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Water Content of Pseudoboehmite: A New Model for Its Structure

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A new model is proposed for the structure of the class of aluminum gels known as pseudoboehmite. This model accounts for the excess water, over that of boehmite, as being coordinated to aluminum ions located on crystallite surfaces. This is in contrast to the accepted practice of locating this excess water as water molecules hydrogen bonded between boehmite like layers. The new model accounts for both nmr and XRD spectra of pseudoboehmite.

INTRODUCTION

Pseudoboehmite is a poorly crystallized alumina with an X-ray diffraction pattern similar to boehmite. It differs from boehmite in several respects. Its lower degree of crystallinity is reflected in broader X-ray diffraction lines and the 020 line (*b* crystallographic dimension) increases from about 6.15 Å in well-crystallized boehmite to as much as 6.6–6.7 Å in pseudoboehmite. The increase in the *b* spacing is accompanied by an increase in the water content over the stoichiometric formula for boehmite, $Al_2O_3 \cdot 1H_2O$. Papee, Tertain, and Biais (*1*) postulated that the excess water is not merely adsorbed on crystallite surfaces, but is located between boehmite-like layers as molecular water, thus accounting for the increase in the *b* dimension of the crystallite.

Lippens (*2*) found as much as 30.7% water in pseudoboehmite. He also showed that the X-ray diffraction pattern must be corrected for continuous factors due to small angle scattering. When this correction was made, he found a linear relationship between the increased *b* dimension and the mole fraction of excess water. The corrected value of *b* was not as large as uncorrected values reported by other workers, but was still larger than that for well-crystallized boehmite. He concurred with the structure proposed by Papee, Tertain, and Biais, placing the excess water between boehmitic layers.

Wefers and Bell (*3*) reviewed the data for pseudoboehmite and postulated a series of reactions leading to a structure similar to the previously proposed structures, i.e., $(AlOOH)_2{:}HOH{:}(HOOAl)_2$. They state, rather clearly, that the excess water is not surface water, but is interlayer water.

There are at least two experimental facts that do not agree with these proposed structures. First, the shift of the 020 line indicates a maximum increase in the crystal spacing of 0.7 Å. It seems unlikely that such a small change could accommodate much interlayer water. The oxide ions in each sheet are close packed. The sheets are not close packed together but are stacked in such a way that zig-zag interlayer chains,

$${}_{\mathrm{O}}\mathrm{H}^{\mathrm{O}}\mathrm{H}_{\mathrm{O}}\mathrm{H}^{\mathrm{O}}$$

form hydrogen bonds, holding the sheets together. In well-crystallized boehmite, the lattice dimension perpendicular to the sheets is $b/2 = 6.15$ Å. This is about 0.5 Å greater than a value calculated for a completely close-packed structure. Thus, about 0.5 Å interlayer spacing is available in boehmite. In pseudoboehmite $b/2$ expands to about 6.7 Å at a maximum, for a total spacing in the interlayer of about 1.1 Å. This spacing is simply not large enough to accommodate the amount of interlayer water required.

The second objection to the accepted structure is found in the wide-line NMR spectrum. Saito and Hagewara (*4*) showed that water adsorbed on transition aluminas exhibits a compound proton spectrum consisting of a broad line attributed to chemically bound OH and a narrow line attributed to physically bound H_2O. The width of the broad line was related to the BET surface area by Pearson (*5*). "Wet" pseudoboehmite also shows a compound spectrum (Fig. 1). The narrow line water can be removed by drying at 100°C under vacuum, and the dry product containing only broad line, chemically bound water (Fig. 2), still has a water content in excess of the boehmite stoichiometry.

An alternative to interplanar water might be that it is due to a defect structure involving cation vacancies. If Al^{3+} ions were missing from the structure, electroneutrality could be provided by protonation of some of the OH or O groups. This would increase the water content. It can be shown, however, that the number of cation vacancies required would be excessive. For example, to account for a composition containing 35% total water, about 60% of the Al^{3+} ions would have to be missing. This seems unrealistic, although this explanation might be less unrealistic for a more highly crystalline material with a smaller water content.

For the reasons outlined above, we sought an alternative model for the structure of pseudoboehmite that would account for the excess water without requiring excessive interplanar water or an unreasonable concentration of defects. The model we propose is really an elaboration of the one first suggested by Shipko and Haag (*6*) in their study of the thermal stability of the hydrous aluminum oxides.

METHODS

Apparatus

Nuclear magnetic resonance spectra were run on a Varian Model DA-100-15D NMR spectrometer. All spectra were fed into a Fabri-Tek instrument computer for data reduction.

X-ray diffraction was accomplished by standard techniques. Crystallite size measurements were made from the line broadening of the 020 peak and consequently refer to the *b* crystallographic dimension.

Materials

The gelatinous boehmite samples used in this study were of several types including two commercial materials, and others prepared by precipitation of an aluminate solution with acid or by hydrolysis of freshly distilled aluminum isopropoxide in water, followed by hydrothermal conver-

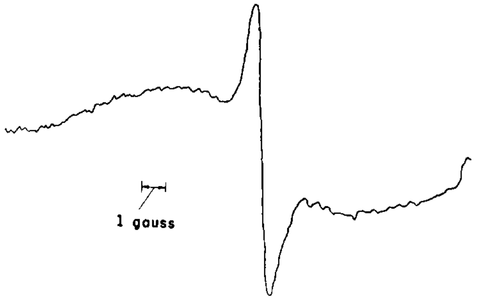


FIG. 1. Proton NMR spectrum of untreated pseudoboehmite.

