

IR Studies of Development of Order in Aluminum Hydroxide Gels

STEVEN L. NAIL *, JOE L. WHITE †, and STANLEY L. HEM **

Abstract □ The usefulness of deuteration in detecting the development of order in aluminum hydroxide gel by IR spectra is demonstrated. By treatment of gel samples with deuterium oxide vapor at room temperature, the relative ease with which deuterioxy-hydroxyl exchange takes place is determined as a function of the age of the gel. The use of scale expansion in conjunction with deuteration allows detection of IR absorbance characteristic of gibbsitic material long before such detection is possible by conventional IR analysis or X-ray diffraction.

Keyphrases □ IR spectroscopy—detection of development of order in deuterated aluminum hydroxide gels □ Aluminum hydroxide gels—deuteration, IR detection of development of order □ Deuteration—aluminum hydroxide gels, related to age of gel

IR spectral analysis of aluminum hydroxide gel detects well-defined absorption bands in the hydroxyl bending and hydroxyl deformation regions of the spectrum as the gel ages (1). These bands represent structural hydroxyls that are part of an ordered structure (2–4). Since each structural unit absorbs IR radiation independently, the detection of order does not depend on the regular successive stacking required to give X-ray diffraction (2). Structural information on amorphous alumina systems was obtained using a generalized Fourier synthesis (5); however, conventional X-ray diffraction was shown to be less sensitive than IR spectral analysis in detecting the early development of order in aluminum hydroxide gel (1).

Treatment of minerals with deuterium oxide vapor leads to conversion of some or all of the hydroxyl groups to deuterioxy groups (4, 6, 7). Since the deuterioxy stretching vibration occurs in the 2700–2200- cm^{-1} region of the IR spectrum, as opposed to 3700–2900 cm^{-1} for the hydroxyl stretching frequency, this exchange is readily detected.

The comparative ease with which hydrogen–deuterium exchange takes place in hydroxyl groups of layer silicates yields information about the accessibility of the hydroxyl groups. In studying the IR spectra of synthetic hydroxyl interlayers in expanding clays, Ahlrichs (7) observed that flushing with deuterium oxide vapor at room temperature removes water and that heating at 100° in deuterium oxide vapor exchanges interlayer hydroxyl but not the clay crystal hydroxyl. Complete replacement of lattice hydroxyl by deuterioxy in beidellite, montmorillonite, saponite, and hectorite is only achieved after repeated treatment at temperatures of 350° or higher (6).

This report demonstrates the usefulness of deuteration in detecting the development of order in aluminum hydroxide gel. By treatment of the gel sample with deuterium oxide vapor at room temperature, the relative ease with which deuteration takes place is determined as a function of the age of the gel. Use of

the scale expansion feature of the spectrophotometer enhances sensitivity in studying spectral changes.

EXPERIMENTAL

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

Preparation of Aluminum Hydroxide Gel—Aluminum hydroxide gel was prepared by the neutralization of 8.5% aluminum chloride hexahydrate solution with 13% ammonium hydroxide to a final pH of 7.0 (8).

Analytical Procedures—The acid-consuming capacity test (9) was modified by titrating to pH 3.5 rather than using bromophenol blue TS, as given in the USP. Duplicate determinations were made for each sample. The antacid property of each gel is given as the percentage of the theoretical acid-consuming capacity.

For X-ray analysis, a gel sample was air dried at room temperature and ground to a fine powder with an agate mortar and pestle. Powder mounts were prepared using aluminum McCreery mounts. The diffraction pattern¹ was recorded from 14 to 27° 2θ under the following conditions: Cu K_{α} radiation, 40 kv, 20 mamp, 500 Hz full scale, and 1°/min scan speed.

IR spectra of the gel samples were obtained² by air drying a 0.10-ml gel sample on a silver chloride window³. The concentration on the window was 0.3 mg of aluminum oxide/ cm^2 .

For deuterium oxide treatment, two matched quartz vacuum cells of square cross-section were used (Fig. 1). One cell was used for the sample, and the other was used for the reference beam of the spectrophotometer. The vacuum cells were fitted with a quartz rod with a ring at the bottom to hold a silver chloride window. A three-way stopcock at the top of the cell was connected by rubber vacuum tubing to the vacuum pump⁴ and to a glass Thunberg tube⁵ containing deuterium oxide.

