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## Role of Carbonate in Acid Neutralization of Aluminum Hydroxide Gel

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**Abstract** □ The role of carbonate in the acid neutralization of a carbonate-containing aluminum hydroxide gel was studied. The pH-stat neutralization reaction was comprised of three phases: an initial, immediately reacting phase; a slow, zero-order phase; and a terminal, fast zero-order phase. The evolution of carbon dioxide and the appearance of aluminum ions were monitored during neutralization. Acid neutralization is believed to occur predominantly at the aluminum-carbonate bond during the slow phase of neutralization. The reaction of structural carbonate disrupts the gel structure and increases the porosity and surface area of the gel. The diffusion of acid into the gel structure is facilitated and accelerates the neutralization rate, as seen in the final phase of the pH-stat titrations. This behavior of carbonate is probably responsible for the rapid and complete neutralization of acid generally observed with carbonate-containing aluminum hydroxide gel.

**Keyphrases** □ Aluminum hydroxide gel—acid neutralization, pH-stat titration, role of carbonate □ Gels—aluminum hydroxide, acid neutralization, pH-stat titration, role of carbonate □ Acid neutralization—aluminum hydroxide gel, pH-stat titration, role of carbonate □ pH-stat titration—aluminum hydroxide gel, acid neutralization, role of carbonate □ Carbonate—role in acid neutralization of aluminum hydroxide gel, pH-stat titration □ Antacids—aluminum hydroxide gel, acid neutralization, pH-stat titration, role of carbonate

Carbonate is an integral part of the aluminum hydroxide gel structure (1). The presence of carbonate in the gel structure contributes to gel stability (2), probably by inhibiting polymerization of the hydroxylaluminum particles and retarding the development of a highly ordered structure. In addition to enhanced stability, carbonate-containing aluminum hydroxide gels usually exhibit a faster acid neutralization rate than is observed in gels stabilized by other anions such as chloride or sulfate (2). The objective of this investigation was to determine the mechanism of acid neutralization in carbonate-containing aluminum hydroxide gels.

#### EXPERIMENTAL

**Materials**—All chemicals used were either official or reagent grade.

**Aluminum Hydroxide Gel Preparation**—Carbonate-containing aluminum hydroxide gel was prepared by the reaction of aluminum chloride, sodium bicarbonate, and sodium carbonate to a final pH of 6.5 (2).

**Analytical Procedures**—The equivalent aluminum oxide content was determined by the ethylenediaminetetraacetic acid titration (3). The acid reactivity was measured using an automated pH-stat method (4).

The carbonate content of the gels was analyzed by a gasometric displacement technique (5) using a Chittick apparatus<sup>1</sup>. The results are expressed as the ratio of millimoles of carbon dioxide evolved to millimoles of aluminum in the gel.

A specially designed glass reaction vessel, with a polytef head and methyl methacrylate top, was fabricated to study the evolution rate of carbon dioxide from the carbonate-containing aluminum hydroxide gels during neutralization with 1.0 N HCl. The reaction assembly consisted of a glass reaction vessel and an airtight head and top, which sealed the system and served as a holder for the electrodes, the titrant delivery tube, and the gas outlet tube connected to the Chittick apparatus.

The glass reaction flask was made of 45-mm o.d. × 100-mm Pyrex glass tubing. The wall thickness was 1.92 mm. The reaction vessel was fabricated with a flat bottom to facilitate the use of a standard 2.54-cm polytef-coated magnetic stirring bar.

The reaction head was fabricated from a 5.08-cm polytef rod (Fig. 1). The bottom side was machined to 41-mm diameter to fit inside the reaction vessel. A groove for a 3.175 × 41.275-mm o.d. O-ring was machined in the circumference of the bottom lip so that a tight press fit was obtained when the reaction vessel was forced over the O-ring.

Appropriately sized holes were drilled through the head to allow the insertion of the electrodes, the titrant delivery tube, and the gas outlet tube. A clear methyl methacrylate top was machined to the same pattern as the head. Eight holes were drilled in the top and threaded in the head to accept binding-head machine screws. The O-rings were fitted over the electrodes, the titrant delivery tube, and the gas outlet and were placed between the top and the head. The openings in the top and head were beveled to compress the O-rings and to seal the head when the machine screws were tightened.

