

Effect of Dilution on Reactivity and Structure of Aluminum Hydroxide Gel

NICHOLAS J. KERKHOF *, JOE L. WHITE †, and STANLEY L. HEM **

Abstract □ Aluminum hydroxide gel loses reactivity upon aging. However, a sharp decrease in reactivity occurs when the gel is diluted with double-distilled water. The loss of reactivity is directly related to the degree of dilution, but dilution with dioxane or the mother liquor has no effect on reactivity. It is hypothesized that dilution with water causes a change in the equilibrium between stabilizing ions incorporated in the gel structure and ions in solution. As the stabilizing ions leave the gel structure to reestablish the equilibrium, a loss of reactivity is observed until a new equilibrium is established.

Keyphrases □ Aluminum hydroxide gel—effect of dilution on reactivity and structure □ Gels—effect of dilution on reactivity and structure of aluminum hydroxide gel □ Acid reactivity—effects of dilution on aluminum hydroxide gel

Aluminum hydroxide gel is a complex material whose structure is not fully understood. Several factors involved in the manufacture of aluminum hydroxide gel have been found to affect acid reactivity, including precipitation temperature (1), pH (2), order of addition of reactants (1, 3), and washing (4). Changes in the acid reactivity of aluminum hydroxide gel were observed to occur following dilution of the gel. This report confirms this observation and proposes a mechanism by which the reactivity of aluminum hydroxide gel is affected by dilution.

EXPERIMENTAL

Materials—All chemicals used were either official or reagent grade. Double-distilled water was used.

Preparation of Aluminum Hydroxide Gel—Aluminum hydroxide gel was prepared by the reaction of aluminum chloride, sodium carbonate USP, and sodium bicarbonate USP at pH 6.5 (2). Aluminum hydroxide gel from two identical precipitations was used to study the effect of dilution. The final volume of each gel was adjusted to produce one gel containing 4.8% Al_2O_3 and a second gel containing 3.6% Al_2O_3 .

A third gel was precipitated and, in place of the usual washing procedure, the mother liquor was immediately separated by vacuum filtration using a buchner funnel with No. 1 filter paper. The solids were maintained as a moist cake while the clear mother liquor was collected. A portion of the mother liquor was used to reconstitute the moist cake to prepare a gel containing 3.9% Al_2O_3 .

Aluminum Hydroxide Gel Dilutions—The aluminum hydroxide gel containing 4.8% Al_2O_3 was used to study the effect of diluting the gel with double-distilled water. Three dilutions were prepared whereby 12.5, 25.0, and 50.0 g of gel were diluted to 100 ml with double-distilled water. Therefore, the samples contained 0.6, 1.2, and 2.4% Al_2O_3 , respectively.

The gel containing 3.6% Al_2O_3 was used to prepare a series of gels to study the effect of dilution with water-dioxane mixtures. Fifty grams of gel was diluted to 100 ml with a water-dioxane mixture containing 0, 25, 50, 75, or 100% dioxane. All diluted gels contained 1.8% Al_2O_3 .

The gel containing 3.9% Al_2O_3 was used to study the effect of dilution with the mother liquor. Fifty grams of the gel was diluted to 100 ml using the mother liquor, an equal mixture of mother liquor and double-distilled water, or double-distilled water. The samples contained 1.95% Al_2O_3 .

Analytical Procedures—The aluminum oxide content was determined by ethylenediaminetetraacetic acid titration (5).

The acid reactivity was monitored by a pH-stat technique similar to the method described by Steinberg *et al.* (6). An automated technique utilizing a pH meter, a titrator, an autoburet, a titration assembly, and a recorder¹ was used.

An appropriate volume of water was added to the reaction vessel and brought to pH 3.0. A volume of sample containing 38 mg Al_2O_3 was then added. The volume of water was adjusted for each sample to produce a reaction volume of 22 ml. The instrument was set to maintain pH 3.0 by adding 1.0 N HCl from the autoburet. The instrument was activated simultaneously with the sample injection. The recorder plotted milliliters of 1.0 N HCl added *versus* time. The acid reactivity of each sample is expressed as T_{50} : the time required to add 50% of the total 1.0 N HCl needed to neutralize the aluminum hydroxide gel at 25°.

