The development of crystalline structure in aluminium hydroxide polymorphs on ageing

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SUMMARY. Infrared absorption spectra of the precipitated solids separated from aluminium-hydroxide solutions below the pH of minimum solubility of $Al(OH)_3$ demonstrate the slow ageing of polymeric Al complexes to gibbsite. On comparison with the spectra of natural gibbsites, shifts in absorption frequency during crystal growth are interpreted in terms of changes in hydrogen bonding as a consequence of deprotonation and stacking of aluminium hydroxide layers to form gibbsite. In alkaline solutions the bayerite polymorph precipitates and IR frequencies are compatible with protonation as aluminate ions associate with the bayerite crystal having a lower crystal energy than its low pH polymorph. The infrared spectrum of nordstrandite, which is probably the stable polymorph in alkaline solution, shows evidence of strongly polarized hydroxyl ions similar to gibbsite.

OF the many studies of the speciation of aluminium-hydroxide solute in water, recent work at the U.S. Geological Survey (Hem and Roberson, 1967; Hem, 1968; Schoen and Roberson, 1970) has provided much useful information on the forms of and controls on aluminium in solution, and the nature of the aluminous solids that precipitate from such solutions. For example, it has been demonstrated that solution pH plays a vital role in controlling the structure of the Al hydroxide precipitates; the gibbsite structure forms when the pH is less than about 5·8 and bayerite when pH > 5·8, although the latter appears to convert to nordstrandite, which may be the stable polymorph in alkaline solutions. In one aspect of investigations into the mechanisms of precipitation, the above investigators demonstrated that, upon ageing of solutions in which the number of bound hydroxyl ions per Al ion (OH_B/Al) ranged initially from 2·0 to 3·0, polymerization of Al–OH octahedra occurred very slowly to produce macromolecules and finally very small, approximately 0·1 μm crystals of gibbsite. The identification of crystallinity in these small quantities of fine-grained precipitates provides many problems and, to date, has been based on X-ray diffraction and electron microscope studies. This paper is a preliminary report of investigations into the use of infrared absorption spectroscopy to study the development of crystalline structure in aluminium hydroxides on ageing. The results of this study tend to confirm the mechanism of formation suggested by the above authors, and also demonstrate a unique way of assessing crystal growth phenomena.

Experimental conditions. The infrared spectra were obtained of the > 0.10 micron solids separated from 3 aluminium solutions ($pH < 5$ and $OH_B/Al < 3.0$) after ageing periods of 11 days, 24 months, and 45 months. The solutions were prepared as described by Hem and Roberson (1967), and the solution characteristics are summarized in table I. The infrared absorption spectra were recorded on a Perkin-Elmer

TABLE I. *Characteristics of aged aluminium solutions*

Sample No.	Ageing period	pH		Al (moles/l.)		OH_B/Al (initial)
		initial	final	initial	final	
G1	11 days	4·79	4·46	4.5×10^{-4}	3.31×10^{-4}	2·10
G2	24 months	4·80	4·35	4.5×10^{-4}	0.61×10^{-4}	2·50
G3	45 months	4·86	4·22	4.5×10^{-4}	1.29×10^{-1}	2·12

TABLE II. *X-ray diffraction data for aluminium hydroxide polymorphs*

Synthetic precipitate N2		Nordstrandite (Hathaway and Schlanger, 1965)		Bayerite (Rooksby, 1961)		Gibbsite (Rooksby, 1961)	
d	I	d	I	d	I	d	I
—	——	—	—	—	—	4·85 Å	100
4·77 Å	100	4·79 Å	100	—	—	—	—
4·72	85	—	——	4·71 Å	100	—	—
4·36	100	4·32	12	4·35	55	4·37	40
—	—	—	——	—	—	4·31	20
4·20	14	4·21	10	—	—	—	—
—	—	—	—	—	—	3·31	10
3·20	20	—	—	3·20	20	3·18	7
—	——	—	——	—	—	2·45	15
2·39	14	2·39	9	—	—	—	——
2·26	12	2·26	15	——	—	—	—
2·22	100	——	——	2·22	60	2·17	8
2·01	11	2·02	8	—	—	2·04	15
1·90	10	1·90	8	—	——	—	—
—	—	—	—	—	——	1·80	10
1·72	35	—	—	1·72	20	1·75	9
—	——	—	—	——	—	1·69	7
1·46	12	——	—	1·46	8	1·46	8