The silver chloride window with the gel film was placed in the quartz holder and inserted into the vacuum cell. The cell was then evacuated, and the spectrum was recorded from 4000 to 2100 cm^{-1} by aligning the vacuum cell containing the sample in the sample beam of the spectrophotometer. The matching cell was placed in the reference beam.

After the spectrum of the untreated sample was recorded, the sample cell was connected to the deuterium oxide source. The evacuated cell was then filled with deuterium oxide vapor and allowed to stand for 5 min at room temperature. The cell was evacuated again, and the procedure was repeated. After two flushings with deuterium oxide, the spectrum was again recorded.

The IR spectrum was also recorded in the hydroxyl deformation region (1100–800 cm^{-1}) using both regular (1×) scale and 5× scale expansion. By using scale expansion, the signal to noise ratio is enhanced by widening the slits to increase the signal while slowing the attenuator response to decrease noise (10).

RESULTS

Figure 2 shows the IR spectra of the fresh gel and of the same gel following deuteration. The broad, diffuse peak in the hydroxyl stretching region of the gel indicates a highly unordered structure (2). The absence of hydroxyl stretching absorbance in the spec-

¹ Norelco, Phillips Electronic Instruments, Mount Vernon, N.Y.

² Harshaw Chemical Co., Cleveland, Ohio

³ Model 421, Perkin-Elmer Corp., Norwalk, Conn.

⁴ "Duo-Seal" vacuum pump, M. W. Welch Manufacturing Co., Chicago, Ill.

⁵ Lab Glass, Inc., Vineland, N.J.

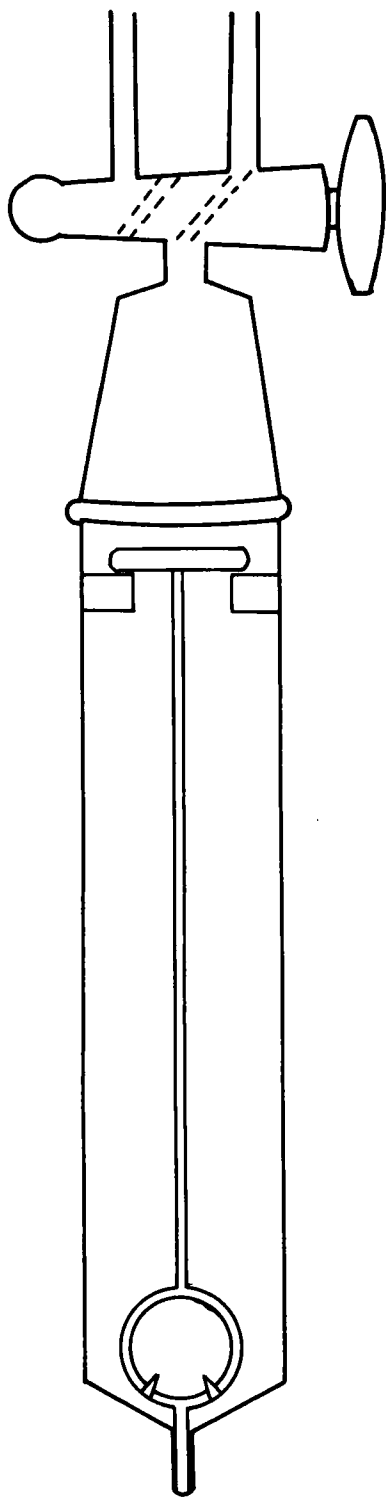


Figure 1—Vacuum IR cell for deuteration studies.

trum of the deuterated gel indicates that all of the water and structural hydroxyl have been exchanged.

Figure 3 shows the IR spectra of the same gel in the 3700–3100- cm^{-1} region for the untreated gel versus the deuterated gel at various times during aging. After 42 days (Fig. 3B), the weak absorbance in the hydroxyl stretching region for the deuterated sample indicates that not all of the hydroxyl groups have been exchanged. The increasing absorbance of the deuterated sample in this region indicates an increase in the relative number of unexchanged hydroxyl groups.

After 74 days of aging (Fig. 3D), the maximum hydroxyl absorbance of the deuterated sample occurs from 3450 to 3515 cm^{-1} .