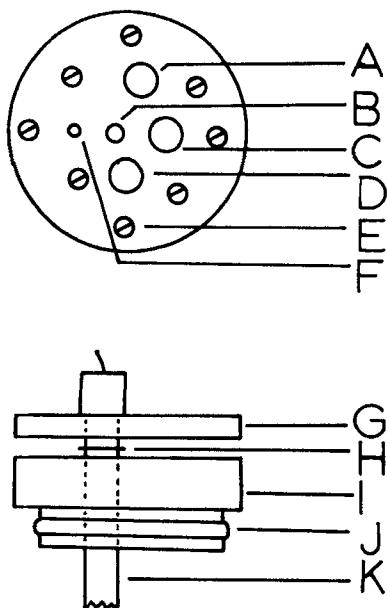
An injection port was included in the reaction head. An appropriately sized hole was machined in the head to accept a high-pressure liquid chromatographic septum.

The reaction vessel, head, and top were combined with the pH-stat titrator and the Chittick apparatus. The sealed reaction vessel replaced the decomposition flask of the Chittick apparatus, and the 25-ml pH-stat autoburet replaced the glass buret.

The following procedure is used to monitor the evolution of carbon dioxide during the neutralization of a sample containing 380 mg equivalent Al<sub>2</sub>O<sub>3</sub> by 1.0 N HCl at pH 3.0. Transfer an appropriate volume of liquid gel, accurately weighed, into the decomposition reaction vessel. Secure the reaction vessel to the reaction head assembly. With the stopcock open to the atmosphere, adjust the leveling bulb to bring the displacement solution to 20.0 ml above the zero mark. Let the system stand 1–2 min to allow the temperature and pressure within the apparatus to equilibrate to room conditions. Then close the stopcock to the atmosphere. Lower the leveling bulb until the level reads zero on the measuring buret.

Using a glass syringe fitted with a 7.62-cm, 22-gauge needle, insert the needle through the injection port septum and slowly add 20.0 ml of

<sup>1</sup> Sargent-Welch Scientific Co., Skokie, Ill.



**Figure 1**—Top and head for pH-stat carbonate analyzer. Key: A, outlet to Chittick apparatus; B, titrant delivery inlet; C and D, electrode ports; E, machine screw; F, injection port; G, methyl methacrylate top; H, O-ring; I, polytef head; J, O-ring; and K, an electrode.

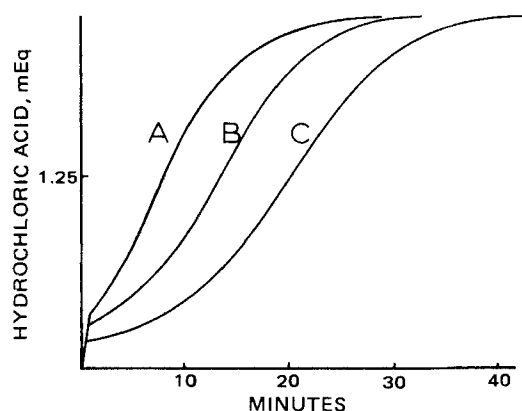
double-distilled water maintained at room temperature. Withdraw the needle and check to see that the level of displacement solution in the measuring tube is at the zero mark. Turn on the magnetic stirrer, previously calibrated at 300 rpm, and activate the pH-stat instrument to maintain pH 3.0 by adding 1.0 N HCl from the autoburet.

As the reaction proceeds, manually lower the leveling bulb to maintain the level of the measuring buret and leveling bulb at the same level. Record milliliters of carbon dioxide evolved with time from the measuring buret. Note the room temperature and atmospheric pressure and convert the volume displaced to standard conditions.