457 grating spectrophotometer after sample preparation using a KBr technique. In addition, the spectra were recorded of two samples (G4 and G5) of natural well-crystallized gibbsite, one sample of synthetic gibbsite produced by the Bayer process, consisting of large crystals > 10 μm (G6), and one sample of synthetic bayerite (B1), prepared as described by Hem and Roberson (1967) and aged for 14 months. The spectra were also recorded of two samples (N1 and N2) of synthetic nordstrandite, which were prepared as described by Schoen and Roberson (1970). It is very difficult

to prepare nordstrandite without contamination from bayerite and so the mineralogies of N1 and N2 were investigated. An X-ray diffractogram gave results shown in table II. The peaks correspond closely to those of bayerite and nordstrandite and those of gibbsite are absent. An electron micrograph of this material (Schoen and Roberson, 1970) showed none of the typical small hexagonal plates (fig. 3) of gibbsite. For this reason, samples N1 and N2 are designated bayerite/nordstrandite.

This report is concerned with an interpretation of the hydroxyl-stretching frequencies. The spectra obtained in this region of the infrared are reproduced in fig. 1 and the frequencies of the observed absorption bands are listed in table III. A selection of spectra between 1200 and 250 cm^{-1} are also included (fig. 2 and table IV) since no data for bayerite or nordstrandite have been published in this range and the gibbsite spectrum down to 100 cm^{-1} presented by Ishii et al. (1967) is of poor quality.

Infrared band assignments. The development of crystalline structure in the material precipitated in acid solution is demonstrated in the general form of the infrared spectra by a progressive sharpening of the absorption bands with ageing time of the sample. This effect is also illustrated in electron micrographs of the three precipitated solids (fig. 3). For sample G1 no clear crystallinity is developed, whereas for sample G3 some well formed hexagonal crystals, approximately 0·1 μm in diameter, are present.
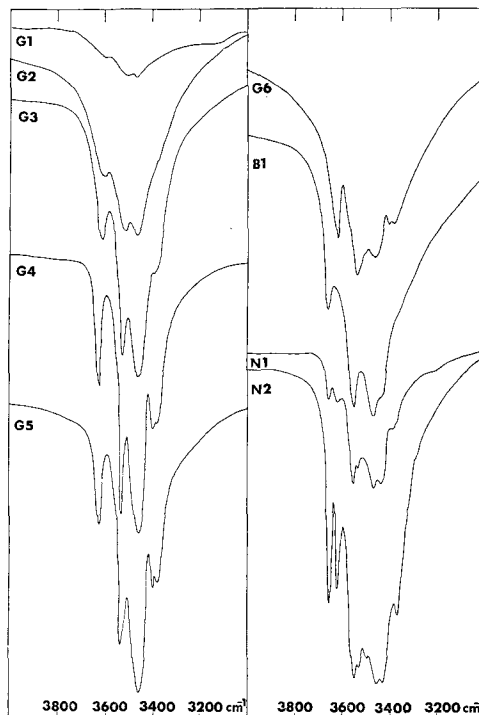
The three high-frequency infrared

FIG. 1. Infrared spectra of the hydroxyl stretching region of aluminium hydroxide polymorphs.
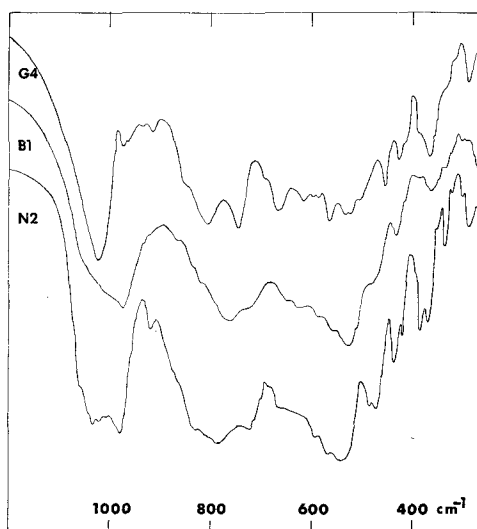

FIG. 2. Infrared spectra in the region 1200–250 cm^{-1} of aluminium hydroxide polymorphs.