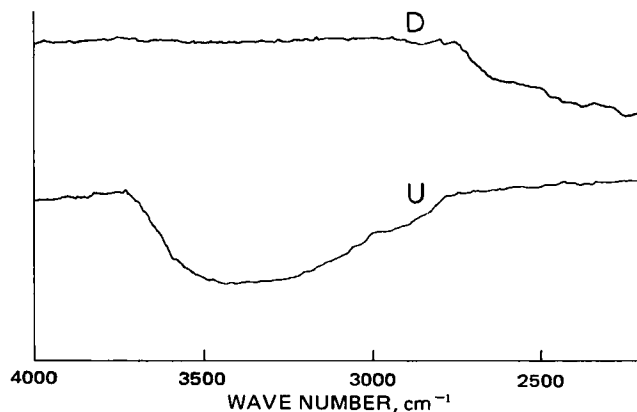


Figure 2—IR spectrum of freshly prepared gel. Key: U, untreated; and D, deuterated.

After 81 days (Fig. 3E), a well-defined peak is seen at 3520 cm^{-1} for the deuterated sample. This peak becomes more intense with continued aging. After 97 days (Fig. 3F), shoulders are seen in the deuterated sample at 3470 and at about 3600 cm^{-1} in addition to the peak at 3520 cm^{-1} . Further aging (Fig. 3G) results in a well-defined band at 3612 cm^{-1} along with the sharp peak at 3520 cm^{-1} and the shoulder at 3470 cm^{-1} .

In the spectra of the untreated gels, the first indication of the 3520- cm^{-1} band is barely perceptible as an inflection point at 3520 cm^{-1} after 81 days (Fig. 3E). After 147 days (Fig. 3G), a sharp peak is seen at 3520 along with shoulders at 3612 and 3470 cm^{-1} .

The use of scale expansion is illustrated in Fig. 4, where the spectra of the untreated and deuterated gels are shown at 5 \times scale expansion. Figure 4A shows the gel after 59 days of aging. The 5 \times spectrum of the deuterated gel shows a maximum absorbance band from 3470 to 3525 cm^{-1} . This band is not discernible in the 1 \times spectrum of the deuterated gel. After 65 days (Fig. 4B), the maximum absorbance band in the expanded scale spectrum of the deuterated gel occurs from 3480 to 3515 cm^{-1} . Finally, after 74 days (Fig. 4C), a sharp peak is seen at 3520 cm^{-1} in the 5 \times spectrum of the deuterated sample. This peak is not resolved in the 1 \times

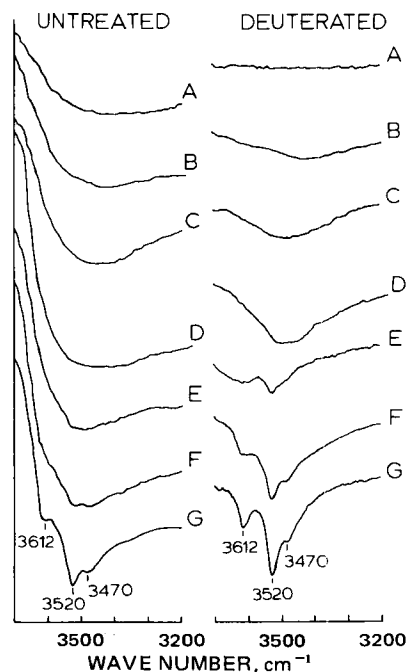


Figure 3—Change in hydroxyl stretching frequency region of IR spectrum of aluminum hydroxide gel for untreated and deuterated samples during aging at 25°. Key: A, fresh precipitate; B, 42 days; C, 59 days; D, 74 days; E, 81 days; F, 97 days; and G, 147 days.