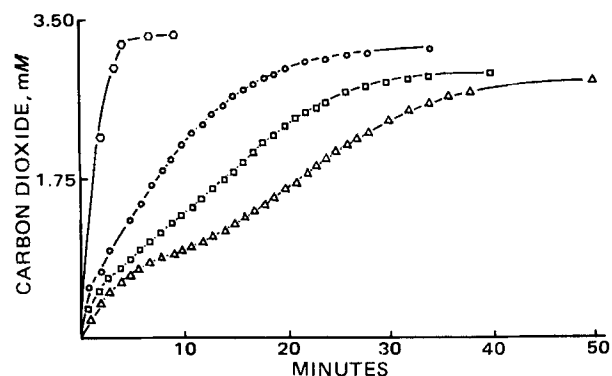
Anhydrous sodium carbonate, dried at 105° for 4 hr, was used to evaluate the specially designed system to monitor the evolution of carbon dioxide during the pH-stat titration. Weighed samples of sodium carbonate were placed in the reaction vessel and decomposed using 1.0 N HCl added by the autoburet. The nine samples analyzed evolved 94.9% of the theoretical amount of carbon dioxide.

The Chittick procedure uses 4 N HCl to decompose the sodium carbonate. When 4 N HCl was used in the autoburet, five replicate determinations using sodium carbonate evolved 99.8% of the expected amount of carbon dioxide. It was concluded that the use of 1.0 N HCl in the pH-stat titration could result in a 5% understatement of the amount of carbon dioxide evolved from the gel. This small error should not interfere with the neutralization study using 1.0 N HCl.

The pH-stat apparatus was calibrated with sodium carbonate and 4.0 N HCl before and after the experiment. Average values of 99.6 and 99.7% of theory were obtained before and after the experiment, respectively,



**Figure 2**—The pH-stat titrgram of carbonate-containing aluminum hydroxide gels aged at 25°. Key: A, 12 months; B, 19 months; and C, 25 months.



**Figure 3**—Evolution of carbon dioxide during pH-stat titration from carbonate-containing aluminum hydroxide gels aged at 25°. Key: O, sodium carbonate solution; O, 12 months; □, 19 months; and Δ, 25 months.

indicating that the system was functioning properly and had remained sealed during the pH-stat titrations.

IR spectra<sup>2</sup> were obtained by air drying a film of the gel on a zinc sulfide<sup>3</sup> window. The best experimental results were obtained with films containing approximately 0.3 mg of aluminum oxide/cm<sup>2</sup>.

IR analysis of partially neutralized aluminum hydroxide gel was obtained by stopping the addition of acid from the autoburet during neutralization. The reacting gel medium was immediately filtered using a 10-ml glass syringe fitted with a filter adapter<sup>4</sup>, prefilter, and 0.45-μm-membrane filter. The total elapsed time was 15 sec. An air-dried film of the collected solids on a zinc sulfide window was prepared as previously described.

Atomic absorption spectrophotometry was used to monitor the appearance of aluminum ions in the reaction medium as the aluminum hydroxide gel was neutralized by 1.0 N HCl at pH 3.0. The addition of acid from the autoburet was stopped at various points during neutralization. The reaction medium was immediately filtered using the previously described filtration assembly. The filtered medium was appropriately diluted with distilled water, and the aluminum content was determined by atomic absorption analysis. An atomic absorption spectrophotometer<sup>5</sup> equipped with a hollow cathode aluminum lamp<sup>6</sup> was used. The aluminum-ion concentration in the reaction medium was calculated by taking the total reaction volume at the time the reaction was stopped as the sum of the volume of distilled water, the volume of gel, and the volume of 1.0 N HCl added to that time as determined from the titrgram.

## RESULTS AND DISCUSSION

The aluminum hydroxide gels studied contained carbonate as an integral part of the gel structure, as demonstrated by IR analysis of the gel. The carbonate band that occurs at 1450 cm<sup>-1</sup> in sodium carbonate split and appeared as two bands at 1525 and 1415 cm<sup>-1</sup>. This splitting of the carbonate band was due to the coordination of carbonate with aluminum in the gel structure (1).