bands observed in the spectra of these samples correspond to OH stretching vibrations of gibbsite, which occur at 3622, 3529, and 3460 cm^{-1} in the spectrum of naturally occurring, well-crystallized minerals. For sample G3 a band was also recorded at 3390 cm^{-1}, close to the (OH) 3396/3384 cm^{-1} absorption doublet of gibbsite. In addition to gibbsite frequencies, absorption features are also present in the spectrum of G1 at 3100 cm^{-1} and also outside the OH stretching region at 1160 and 1085 cm^{-1} (the latter band is present at 1100 cm^{-1} in G2). These are very weak absorptions and can be only tentatively assigned, but all correspond to infrared frequencies of boehmite cited by Wickersheim and Korpi (1965) and Fripiat *et al.* (1967). Although some

TABLE III. *Hydroxyl stretching frequencies (cm^{-1}) of aluminium hydroxide polymorphs*

Gibbsite						Bayerite	Bayerite/ nordstrandite	
G1	G2	G3	G4	G5	G6	B1	N1	N2
3590	3600	3610	3622	3623	3623	3655	3655	3655
—	—	—	—	—	—	—	3620	3621
3500	3510	3515	3529	3527	3527	3550	3550	3550
—	—	—	—	—	—	—	3530	3530
3470	3560	3450	3460	3460	3460	3470	3460	3460
—	—	—	—	—	—	—	3440	3430
—	—	3390	3396	3396	3396	3410	3390	3400
—	—	—	3384	3385	3384	—	3370	3370
3100	—	—	—	—	—	—	—	—

Samples G1, G2, G3, B1, N1, and N2 are synthetic precipitates; G6 was produced by the Bayer process (kindly supplied by V. C. Farmer); G4 is a well crystallized natural gibbsite from Guyana (supplied by V. C. Farmer), and G5 a natural gibbsite from Minas Gerais, Brazil (Wards Natural Science Establishment, Inc.).

workers have reported pseudoboehmite in freshly precipitated aluminium hydroxides, such material may be too poorly ordered to be assigned a boehmite structure, and more study is required before these bands in G1 and G2 can be interpreted.

The infrared bands of the large crystals of synthetic gibbsite G6 appear at frequencies almost identical to those of well crystallized gibbsite. For the synthetic bayerite precipitate B1 the two low-frequency bands are missing but the three bands that are present similarly correspond to those of gibbsite although they occur at slightly higher frequencies. Spectra of the bayerite/nordstrandite precipitates are more complex than this. With the exception of the low-frequency doublet, two absorption bands correspond to each single band in the spectra of gibbsite and bayerite.

Interpretation and discussion. The hydroxyl-stretching bands assigned to the gibbsite structure in the spectra of G1, G2, and G3 differ from each other and also from those of naturally occurring, well crystallized gibbsite in two ways. Firstly, the band–absorbance ratios are not the same for the 3 samples studied and all differ from those

reported by Frederickson (1954) and by Kolesova and Ryskin (1959) in their published spectra of gibbsite. Secondly, the frequencies of these stretching bands do not coincide exactly with those of gibbsite and also differ from one sample to another. That the band–absorbance ratios differ from published spectra is not surprising since these ratios are extremely sensitive to the method of sample preparation, particularly the
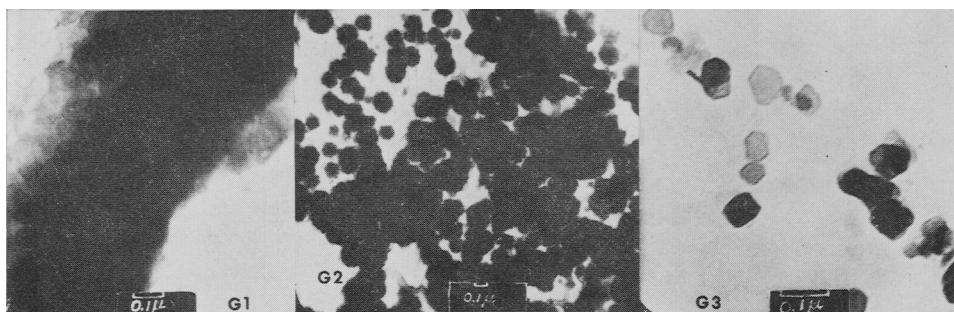

FIG. 3. Electron micrographs of synthetic gibbsite crystals.