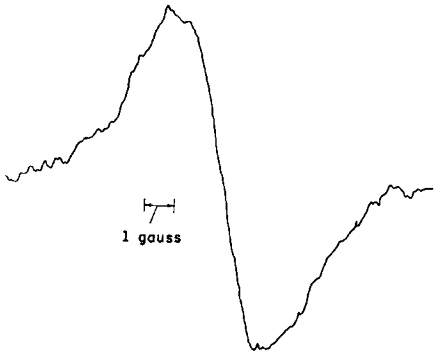


FIG. 2. Proton NMR spectrum of pseudoboehmite after 100°C overnight evacuation.

sion to increase the crystallite size. Details of the conditions are given as a footnote in the tables of data.

Water Analysis

The concentrations of physically and chemically bound water were determined by a method previously described (*5*, *7*, *8*). This analysis uses the intensity of the narrow and broad lines to measure, respectively, the concentration of physically and chemically bound water. The narrow line, physically bound water, may be measured in the presence of chemically bound water, but in order to measure the chemically bound water, the physically bound water must be removed. This can be accomplished by heating the sample under vacuum at 100°C, but a complication is introduced in that some chemically bound water is also lost. This is corrected for gravimetrically by measuring the weight loss and, therefore, the total water loss, physical and chemical, at 100°C. Subtracting the known concentration of physical water from the weight loss gives the chemical water loss at 100°C. Thus, $C_c = C_m + \Delta W - P$ where C_c is the corrected concentration of chemically bound water, C_m is the chemically bound water measured by NMR after 100°C heating, ΔW is the weight loss at 100°C, and P is the concentration of physically bound water measured by NMR. All concentrations are percent by weight of the "wet" sample (before heating).

Alternatively, the analysis can be performed by measuring the physically bound water from the narrow NMR line, then subtracting this from the loss on ignition at temperatures sufficiently high to dehydrate the sample completely. We found it easier to do the analysis by the first method, but several analyses were performed both ways with good agreement between the methods if proper care was taken with the LOI measurement, i.e., platinum crucibles were used, and the temperature was sufficiently high to convert the alumina to αAl_2O_3. The analysis could probably be done more efficiently with the pulsed NMR technique described by Zimmerman, Holme, and Lasater (*9*), but not available to us.

PROPOSED STRUCTURE OF PSEUDOBOEHMITE

We have rejected the classical explanation for the excess water in pseudoboehmite for two reasons as stated before, (1) dried (physically adsorbed molecular water removed) pseudoboehmite still contains an excess of water over the formula $Al_2O_3 \cdot 1H_2O$, and (2) there is not enough interlayer space in a boehmite lattice to accommodate the excess water.

The NMR spectra show that excess water is not physically adsorbed molecular water. It could, however, be either OH or H_2O coordinated to Al^{3+} on the surface of crystallites. Either species would be expected to contribute to the broad line portion of the spectrum.

Consider, first, a generalized crystallite without regard to structure or composition. For convenience, we choose a crystallite having the relative dimensions of a boehmite unit cell such that $a = na_0$, $b = nb_0$, and $c = nc_0$ where a_0, b_0, and c_0 are the unit cell dimensions 2.9, 12.2, and 3.7 Å, and n is a constant. We assume the surface of the crystallite to consist entirely of OH groups and assign a value of 10 Å^2 per OH group. The calculated water content of such a crystallite (with an anhydrous interior) is shown as a function of b in Fig. 3. As b becomes small the water

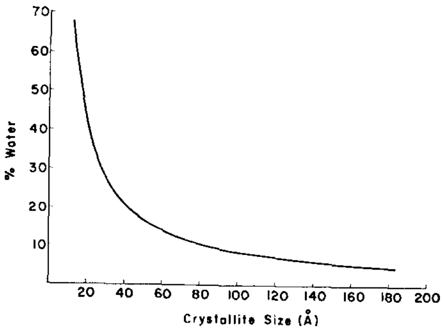


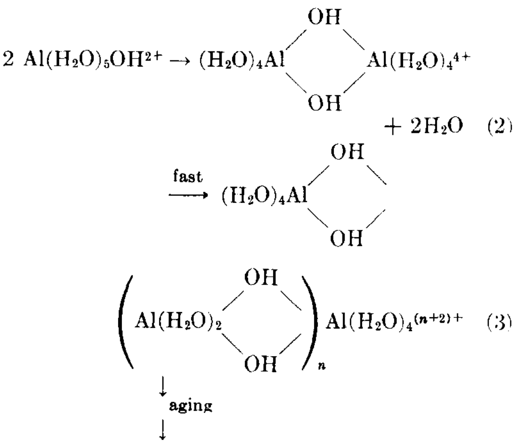
FIG. 3. Surface water content of a model crystallite containing Al on surface groups at 10 Å^2/oxygen.

content increases abruptly, reflecting the very large increase in specific surface with a decrease in crystallite size. The importance of this argument is that the pseudoboehmites generally prepared in commercial processes or in the laboratory have crystallite sizes in the range <50 Å, and the water contents of 20–30% are usually found with the smaller crystallite material. This analysis shows that materials of this type do have a sufficiently large surface area to accommodate all of the excess water observed. We note, in passing, that it is also conceivable that an oxide with an anhydrous bulk structure, even αAl_2O_3, could have a composition approaching that of a trihydrate if it were composed of small enough crystals and its surface were completely hydrated.