The acid neutralization of carbonate-containing aluminum hydroxide gel appears to consist of three phases when studied using the pH-stat technique (4): an initial, immediately reacting phase; a slow zero-order phase; and a terminal, fast zero-order phase. This reactivity pattern was somewhat unexpected because, for example, the dissolution rate of a suspension generally decreases as dissolution occurs due to the higher solubility and more rapid dissolution rate of the small particles in the suspension.

To understand the reaction mechanism responsible for the unexpected reactivity pattern, the rates of acid neutralization and carbon dioxide evolution were determined for three carbonate-containing aluminum hydroxide gels aged for 12, 19, and 25 months at 25°. As seen in Fig. 2, the gels all exhibited the same reactivity pattern. As previously reported (4), the effect of aging was to decrease the amount of immediately reacting material and to reduce  $k_{II}$  and  $k_{III}$ , the zero-order rate constants for the slow phase and the final fast phase, respectively.

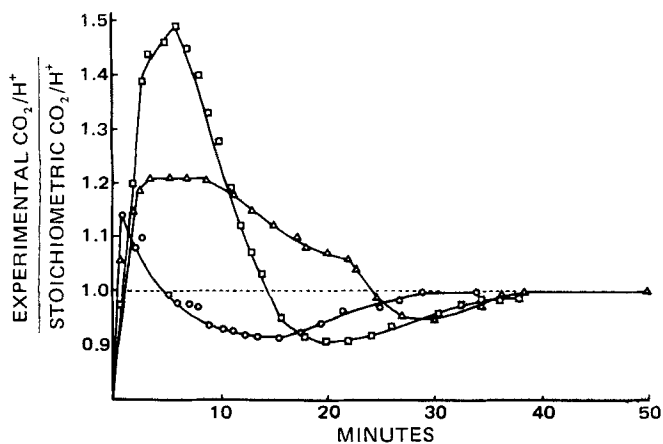
<sup>2</sup> Model 421, Perkin-Elmer Corp., Norwalk, Conn.

<sup>3</sup> Irtan 2, Eastman Kodak Co., Rochester, N.Y.

<sup>4</sup> Micro-Syringe holder, Millipore Corp., Bedford, Mass.

<sup>5</sup> Model 290B, Perkin-Elmer Corp., Norwalk, Conn.

<sup>6</sup> Perkin-Elmer Corp., Norwalk, Conn.



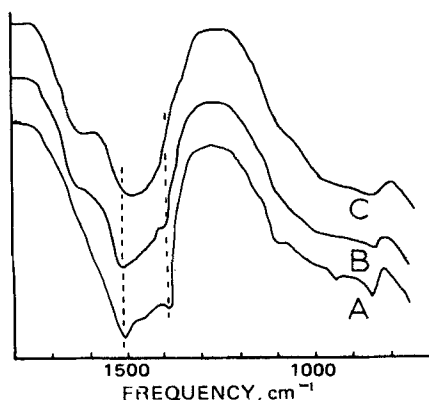
**Figure 4**—Experimental ratio of evolved carbon dioxide to acid neutralized compared to the stoichiometric ratio of total carbonate in the gel to total acid neutralized during pH-stat titration of carbonate-containing aluminum hydroxide gels aged at 25°. Key: O, 12 months; □, 19 months; Δ, 25 months; and - - -, expected behavior.

Carbon dioxide evolution from these gels followed a somewhat different pattern (Fig. 3). The carbon dioxide evolution rate was greatest during the first 10 min, which corresponds to the slow phase of the acid neutralization curve.

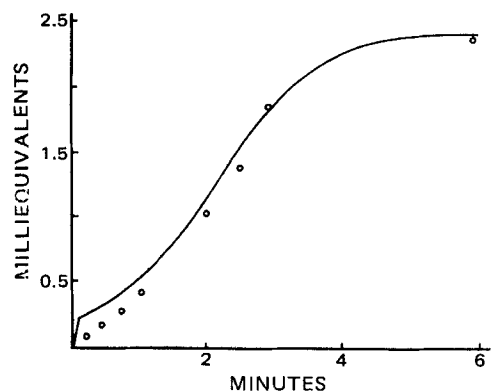
Carbon dioxide evolution from a solution of sodium carbonate is shown in Fig. 3. A comparison of the evolution of carbon dioxide from a sodium carbonate solution and from the aluminum hydroxide gels supports the hypothesis that carbonate is part of the gel structure. Carbon dioxide was evolved at a constant, rapid rate from the sodium carbonate solution. Carbonate was released much more slowly from aluminum hydroxide gel and at a rate that varied during neutralization.