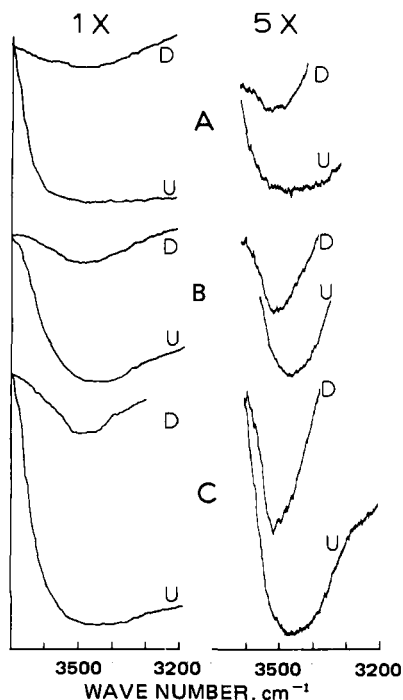


Figure 4—Change in hydroxyl stretching frequency region during aging by regular (1X) scale and 5X scale expansion for both untreated (U) and deuterated (D) samples. Key: A, 59 days; B, 65 days; and C, 74 days.

spectrum of the deuterated sample.

Scale expansion also is useful in examining the hydroxyl deformation region of the spectrum (Fig. 5). When using the 1X scale, the hydroxyl deformation absorbance appears as a broad band centered at about 900 cm^{-1} for a fresh gel (1). The better resolution of scale expansion shows a peak at 880 cm^{-1} (Fig. 5A). Continued aging leads to the disappearance of the 880 cm^{-1} band and the appearance of another band at 970 cm^{-1} . After 74 days, another sharp peak appears at 1020 cm^{-1} (Fig. 5E). By this time there is no evidence of a peak at 880 cm^{-1} . With further aging, the intensity of the 1020-cm^{-1} peak increases relative to the peak at 970 cm^{-1} (Fig. 5F). After 80 days, the 1020-cm^{-1} peak is easily identifiable by the 1X scale.

The X-ray diffraction pattern of the gel at various aging times is seen in Fig. 6. The first evidence of crystallinity is seen after 94 days of aging (Fig. 5C), at which time a broad peak is seen from 18.4 to $19.6^\circ 2\theta$ (4.82 – 4.52 \AA) and a sharper peak is seen at $20.35^\circ 2\theta$ (4.36 \AA). Even after 189 days of aging, the peak at $18.5^\circ 2\theta$ (4.80 \AA) remains relatively diffuse and of low intensity. While the 4.80 - and 4.36 - \AA spacings correspond to the interplanar spacings for gibbsite, the relative intensities are reversed from those of highly crystalline gibbsite (11).

A plot of the log of the acid-consuming capacity of the gel versus time at room temperature is shown in Fig. 7. As previously reported (1, 8), the loss in acid reactivity follows apparent first-order kinetics (slope = $-3.10 \times 10^{-3}/\text{day}$, $r = 0.99$). Although the gel used in this study was prepared under the same conditions of pH of precipitation, rate of addition of base, and washing and contained the same amount of chloride (0.35% w/v) as the earlier gel (1), the rate constant for loss of reactivity was $7.13 \times 10^{-3}/\text{day}$ in contrast to a rate constant for the previous gel of $13.65 \times 10^{-3}/\text{day}$. The reason for the observed difference in behavior is not known.

DISCUSSION

The initial precipitate resulting from the reaction of a soluble aluminum salt with base is probably a highly random structure. With aging, structural rearrangement occurs to form a more stable system. For example, a polymerization-like process may occur to produce a more highly ordered system which is resistant to attack by acid (12–15). The end-product of this process is a crystalline

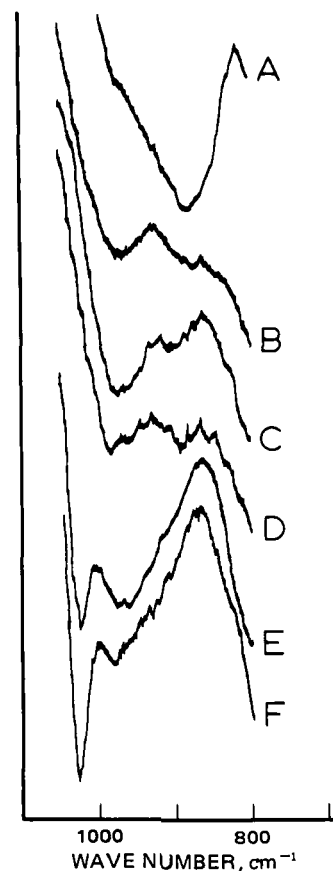


Figure 5—Change in hydroxyl deformation frequency of IR spectrum during aging at 25° by 5X scale expansion. Key: A, fresh precipitate; B, 45 days; C, 52 days; D, 65 days; E, 74 days; and F, 81 days.

form of aluminum hydroxide (16–20). Under the conditions used in preparing the gel for this study, it was determined that gibbsite is the primary crystalline phase that develops on aging (1). Highly crystalline gibbsite has bands in the hydroxyl stretching region of the IR spectrum at 3612 , 3520 , 3440 , and 3395 cm^{-1} and bands in the hydroxyl deformation region at 1030 and 970 cm^{-1} (21).