RESULTS AND DISCUSSION

Aluminum hydroxide gel becomes less reactive upon aging. However, as seen in Fig. 1, the increase in T_{50} was greatest during the first days after precipitation or dilution with double-distilled

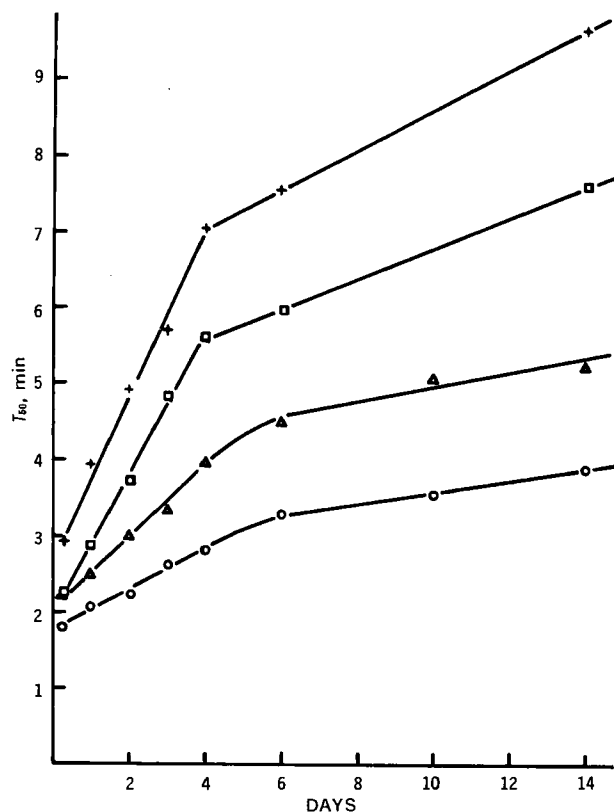


Figure 1—Change in T_{50} during aging at 25°. Key: O, undiluted gel containing 4.8% Al_2O_3 ; and gel diluted with double-distilled water to contain: Δ, 2.4% Al_2O_3 ; □, 1.2% Al_2O_3 ; and +, 0.6% Al_2O_3 .

¹ pH meter PHM 26, titrator TTT 11, autoburet ABU 12 (2.5 ml), titration assembly TTA 3, and recorder SBR 2, all from Radiometer, Copenhagen, Denmark.

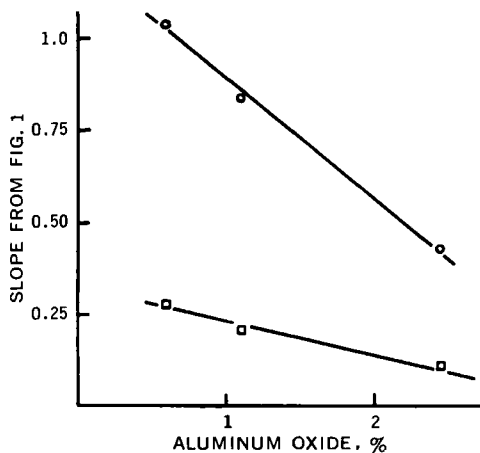


Figure 2—Effect of dilution with double-distilled water on the rate of change of acid reactivity. Key: \circ , initial period; and \square , long-term period.

water. An initial sharp decrease in reactivity was observed during the first 4–6 days. The initial rate of loss of reactivity was directly related to the degree of dilution (Fig. 2). The gel diluted to 0.6% Al_2O_3 had the greatest increase in T_{50} during the first several days. The undiluted sample of the freshly precipitated gel also lost reactivity more sharply during the first several days following precipitation, but the increase in T_{50} during the first 4 days was from 1.8 to 2.8 min compared to an increase from 2.9 to 7.0 min for the most dilute sample.

A much smaller increase in T_{50} occurred for all dilutions as well as the undiluted gel after the initial period. The rate of loss of reactivity in this later period also was directly related to dilution (Fig. 2). The samples were monitored for 112 days, and the rate of loss of reactivity was constant for each gel after the initial period. The rate of loss of reactivity in the second period appears to represent the loss of reactivity normally observed during the aging of aluminum hydroxide gel.

The series of gels containing 1.8% Al_2O_3 but diluted with varying ratios of double-distilled water–dioxane produced the same pattern of increasing T_{50} (Fig. 3) as was observed when the gels were diluted with double-distilled water. It appears that dilution with dioxane has no effect on reactivity since the sample diluted with 100% dioxane had virtually the same reactivity profile as the freshly precipitated, undiluted gel (Table I). However, the concentration of water in the diluting solution was important. A greater initial increase in T_{50} was observed as the concentration of water in the diluting solution was increased.