As a more specific model for the structure of pseudoboehmite, we propose that it is nothing more than an aggregate of ultra-small boehmite-like crystallites. The X-ray diffraction techniques used in this study can detect a boehmitic pattern in crystallites as small as about 25 Å (the 020 line, *b* dimension). It is not a very large conceptual step from the hydrolytic polymers in aluminum salt solutions (the dimer, $Al_2(H_2O)_8(OH)_2^{4+}$, for example) to the small boehmite-like crystallites capable of giving an X-ray diffraction pattern. We thus make considerable use of the concepts of coordination chemistry and the chemistry of hydrolytic polymers of metal ions in building model structures.

The species of ions existing in partially hydrolyzed solutions of aluminum salts has been extensively studied, and Smith has written a good review of the work (*10*). Most of the data were obtained from pH measurements on dilute aluminum salt solutions by titration with bases. The results are ambiguous for several reasons: (1) equilibrium is slowly established, (2) several different hypotheses give equally satisfactory fits to the data, and (3) the role of the anions in the solution is uncertain. In our opinion the most reasonable interpretation for the hydrolytic polymerization of the aluminum ion is the series of reactions:

$$Al(H_2O)_6^{3+} \rightarrow Al(H_2O)_5OH^{2+} + H^+ \quad (1)$$



$$2\,Al(H_2O)_5OH^{2+} \rightarrow (H_2O)_4Al\overset{OH}{\underset{OH}{\diamond}}Al(H_2O)_4^{4+} + 2H_2O \quad (2)$$

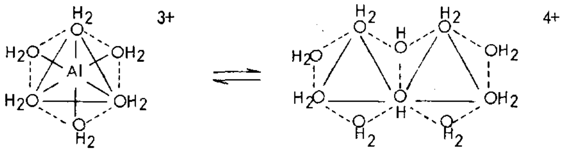
$$\xrightarrow{\text{fast}} \left((H_2O)_4Al\overset{OH}{\underset{OH}{\diamond}}\;\; Al(H_2O)_2\overset{OH}{\underset{OH}{\diamond}}\right)_n Al(H_2O)_4^{(n+2)+} \quad (3)$$

$$\downarrow \text{aging}$$

or

$$\xrightarrow{\text{slow}} Al_6O_3(OH)_9(H_2O)_{12}^{3+} \text{ or } Al_8O_4(OH)_{12}(H_2O)_{14}^{4+} \quad (4)$$

These reactions are represented structurally as:



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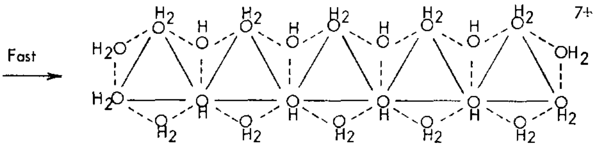
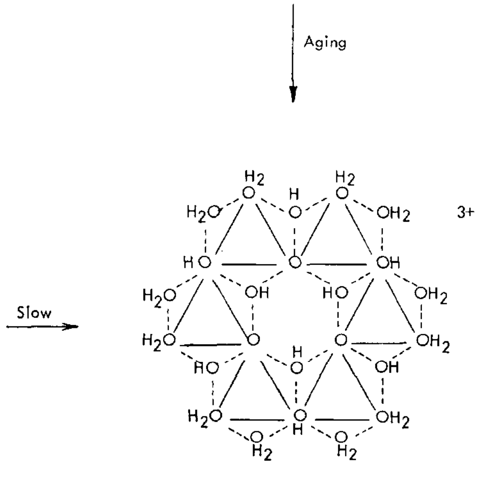
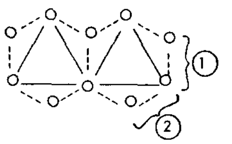


(6)



(7)

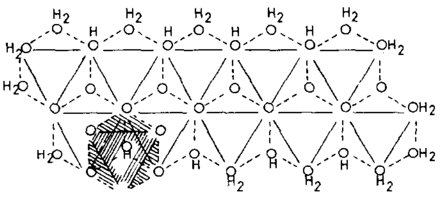
The product of Eq. (6), an infinite series of chains, has a structural similarity to boehmite, that of Eq. (7), a ring structure, has a similarity to gibbsite or bayerite. Note that the structures differ in the way the octahedra share edges. Consider



(8)

If the third octahedron condenses in position 1 a chain will result, but if it condenses in position 2 the beginning of a ring will result. The product may depend on a balance between thermodynamic and kinetic factors, but the conditions and mechanisms governing boehmitic-like materials vs gibbsite or bayerite are not completely clear.

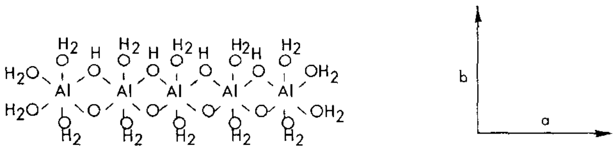
The structure of boehmite is related to the chain type of hydrolytic polymers in the following way.



(9)

This structure represents two $5Al^{3+}$ ion chains condensed into a double chain. The start of a third chain is shown by a shaded octahedron. Note the structural formalism which we adopt as a general rule [Paulings electrostatic valence rule *(11)*]: (1) oxygen species bound to only one Al^{3+} ion are H_2O, (2) oxygen species shared by two Al^{3+} are OH, and (3) oxygen species shared between 3 Al^{3+} are O^{2-}. This rule permits a calculation of the water content for any chosen aggregate of aluminum ions. Part (1) can be modified, as needed, to permit removal of H^+ from bound H_2O to satisfy electroneutrality.