Treatment of aluminum hydroxide gel with deuterium oxide

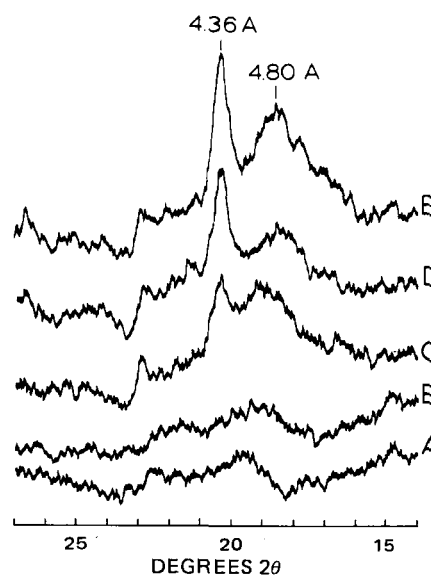


Figure 6—Change in X-ray diffraction pattern of aluminum hydroxide gel during aging at 25° . Key: A, 56 days; B, 78 days; C, 94 days; D, 115 days; and E, 189 days.

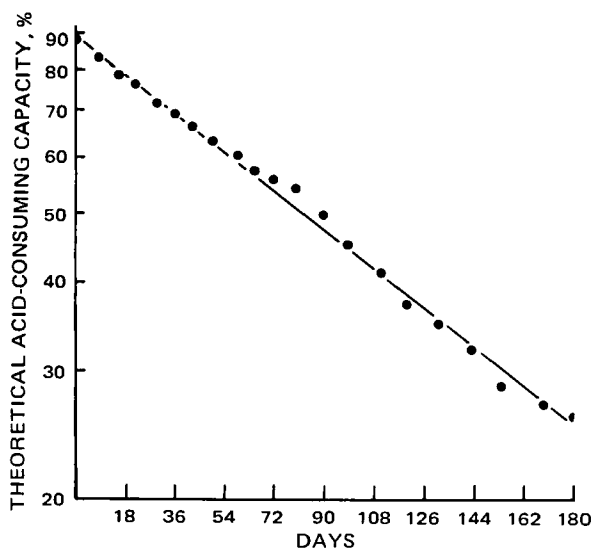


Figure 7—Change in acid-consuming capacity of aluminum hydroxide gel during aging at 25°.

vapor at room temperature enhances the sensitivity of IR spectral analysis in observing the development of order in the gel. In the freshly precipitated gel, which is fully reactive by the USP acid-consuming capacity test, all structural hydroxyl groups are exchanged. This condition indicates ready accessibility of the hydroxyl groups to deuterium oxide vapor. The residual hydroxyl stretching absorbance following deuteration of aged samples indicates that the accessibility of the structural hydroxyl groups is diminished. The magnitude of this residual absorbance increases with age, and the maximum absorbance occurs within a narrower frequency range with age. The observation of the narrowing of the range of maximum absorbance of deuteration-resistant hydroxyl is facilitated by use of scale expansion. The deuteration-resistant hydroxyl absorbance becomes more specific until a sharp band is seen at 3520 cm^{-1} , corresponding to a major gibbsite peak.

The development of distinct bands resistant to deuterium oxide exchange indicates that the chemical environment of the hydroxyl groups is becoming more uniform; *i.e.*, the structure is more highly ordered. The first indication of the development of order in the gel by IR analysis is seen after 43 days of aging by the residual hydroxyl stretching absorbance following deuteration. At this time, the acid-consuming capacity is 67% of the theoretical capacity. A distinct peak at 3520 cm^{-1} following deuteration is seen by 5X scale expansion after 74 days, when the gel is 54% reactive. The first evidence of crystallinity by conventional X-ray diffraction is seen after 94 days, corresponding to 44% reactivity. Thus, while the acid-consuming capacity is the most sensitive indicator of developing order, the application of deuteration is of considerable value in relating structural changes on aging to decreased acid reactivity.