The relationship between carbon dioxide evolution and acid neutralization is seen more clearly if the experimental ratio of evolved carbon dioxide to acid neutralized ( $\text{CO}_2/\text{H}^+$ ) is compared to the stoichiometric ratio of total carbonate in the gel to the total acid neutralized. The stoichiometric ratio of total carbonate in the gel determined by the Chittick procedure to the total acid neutralized was 0.135 in the 12-month gel, 0.120 in the 19-month gel, and 0.115 in the 25-month gel. The experimental ratio of evolved carbon dioxide to acid neutralized differed from the stoichiometric ratio (Fig. 4). During the first two phases of the neutralization reaction, more carbon dioxide than expected was liberated. Less carbon dioxide was evolved than predicted during the final phase of neutralization.

The role of carbonate in neutralization was further studied by comparing the IR spectra of the gel before neutralization and after partial neutralization. Figure 5 shows that the gel aged 12 months had a split carbonate band, indicating that carbonate was coordinated with aluminum. After the gel was 15% neutralized, the split band was less pronounced. At 50% neutralization, the carbonate band appeared as a single band at  $1470\text{ cm}^{-1}$ . A small degree of interaction still existed between carbonate and aluminum at this point since the band was shifted from



**Figure 5**—IR spectrum of a carbonate-containing aluminum hydroxide gel aged 12 months at 25°. Key: A, unreacted, B, after 15% neutralization, and C, after 50% neutralization.



**Figure 6**—Appearance of aluminum ion during pH-stat titration of carbonate-containing aluminum hydroxide gel aged 1 day at 25°. Key: —,  $\text{H}^+$  consumed; and O,  $\text{Al}^{3+}$  in solution.

the normal position at  $1445\text{ cm}^{-1}$ . These changes in the IR spectrum during neutralization indicate that the association between carbonate and aluminum is destroyed during the early phases of neutralization. Evidence of coordination with aluminum was virtually gone by the time the gel was 50% neutralized.

The milliequivalents of aluminum ion appearing in solution was less than the milliequivalents of acid neutralized during the first two phases of the pH-stat titration. The result is seen in Fig. 6 for a carbonate-containing aluminum hydroxide gel aged 1 day. Similar behavior was observed after the gel was aged for 40 and 193 days at 25°.

The slow appearance of aluminum ion is consistent with the high ratio of evolved  $\text{CO}_2/\text{H}^+$  during the early phases of the neutralization reaction. The early acid attack appeared to occur predominantly at the aluminum-carbonate bonds. The appearance of aluminum ions, which were only generated by the complete neutralization of the aluminum hydroxide gel, was delayed. The milliequivalents of aluminum ion in solution was equal to the milliequivalents of acid neutralized during the third phase of the neutralization reaction where the predominant reaction was the attack of aluminum-hydroxyl bonds by protons.

Aluminum hydroxide gel may be considered to have a polymeric structure consisting of aluminum atoms joined by double hydroxide bridges, which may ultimately form a large, ordered structure. Carbonate appears to replace a hydroxyl in the double hydroxide bridges. The carbonate in the gel structure readily reacts with acid during neutralization. The initial acid reaction with carbonate disrupts the gel structure and causes an increased porosity and surface area. This facilitates the diffusion of acid into the gel and causes an accelerated neutralization rate, as seen in the third phase of the pH-stat titrations of aluminum hydroxide gel. This unique role of carbonate is probably responsible for the rapid and complete neutralization of acid generally observed with carbonate-containing aluminum hydroxide gel.

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