Because this structural notation becomes increasingly difficult to visualize, we will change the notation to that described by Lippens *(2)* and others. Each chain can be written as:

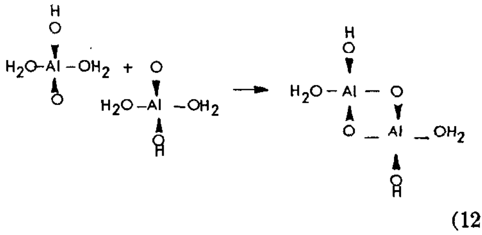


(10)

where the chain lies along the *a* crystallographic axis. The water molecules completing the aluminum ion coordination extend in the *c* direction except for the four terminal water molecules shown in the *a–b* plane. If we rotate the chain so that we look down the *a* direction, we see

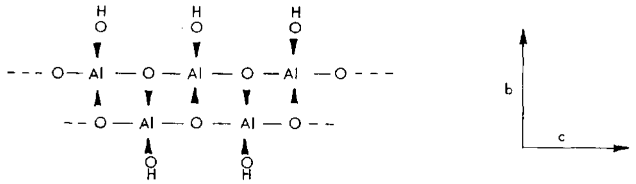
(11)

Boehmite can be considered to be the condensation product of such chains, that is,



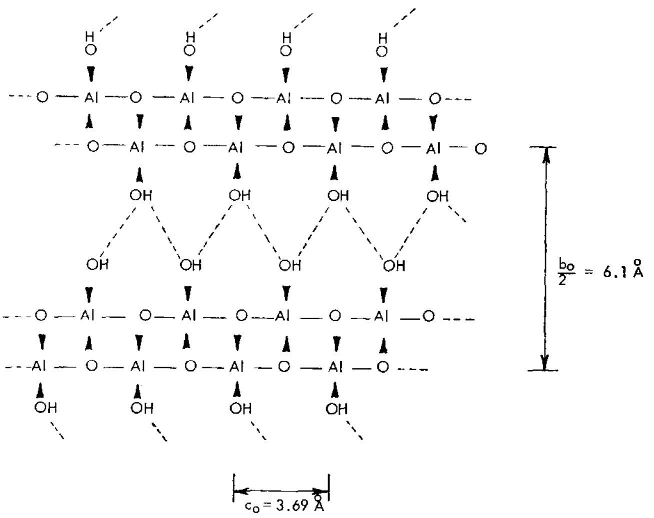
(12)

or extended infinitely in the *c* direction,



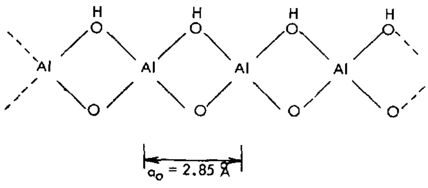
(13)

This forms a sheet, four oxide ions thick. In boehmite these sheets are held together by hydrogen bonds, and the final structure is represented as



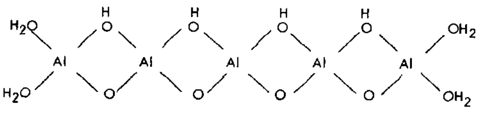
(14)

or, in the *a* direction,



(15)

The stoichiometry, AlOOH, can be seen in these chains. For each Al^{3+} there is one OH^- and one O^{2-}, *except at the end of the chain.*



(16)

If the chain is very long, the four terminal water molecules make a negligible contribution to the formula. The formula for this particular chain is $Al_n(OH)_{n-1}O_{n-1}4H_2O$ where n is the number of Al atoms per chain, but as n becomes very large, the difference between n and $n - 1$ becomes negligibly small and n becomes very large compared to 4 so the formula approaches AlOOH as $n \rightarrow \infty$.

In pseudoboehmite, n is not large, and the terminal water molecules cannot be ignored. We will show that pseudoboehmite can be considered to be ultramicrocrystalline boehmite where all of the excess water is simply this terminal water on the crystallite surfaces.

A boehmite microcrystal can be written schematically in the following way. We assume that the microcrystallite boehmite adopts dimensions in proportion to its unit cell dimensions. There is no real physical basis for this assumption, but it does give us a basis on which to develop a working model. As an illustration, consider the condensation of chains, four Al^{3+} ions long. In order to fit our assumption that $a/c =$

a_0/c_0, we must condense seven such chains. This aggregate consists of two terminal chains for formula $Al_4(H_2O)_7(OH)_3O_4^+$. The five intermediate chains all have the formula $Al_4(H_2O)_3(OH)_3O_4^+$. In the general case, we have

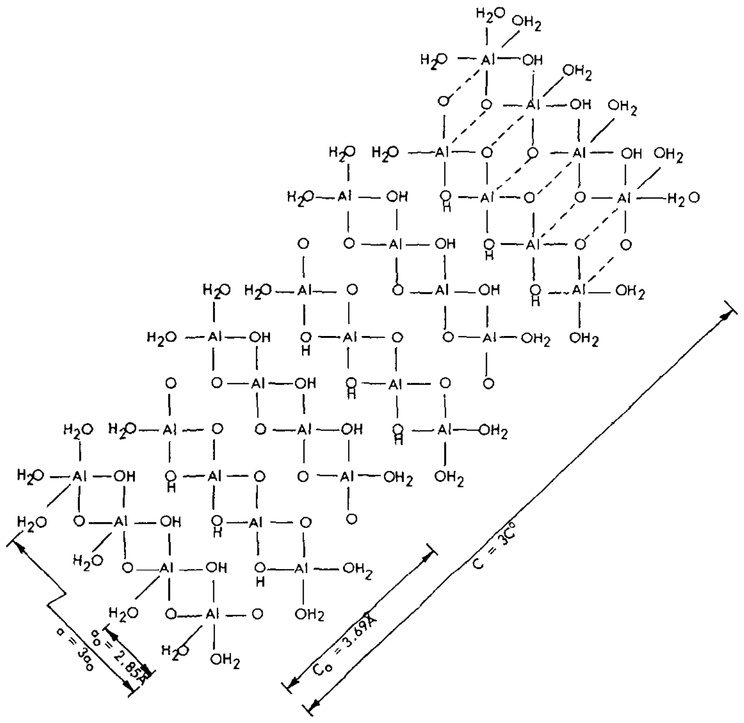
$$\begin{aligned}&\text{Terminal chains}\\ &\qquad 2 \times Al_n(H_2O)_{n+3}(OH)_{n-1}O_n^+\\ &\text{Intermediate chains}\\ &\qquad (2n-3)Al_n(H_2O)_3(OH)_{n-1}O_n^+\end{aligned} \tag{17}$$