Spectral changes in the hydroxyl deformation region also show the gradual development of a gibbsite structure. Three different peaks are seen during the aging process. The first is at 880 cm^{-1} and is subsequently replaced by a band at 970 cm^{-1} and later by a sharp peak at 1020 cm^{-1} . The 1020-cm^{-1} and 970-cm^{-1} peaks are associated with the gibbsite structure. The structural significance of the early peak at 880 cm^{-1} is not known.

The reversal in the relative intensities of the 4.80- and 4.36-Å peaks in the X-ray diffractogram of the gel studied in comparison

to highly crystalline gibbsite may also yield information on the structure of the gel. According to Schoen and Roberson (22), diffraction from the (002) or basal planes gives rise to the 4.80-Å peak. The width of this peak indicates that the crystallites are relatively small in the basal or *c*-axis direction. The 4.35-Å peak is caused by reflection from the (100) plane. The relatively intense nature of this reflection indicates preferential growth in the *ab* plane. Thus, a thin platelet structure is suggested.

REFERENCES

- (1) S. L. Nail, J. L. White, and S. L. Hem, *J. Pharm. Sci.*, **64**, 1166(1975).
- (2) V. C. Farmer, *Clay Miner.*, **7**, 373(1968).
- (3) V. C. Farmer and J. D. Russell, *Clays Clay Miner.*, **15**, 121(1972).
- (4) V. C. Farmer, J. D. Russell, and J. L. Ahlrichs, *Trans. Int. Congr. Soil Sci.*, **9th**, 3, 101(1968).
- (5) A. J. Leonard, F. Van Cauwelaert, and J. J. Fripiat, *J. Phys. Chem.*, **71**, 695(1967).
- (6) J. D. Russell, V. C. Farmer, and B. Velde, *Min. Mag.*, **37**, 869(1970).
- (7) J. L. Ahlrichs, *Clays Clay Miner.*, **16**, 63(1968).
- (8) S. L. Hem, E. J. Russo, S. M. Bahal, and R. S. Levi, *J. Pharm. Sci.*, **59**, 317(1970).
- (9) "The United States Pharmacopeia," 17th rev., Mack Publishing Co., Easton, Pa., 1965, p. 27.
- (10) "Instruction Manual, Perkin-Elmer Model 421 Spectrophotometer," Instruments Division, Perkin-Elmer Corp., Norwalk, Conn.
- (11) K. Wefers and G. M. Bell, Technical Paper No. 19, Alcoa Research Laboratories, 1972.
- (12) R. W. Smith and J. D. Hem, Geological Survey Water-Supply Paper 1827-D, U.S. Government Printing Office, Washington, D.C., 1971.
- (13) J. D. Hem and C. E. Roberson, Geological Survey Water-Supply Paper 1827-A, U.S. Government Printing Office, Washington, D.C., 1967.
- (14) P. H. Hsu and T. F. Bates, *Min. Mag.*, **33**, 749(1964).
- (15) P. H. Hsu, *Soil Sci. Soc. Amer. Proc.*, **30**, 173(1966).
- (16) E. C. Marboe and S. Bentor, *Silic. Ind.*, **26**, 389(1961).
- (17) R. C. Turner and G. J. Ross, *Can. J. Chem.*, **48**, 723(1970).
- (18) R. J. Barnhisel and C. I. Rich, *Soil Sci. Soc. Amer. Proc.*, **29**, 531(1965).
- (19) P. H. Hsu, International Committee for the Study of Bauxites and Aluminum Oxides-Hydroxides, 3 Congress, Nice, France, 613(1973).
- (20) G. J. Ross and R. C. Turner, *Soil Sci. Soc. Amer. Proc.*, **35**, 389(1971).
- (21) J. L. White, *Soil Sci.*, **112**, 22(1971).
- (22) R. Schoen and C. E. Roberson, *Amer. Mineral.*, **55**, 43(1970).

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* To whom inquiries should be directed.