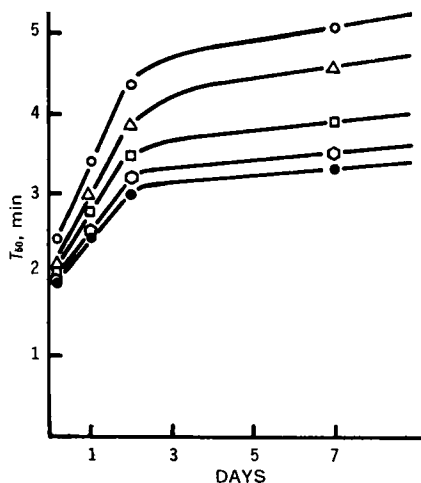


Figure 3—Effect of dilution with varying double-distilled water–dioxane mixtures. Key: \bullet , 100% dioxane; \circ , 25% water–75% dioxane; \square , 50% water–50% dioxane; \triangle , 75% water–25% dioxane; and \circ , 100% water.

Table I—Acid Reactivity of Gel Diluted with Dioxane Compared to Undiluted Gel

Days	T_{50} , min	
	Undiluted Gel Containing 3.6% Al_2O_3	Gel Diluted with Dioxane to 1.8% Al_2O_3
0.25	2.0	2.0
1	2.5	2.5
2	3.3	3.0
7	3.4	3.3
14	4.5	3.9
28	4.7	4.6
56	5.2	5.4
112	8.1	8.9

The rate of change in T_{50} during the initial period was directly related to the concentration of water in the water–dioxane diluting mixtures (Fig. 4). A much smaller rate of change of acid reactivity occurred after the initial period. The later increase in T_{50} also was directly related to the concentration of water in the water–dioxane diluting mixtures (Fig. 5).

The pattern of a sharp decrease in reactivity followed by a slow rate of loss of reactivity following precipitation or dilution of aluminum hydroxide gel with water suggests the establishment of an equilibrium condition. Several reports (2, 7–9) indicated that ions present in the precipitation solution may be incorporated in the gel structure. These ions act to stabilize the aluminum hydroxide gel structure.

It was hypothesized that dilution with water alters the equilibrium between ions in the gel structure and in solution. When equilibrium is reestablished, the concentration of stabilizing ions in the gel structure is reduced. The reactivity of the gel reflects this change in concentration of stabilizing ions and a sharp decrease in reactivity occurs until a new structure is established. The new structure then changes at a rate related to the concentration of ions present in the gel structure and a constant, long-term loss of acid reactivity is observed.

A final series of dilutions was prepared to test this hypothesis. Fifty grams of the gel containing 3.9% Al_2O_3 was diluted to 100 ml with the mother liquor, an equal mixture of mother liquor and water, or double-distilled water. All sample dilutions contained 1.95% Al_2O_3 . Figure 6 indicates that dilution with the mother liquor did not affect reactivity since the increase in T_{50} was virtually identical for the freshly prepared undiluted gel and for the sample diluted with mother liquor. The sample diluted with water had a sharp initial increase in T_{50} . The water–mother liquor dilution was intermediate in effect.

The unwashed gel was more reactive than either of the gels used for the water dilution or dioxane dilution experiments. The washing operation probably causes the loss of stabilizing ions from the

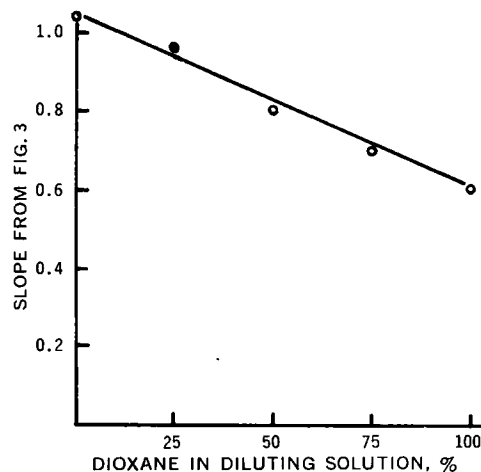


Figure 4—Effect of dilution with varying double-distilled water–dioxane mixtures on the initial rate of loss of acid reactivity.