This will always give the correct number of chains in relation to n so that $a/c = a_0/c_0$, where a and c are crystallite dimensions and a_0 and c_0 are unit cell dimensions.

To apply this general formula to a specific case, let $n = 4$.

$$\begin{aligned}2\,Al_4(H_2O)_6(OH)_3O_4^+ &\\ &= Al_8(H_2O)_{14}(OH)_6O_8^{2+}\\ 5\,Al_4(H_2O)_3(OH)_3O_4^+ &\\ &= \underline{Al_{20}(H_2O)_{15}(OH)_{15}O_{20}^{5+}}\\ &= Al_{28}(H_2O)_{29}(OH)_{21}O_{28}^{7+}\end{aligned} \tag{18}$$

to neutralize the +7 ionic charge we withdraw 7 H^+ ions (from 7 H_2O, making 7 OH^-) and get $Al_{28}(H_2O)_{22}(OH)_{28}O_{28}$. Dividing by 28, we get $AlOOH \cdot 0.785\ H_2O$ or multiplying by 2, we get $Al_2O_2(OH)_2 \cdot 1.57\ H_2O$ or $Al_2O_3 \cdot 2.57\ H_2O$, which has a formula weight of $102 + 2.57 \times 18 = 148.3$ and contains $(46.3/148.3) \times 100 = 31.3\%$ H_2O. A structural model for one layer with the composition is illustrated below:



(19)

Unfortunately, the model relates to the a and c dimensions, but the b dimension is the only one easily measurable. We can assume, however, that $a:b:c::a_0:b_0:c_0$, thus $a = (n-1)a_0$, $b = (n-1)b_0$, and $c = (n-1)c_0$. The ratio of crystallographic dimensions to unit cell dimensions can be used as an adjustable parameter. Smaller values of a and c in relation to b will result in higher water contents for a given experimental value of b, and, in fact, we find a slightly better fit with experimental data for $b = nb_0$.

TABLE 1

WATER CONTENT OF PSEUDOBOEHMITE AS A FUNCTION OF CRYSTALLITE SIZE

Sample No.	Description	Crystal size (Å)	Chem. water (%)	Chem. water after 100°C	% Chem. water lost at 100°C	Phys. water	Relative[c] X-ray intensity (020 line)
1	Laboratory sample[a]	24	39.6	25.0	36.9	10.1	0.76
2	Commercial sample	35	36.2	25.1	30.7	7.1	0.57
3	Isopropoxide hydrolysis aged at 25°C	38	30.6	23.0	24.8	8.1	0.87
4	Laboratory sample[a]	38	34.0	31.3	8.7	9.0	0.54
5	Isopropoxide hydrolysis, aged 18 hr, 130°C[b]	53	29.0	14.9	48.2	6.4	0.81
6a	Isopropoxide hydrolysis, aged 18 hr, 150°C	65	35.2	16.4	53.4	5.6	0.89
6b	Isopropoxide hydrolysis, aged 18 hr, 150°C, then dried 1 hr, 40°C	74	31.9	17.1	46.3	5.7	0.99
7	Commercial sample	85	24.6	19.4	21.2	2.6	1.17
8	Isopropoxide hydrolysis, aged 18 hr, 200°C	198	21.7	18.2	16.1	3.4	—

[a] Prepared by acidifying sodium aluminate solution with nitric acid.

[b] Distilled aluminum isopropoxide was poured into cold distilled water with stirring. The product was filtered and air-dried. About 40 g of dried product was heated in a sealed bomb with 40 ml of distilled water for 18 hr. This product was air-dried and ground in a mortar.

[c] Measured relative to a laboratory reference standard.

RESULTS

The water contents and crystallite sizes for a variety of pseudoboehmite samples are tabulated in Table 1. The percent chemically bound water in the air dried samples is plotted as a function of crystallite size (b dimension) in Fig. 4. The solid curve is the water content calculated from the model structures assuming (1) $b = nb_0$, and (2) $a:b:c::a_0:b_0:c_0$, where n is the number of Al^{3+} ions per chain in the a direction. The experimental points fit the calculated curve quite well. Also, in Fig. 4, we show some previously unpublished data of P. L. Anderson from this laboratory on a series of pseudoboehmite samples that had been dried at 120°C. The water contents, determined before we had NMR capability, are loss-on-ignition values. The lower water contents are a reflection of the fact that drying at 120°C removes not only the physically bound water, but considerable chemically bound water as well. From Table 1 it can be seen that about 20–50% of the total chemically bound water is lost under vacuum at 100°C. If a correction for this loss of about that magnitude were added to the water contents of the samples comprising the dotted curve, it also would probably fit the theoretical curve. Even without the correction it can be seen that the water content increases as the crystallite size decreases as required by the model.