TABLE IV. 1200–250 cm^{-1} frequencies of aluminium hydroxide polymorphs

Gibbsite (G4)	Bayerite (B1)	Bayerite/ nordstrandite (N2)	Gibbsite (G4)	Bayerite (B1)	Bayerite/ nordstrandite (N2)	Gibbsite (G4)	Bayerite (B1)	Bayerite/ nordstrandite (N2)
1022	—	1030	595	—	—	410	—	412
970	972	975	584	580	585	380	—	378
915	—	915	561	555	562	365	—	363
835	—	825	531	525	538	—	355	345
804	770	780	520	—	—	328	330	330
746	720	712	504	—	—	310	315	315
690	—	—	—	475	475	—	—	297
667	630	660	450	—	462	282	—	280
618	—	—	424	428	430			

mineral particle size. The spectra of the three synthetic gibbsite samples examined (G1, G2, and G3) were all obtained from similarly sized particles using identical sampling techniques and there is some justification in using variations in the absorbance ratios of these samples for spectral interpretation. However, the effect of even small variations in gibbsite particle size on band absorbance measurements is not known, and so the results of this type of spectral analysis cannot be considered conclusive.

In the following discussion, a relationship between frequency shifts and gibbsite crystallinity is considered. The frequency shifts between G1 and G3 could in part arise from the distortion of peak maxima due to the overlapping of a weak band (crystalline phase) and a broad band (amorphous phase). In addition, particle size and shape can affect frequencies (Ruppin and Englman, 1970). However, their compatibility with pH

changes in the mother liquor and with structural theories for gibbsite precipitation, as outlined below, lead us to believe that the observed frequency trends are related to differences in the nature of the precipitated solid phases.

With the development of gibbsite crystallinity, there is an increase in the vibrational frequency of the two high-frequency bands of the synthetic precipitates (equivalent to 3622 and 3529 cm^{-1} for well crystallized gibbsite) and a decrease for the low-frequency band (equivalent to the gibbsite 3460 cm^{-1} band). Absorption corresponding to the gibbsite 3396/3384 cm^{-1} doublet is only in evidence in sample G3 and so frequency trends are not known for these modes.

The frequency shifts of the high-frequency OH bands are compatible with a progressive weakening of hydrogen bonds of hydroxyls with coordinated water molecules and non-structural hydroxyls because of a relative decrease in the polarizing power of the Al ion affecting these hydroxyls on polymer formation. Hem and Roberson (1967) showed that the predominant Al complex between pH 4·0 and 5·8 is $Al(OH)(H_2O)_5^{2+}$; in this case the full polarizing power of the aluminium ion affects a single hydroxyl ion. On polymerization of this monomer, e.g. to form a single ring structure, $2Al(OH)(H_2O)_5^{2+} \rightarrow Al_2(OH)_2(H_2O)_8^{4+} + 2H_2O$ and $3Al_2(OH)_2(H_2O)_8^{4+} \rightarrow Al_6(OH)_{12}$ $(H_2O)_{12}^{6+} + 6H^+ + 6H_2O$, additional Al ions are brought to bear and deprotonation occurs. As a consequence of this, the proportion of Al ions with unsatisfied positive charges on the perimeter of the enlarging polymeric groups decreases with increasing crystallinity. As the structures increase in size the non-structural OH becomes less significant and it is this effect that appears to be manifested in the infrared frequency shifts of the high-frequency bands. The solutions from which the three precipitated solids were obtained showed a decline in pH on ageing (table I). In weakly acid solutions similar to these Hem and Roberson (1967) showed that the *rate* of decline of pH appears to decrease with time of ageing. This is in agreement with a decrease in deprotonation following a decrease in the polarizing power of the Al ions affecting the surface of the gibbsite structure until the well-crystallized mineral is developed. Comparison of the (OH) frequencies of G3 with those of natural gibbsite (table III) shows that this has not fully occurred as is confirmed by the electron micrograph of this sample (fig. 3).