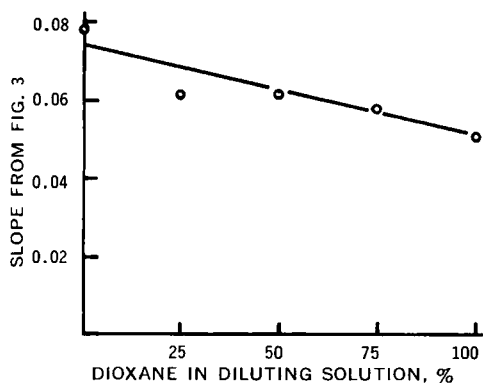


Figure 5—Effect of dilution with varying double-distilled water–dioxane mixtures on the long-term rate of loss of acid reactivity.

gel and results in a less acid reactive gel. Further experiments are in progress to determine the effect of washing on acid reactivity.

These results support the previous hypothesis, because the equilibrium between ions in the gel structure and ions in solution would not be affected by dilution with the mother liquor or dioxane. Dilution with water always caused a sharp loss of reactivity.

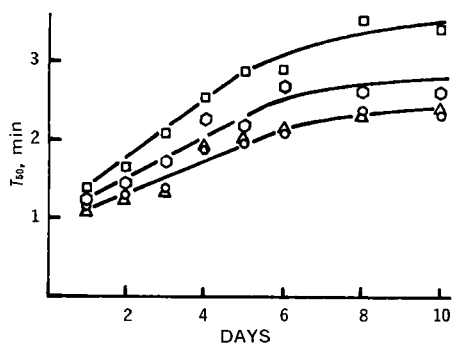


Figure 6—Effect of dilution with mother liquor. Key: ○, undiluted gel containing 3.9% Al_2O_3 ; and gel diluted to 1.95% Al_2O_3 with: △, mother liquor; ○, 50% mother liquor–50% double-distilled water; and □, double-distilled water.

The change in reactivity was directly related to the amount of water added to the gel. The important stabilizing function of ions incorporated in the gel structure is illustrated by this study.

The composition of the solution used to dilute the gel has an important effect on the long-term acid reactivity of the aluminum hydroxide gel. A carefully designed diluting solution will minimize the loss of acid reactivity normally observed with aluminum hydroxide gels, resulting in increased efficacy and longer shelflife.

The composition of the solution and the technique used to wash the gel may likewise affect the acid reactivity of the gel.

This study emphasizes the complex structure of aluminum hydroxide gel. The preparation of aluminum hydroxide gel requires a carefully controlled manufacturing procedure to produce a highly reactive gel of uniform quality.

REFERENCES

- (1) J. A. Lewis and C. A. Taylor, *J. Appl. Chem.*, **8**, 223(1958).
- (2) S. L. Hem, E. J. Russo, S. M. Bahal, and R. S. Levi, *J. Pharm. Sci.*, **59**, 317(1970).
- (3) D. Papee, R. Tertian, and R. Biais, *Bull. Soc. Chim. Fr.*, **1958**, 1301.
- (4) R. H. Green and S. L. Hem, *J. Pharm. Sci.*, **63**, 635(1974).
- (5) "The United States Pharmacopeia," 18th rev., Mack Publishing Co., Easton, Pa., 1970, p. 26.
- (6) W. H. Steinberg, H. H. Hutchins, P. G. Pick, and J. S. Lazar, *J. Pharm. Sci.*, **54**, 625(1965).
- (7) R. J. Barnhisel and C. I. Rich, *Soil Sci. Soc. Amer. Proc.*, **29**, 531(1965).
- (8) P. H. Hsu, International Committee for the Study of Bauxites and Aluminum Oxides-Hydroxides, 3 Congrès, Nice, 1973, p. 613.
- (9) G. J. Ross and R. C. Turner, *Soil Sci. Soc. Amer. Proc.*, **35**, 389(1971).

ACKNOWLEDGMENTS AND ADDRESSES

Received July 24, 1974, from the *Department of Industrial and Physical Pharmacy and the †Department of Agronomy, Purdue University, West Lafayette, IN 47907

Accepted for publication November 11, 1974.

Supported in part by a David Ross Fellowship (to N. J. Kerkhof).

This article constitutes Journal Paper No. 5634, Purdue University Agricultural Experiment Station, West Lafayette, IN 47907

* To whom inquiries should be directed.