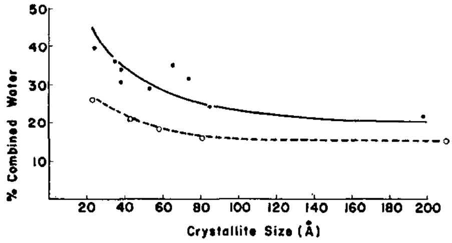


FIG. 4. Measured compared to theoretical chemical water content.

DISCUSSION

Water Content of Pseudoboehmite

To reiterate the argument used to develop a model for the purpose of calculating the water content of a crystallite of pseudoboehmite, we assume that the term, pseudoboehmite, includes every polymeric aggregate from $Al_2(H_2O)_4(OH)_2^{4+}$ to some relatively well crystallized boehmite with the exception of those aggregates having a bayerite or gibbsite like ordering of AlO_6 octahedra. In practice, the term, pseudoboehmite, would include only those aggregates that are large enough to precipitate from solution and would include the X-ray amorphous gels, as well as those materials which give rise to broadened X-ray diffraction patterns of boehmite. We recognize that it should be possible to prepare an amorphous gel having an atomic ordering characteristic of gibbsite or bayerite. In view of the rapid growth rate of gibbsite on bayerite once nucleation occurs, it is our opinion that gels which do not age into these phases, but instead age into pseudoboehmite, do not contain bayerite or gibbsitic ordering.

Consider the ion, $Al(H_2O)_6^{3+}$. If this ion is imagined to form a hypothetical monomer containing precipitate by removing H^+ from it, the composition would be $Al(H_2O)_3(OH)_3$ containing 61.4% water. If the ion polymerizes, then precipitates, the next hypothetical stage would be the dimer, $Al_2(H_2O)_4(OH)_6$, containing 55.5% water. If longer polymer chains are built up, it can easily be shown that a limiting content of 46.7% water is reached when the effects of the terminal groups become negligible. If we hypothesize double chains, the water content again reaches a limiting low value as the chain length increases, but the limiting value is lower than that for a single chain (about 37% water). To extend this argument to something that would be recognizable as a boehmite structure by X-ray diffraction would require only that the chains condense together into boehmite-like sheets which stack upon one another. These structures are similar to the micelles proposed by Marboe and Bentur for gelatinous aluminas (*12*).

The water contents of the boehmitic-like aggregates depend primarily on the crystallite dimensions *a* and *c*. As *a* and *c* become large, the coordinated H_2O content becomes negligible. It is possible to define two extremes. In one case, the crystallites are nearly equiaxial, *a*, *b*, and *c* being the same order of magnitude. This is the model we chose to make use of the experimentally measurable value of *b*. In the other extreme, *a* and *c* are the same order of magnitude and are much larger than *b*. Boehmite crystallizes in orthorhombic plates, the plate width and length being the *a* and *c* dimensions with *b* the thickness. Vedder and Vermilyea (*13*) observed pseudoboehmite platelets about five times as long and wide as they were thick. If we assume the 198 Å (*b*) crystallites of Fig. 4 to be crystallized in this mode, *a* and *c* would be about 1000 Å. Consideration of the generalized formula (formula 17) shows that as n (number of Al^{3+} per chain) becomes large, the composition approaches $Al_{2n^2}(H_2O)_{6n}(OH)_{2n^2}O_{2n^2}$. For a 1000 Å crystallite n would be about 350, and the coordinated H_2O would be negligible. We measure 21.7% water in this sample, which would seem to be too high for a platelet modification but which fits the theoretical curve for a more nearly equiaxial crystal modification.

The equiaxial mode receives some support from one transmission electron microscopic (TEM) examination. One sample, shown by X-ray diffraction (XRD) to have a 35 Å average crystallite size showed mostly discreet, approximately equiaxial particles of about 35 Å diameter along with a few larger platelike crystallites. Obviously, more work is required on crystallite size and morphology before these questions can be answered conclusively. It should be possible, by XRD, to obtain size estimates of the *a* and *c* dimensions. It is possible that some of the more important properties of gels and pseudoboehmites, such as acid solubilities, surface areas, surface activities, and aging characteristics, depend more on relative crystallite dimensions than they do on the absolute sizes.

Based on these observations, we conclude that the peripheral coordinated water model developed here accounts for the NMR spectra and water contents of small crystallite pseudoboehmite (<80 Å) very well. There is more uncertainty for larger crystallite material because of a lack of information on crystal morphology.

The alternate proposal, interlayer water, is a much less likely proposal, especially for the smaller crystallite materials, for the following reasons: clay minerals such as montmorillonite and vermiculite absorb and bind large quantities of water with an accompanying expansion of the lattice to accommodate it. The lattice expansions occur in approximately integral numbers of water molecule monolayer thicknesses, i.e., about 3 Å per monolayer (*14*). In pseudoboehmite the maximum expansion is only about 0.6 Å, or even only 0.4 Å if the correction for continuous factors due to small angle scattering is applied according to Lippens (*2*). This is hardly enough to accommodate interlayer water. To our knowledge, this point has never been raised in the literature, and we assume the implication is that the 0.6 Å expansion is an average value and that interlayer regions exist where the expansion is sufficient to accommodate a water monolayer, even though the average expansion is much smaller than this. While this may be a tenable argument for crystallites with large *a* and *c* dimensions, it seems less plausible for smaller crystallites. Furthermore, we might expect to find a decrease in the concentration of interlayer water with a decrease in crystallite size rather than the observed increase, because as the size decreases the relative number of interlayer water sites should decrease.