As can be seen from table III, on gibbsite-crystal growth there is a decrease in the frequency of the low-frequency OH band down to 3450 cm^{-1} in the spectrum of sample G3. Fripiat *et al.* (1965), using the attenuated total reflectance (ATR) technique to study the Al cation in aqueous solution, recorded a single (OH) frequency at 3480 cm^{-1}, which these workers suggested was due to hydroxyls directly bonded to aluminium in a polymer of the general formula $Al[(OH)_8Al_3]_n^{4+}$. The observed frequency trend $Al_{(aq)} > G1 > G2 > G3$ can be interpreted as an increase in hydrogen bonding of inner hydroxyls to those in superposed layers as the crystals grow. As crystallinity develops, bonds form between the negatively charged corners of tetrahedral hydroxyl ions in one layer and the positively charged corners of hydroxyl ions in adjacent layers. This crystallization process is in agreement with the structure of gibbsite (Megaw, 1934), where strong attraction of ionic hydroxyls in adjacent layers cause the hydroxyl ions to arrange themselves vertically above each other. This inter-

pretation, however, is inconsistent with the frequency of this band in natural gibbsites. The spectra in fig. 1 show absorption at 3460 cm^{-1} and not at frequencies below 3450 cm^{-1} as might be expected. Of the workers who have published spectra of gibbsite only Frederickson (1954) reports this band at a significantly lower frequency (3428 cm^{-1}). The reason for these discrepancies is not known. An examination of the spectra of synthetic gibbsites after further ageing is required before this frequency trend can be confidently explained. Schoen and Roberson (1970) have demonstrated from X-ray evidence that ageing of gibbsite formed at low pH values results in an increase in the size of crystallites. The observed I.R. frequency shifts between G1 and G3 as compared with well-crystallized gibbsite also appear compatible with crystal growth on ageing of gibbsite in the mother liquor by the mechanism proposed by Hem and Roberson (1967).

Ageing of gibbsite occurs by deprotonation of polymeric cationic Al complexes on attachment to the gibbsite crystallite until the polarizing power of the aluminium ions is balanced in a stable gibbsite structure. For bayerite precipitation, however, the aluminate ion, $Al(OH)_4^-$, is the dominant Al species in solution and the strong polarizing power of the Al ion is balanced by the excess negative charge. Hence, on ageing of bayerite, aluminate ions are added to the bayerite crystal, $Al(OH)_3 + Al(OH)_4^- + H^+ \rightarrow 2Al(OH)_3 + H_2O$, and protonation rather than deprotonation occurs, causing an upward drift in solution pH with ageing and a decrease in OH stretching frequency.

Bayerite B1 absorbs at higher I.R. frequencies than the gibbsites studied here. This can be related to the weakly polarized hydroxyl ions in bayerite resulting in longer OH–OH bonds and a smaller crystal energy than the strongly polarized ions in gibbsite (Schoen and Roberson, 1970). Because of this smaller crystal energy the polarization of the hydroxyl ion in bayerite should slowly increase with ageing to form a more stable polymorph. Schoen and Roberson (1970) suggest that this stable mineral is not gibbsite but nordstrandite, which has an intermediate structure containing both weakly and strongly polarized hydroxyl ions. It is difficult to synthesize a pure sample of nordstrandite without admixed bayerite. The infrared spectra of two samples of bayerite/nordstrandite aged from strongly alkaline solutions exhibit frequencies similar to a mixture of gibbsite and bayerite. Since gibbsite is absent, the infrared spectra give evidence of both weakly and strongly polarized hydroxyl ions, the former due to bayerite and also perhaps nordstrandite, and the latter due to nordstrandite alone.

The results of this preliminary investigation are not sufficiently conclusive to make specific assignments for each OH stretching band. The frequency trends for the two high-frequency bands (at 3622 and 3529 cm^{-1} for well-crystallized gibbsite and bayerite) suggest that these modes are either surface hydroxyls or else strongly influenced by the surface reactions occurring on crystal growth. The 3460 cm^{-1} band, however, shows frequency-trends inconsistent with the surface protonation or deprotonation reactions and is more likely to be due to inner hydroxyls. These conclusions are in general agreement with band–absorbance ratio data for the synthetic gibbsite precipitates. These data show that there is an increase in absorbance of the low-frequency band (3460 cm^{-1}) with respect to the two high-frequency bands (3622 and

3529 cm^{-1}) on development of crystalline structure. On building up the gibbsite struc-
ture there is a decrease in surface area per unit volume and hence a relative decrease
in surface hydroxyls. However, calculation shows that even with small crystals, 50 Å
thick, the ratio of hydroxyls on the crystal surface (oo1 faces) to internal hydroxyls is
only $1:10$ and it seems unlikely that purely surface hydroxyls would be so predominant
in the spectra of highly crystalline gibbsite. It may be that the two high-frequency
bands are due to interlayer bonds and the low-frequency band is due to bonds within
layers.

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