum hydroxide gel, effect of sorbitol □ Antacids—aluminum hydroxide gel, aging mechanism studied, effect of sorbitol □ Sorbitol—effect on aging mechanism of aluminum hydroxide gel

Previous investigations (1, 2) demonstrated that a polymer model can be used to describe the structure and aging characteristics of aluminum hydroxide gel precipitated by the reaction of aluminum chloride or aluminum sulfate solution with sodium hydroxide or strong ammonia solution to a final pH of 7.0. The purpose of this investigation was to study the effect of sorbitol on the initial precipitate and on the aging characteristics of a gel prepared from aluminum chloride solution and strong ammonia solution at pH 7.0.