A second argument used by Papee, Tertain, and Biais against a surface water theory, is that the water content did not increase with an increase in surface area. We have shown, however, that the surface area available to an absorbing gas is not necessarily the same as that available to water built into the lattice surface during its formation (*7*). Crystallites as small as 25 Å will have a total surface area on the order of 1000 m^2/g, but packing of these crystallites can reduce the accessible surface; thus, the BET surface area does not give a correct representation of the true, hydrated surface.

Expansion of the Lattice

The expansion of the lattice in the *b* dimension can be accounted for also as a function of crystallite size with the peripheral coordinated water model. The individual sheets are bound together by zigzag chains of hydrogen bonds extending in the *c* direction. At the ends of the *a* and *c* chains, the terminal groups are H_2O, rather than the OH or O groups comprising the interior part of the chains. The double protonation of these oxygens should result in a smaller attractive force between sheets than that provided by the $\overset{H}{\underset{O}{\cdots HO}}$ bonds. Figure 5 shows the molecular ratio, H_2O/OH, calculated from the model, as a function of *b*. Values of *b* and the crystallite stoichiometry are the same in this plot as those used to calculate the theoretical water content vs *b* curve of Fig. 4. Figure 6 shows a plot of the measured lattice expansion as a function of crystallite size.

These experimental points represent not only the samples used in this water content study, but also other commercial and laboratory specimens of pseudoboehmite evaluated for other purposes in this laboratory. Both curves undergo the greatest

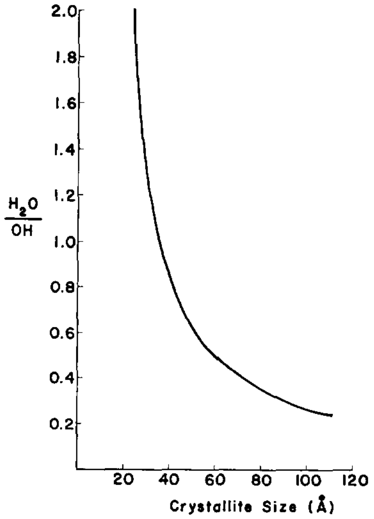


FIG. 5. Theoretical ratio of peripheral water to hydrogen bond sites as a function of crystallite size.

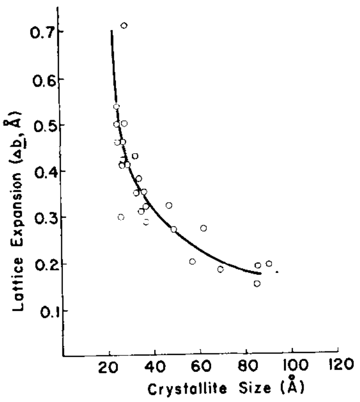


FIG. 6. Lattice expansion as a function of crystallite size.

change at values of *b* below about 60 Å and approach limiting values above this size. Figure 7 combines the curves of Figs. 5 and 6 to show the linear relation between the lattice expansion and the ratio of peripheral H_2O (considered to be repulsive) and OH (considered to be attractive).

NMR Spectrum of Well-Crystallized Boehmite

The interlayer water theory is in accord with the NMR spectrum of well-crystallized boehmite. Boehmite has a compound spectrum, suggesting that it contains a small concentration of molecular water. This water cannot be removed without disrupting the crystal by heating to its decomposition temperature. Fripiat and Touillaux (*15*) attempted to account for this spectrum by suggesting that the zigzag OH···OH interlayer hydrogen bond chains contain defects resulting from the transfer of H^+ from one OH^- ion to another to form O^- and H_2O^+. It would seem, however, that all protons would be readily exchangeable under these conditions, averaging out the spectrum into a single line.

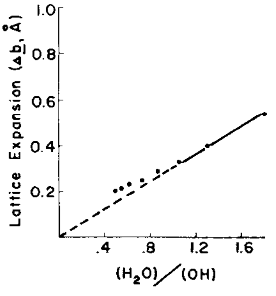


FIG. 7. Relationship between lattice expansion and ratio of peripheral water to hydrogen bond sites.

Fripiat and Touillaux ran the proton NMR spectrum of boehmite as a function of temperature and showed that the narrow line decreased in intensity as the temperature was lowered and vanished at about 128 K. We would suggest that an alternate explanation of the boehmite NMR spectrum is that the narrow line is due to molecular water trapped in the boehmite hydroxyl double layer during crystallization. This has already been postulated by Fraissard and Imelik (*16*). Water so trapped would behave like water condensed in a capillary and would exhibit a depressed freezing point. The relationship between the radius of the capillary and the freezing point of the condensed water can be estimated by an equation developed by Higuti (*17*) and used by Resing and coworkers (*18*) in their study of nuclear magnetic resonance relaxation times of water absorbed on charcoal. This equation is

$$(T_0 - T)/T_0 = 2M\sigma/rPL, \qquad (20)$$

where T is the freezing point of the liquid condensed in a capillary of radius r, and M, P, σ, and L are the molecular weight, surface tension, density, and heat of fusion of the liquid. Using room temperature values for the constants in the above equation and 128 K from Fripiat's data on boehmite, a diameter of about 8×10^{-8} cm (8 Å) is calculated for the capillary in which the water is condensed. This is within an order of magnitude of the measured distance between the hydroxyl layers in boehmite. (A monolayer of water would be expected to be about 3 Å in thickness.)

We suggest then that the water responsible for the narrow component of the spectrum of relatively well-crystallized boehmite is interlayer molecular water and is very difficult to remove because of the large *a* and *c* dimensions of the platelets between which it is trapped. This effect might be expected to extend down into the larger size range of pseudoboehmite crystallites. It cannot account for the excess water of the 198 Å sample of Fig. 4, however, as this sample had 21.7% chemically bound water (broad nmr line) compared to the 15% required for boehmite.

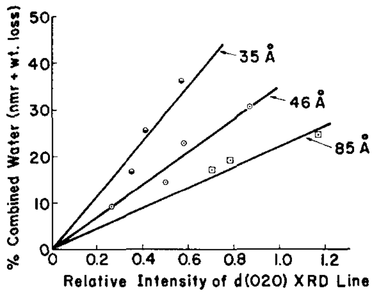


FIG. 8. Combined water vs intensity of XRD *d* (020) line.

Comparison of NMR and X-Ray Data and the Effect of Dehydration of Pseudoboehmites

In a recent paper Gerdes and Ayers (*19*) show that the area under the 020 reflection of the X-ray diffraction pattern of gelatinous boehmite can be related to the differential loss on ignition (DLOI) between 350°C and 1000°C. The DLOI is only an approximate measure of the concentration of chemically bound water in the sample because, as we have shown, considerable chemical water is lost at temperatures lower than 350°C. Data in Table 2 shows the water contents and X-ray diffraction data for three samples of pseudoboehmite. These samples were selected to cover a range of crystallite sizes. Note that, although evacuation at elevated temperature reduces both the chemically bound water content and (020) line intensity, it does not change the crystallite size. Figure 8 shows the relationship which exists between the combined water content of these samples and the intensity of the (020) line in their X-ray diffraction pattern. This data agrees with the finding of Gerdes and Ayers that the (020) line is related to DLOI, but also shows that crystallite size can affect the intensity of the XRD pattern. The effect of crystallite size can only be seen, however, on data covering a wide range of crystallite size such as those shown in Fig. 8. The data in Table 2 can be used to derive Eq. (21):

$$[H_2O] = 21.97 - 0.3757\ (\text{Cryst. Size}) + 33.16\ (\text{Int. 020 line}) \qquad (21)$$

which gives the water content as a function of crystallite size in Angstroms and the relative intensity of the 020 XRD line. Table 3 compares calculated to measured

TABLE 2

WATER CONTENTS AND XRD ANALYSIS OF PSEUDOBOEHMITES

Sample no.	Sample description	Temperature of evacuation (°C)	% Phys. water	% Chem. water	Relative X-ray response[b]	Crystal size (Å)
1A	Commercial sample	None	7.09	36.2[a]	0.57	35
1B	Commercial sample	100	—	25.5	0.41	32
1C	Commercial sample	200	—	16.73	0.35	35
2A	Hydrol. isopropoxide	None	8.10	30.6	0.87	38
2B	Hydrol. isopropoxide	100	—	23.0	0.58	49
2C	Hydrol. isopropoxide	200	—	14.65	0.50	49
2D	Hydrol. isopropoxide	300	—	9.40	0.26	46
3A	Commercial sample	None	2.62	24.6	1.17	85
3B	Commercial sample	100	—	19.35	0.78	85
3C	Commercial sample	200	—	17.13	0.70	85

[a] Calculated from measured concentration of physically adsorbed (phys.) water and weight loss at 100°C evacuation and the concentration of chemically (chem.) bound water after 100°C evacuation, or,

% chem. water = % chem. water (NMR) + [% wt loss (100°C) − % phys. water].

[b] Intensity of (020) line relative to arbitrarily selected standard.

TABLE 3
Calculated and Measured Water Contents of Pseudoboehmite

Sample No.	Crystal size (Å)	Relative 020 intensity	Measured water content %	Calculated water content[a]	Residual
1A	35	0.57	36.2	27.7	+8.5
1B	32	0.41	25.5	23.5	+2.0
1C	38	0.35	16.7	19.3	−2.6
2A	38	0.87	30.6	32.4	−1.8
2B	49	0.58	23.0	22.7	+0.3
2C	49	0.50	14.65	20.1	−5.4
2D	46	0.26	9.40	13.3	−3.9
3A	85	1.17	24.6	28.8	−4.2
3B	85	0.78	19.35	15.90	+3.5
3C	85	0.70	17.13	13.24	+3.9
					Average = +0.3

[a] Calculated using Eq. 8.

water contents using data in Table 2 and Eq. (21).

Figure 9 shows a plot of the relative X-ray intensity of the 020 line vs the crystallite size (data of Table 1). An excellent linear fit is seen. One possible interpretation of these results is as follows. When a fully hydrated crystallite exists, the peripheral coordinated water must be sufficiently distorted in its lattice position relative to the interior oxygen comprising the boehmite-like structure that it doesn't contribute to the X-ray diffraction spectrum. Thus, as the crystallite decreases in size, the number of these peripheral oxygens relative to the interior boehmitic oxygens increases and the X-ray intensity falls. To account for the dehydration curves of Fig. 8, we would have to conclude that, when a pseudoboehmite crystallite is heated under vacuum, it loses water from the surface, but then a migration of oxygen species from the interior occurs to refill the surface positions, resulting in a loss of water from the interior of the crystallite. If only surface water were lost, a decrease in X-ray intensity would not be expected if the interpretation of a noncontributing (XRD) surface oxygen is correct.

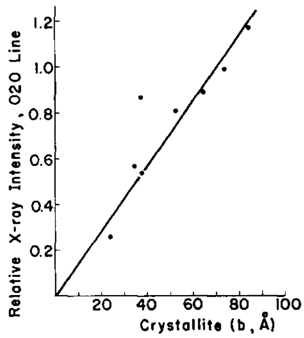


Fig. 9. Relationship between X-ray intensity (020 line) and crystallite size.

Acknowledgments

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