

## Conditions for the formation of bayerite and gibbsite

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**SUMMARY.** Aluminium hydroxide gels have been prepared by the hydrolysis of amalgamated aluminium in water and by precipitation from aluminium salt solutions with an anion exchange resin in the hydroxyl form. The products crystallizing from such gels have been examined by electron microscopy and by X-ray and electron diffraction. Bayerite crystallizes as cone or pyramid-shaped particles and gibbsite as hexagonal plates or prisms. Two types of gel are postulated. The first type, pseudoboehmite, predominates in the absence of acids, is uncharged and rapidly crystallizes to bayerite; the second type, pregibbsite gel, occurs in carboxylic acid solutions, is positively charged and, in the absence of inorganic anions, crystallizes slowly to gibbsite.

**SYNTHETIC** hydrated aluminium oxides have been extensively studied because of their adsorptive properties for enzymes and viruses and because of their significance in pedology. Three crystalline trihydroxides (gibbsite, bayerite, and nordstrandite) are known, together with various amorphous forms. Gibbsite occurs widely in nature but until recently (Bentor *et al.*, 1963) bayerite had been known only in synthetic preparations. Nordstrandite was first reported in synthetic preparations by Van Nordstrand *et al.* (1956) and has since been found in natural deposits (Hathaway and Schlanger, 1965).

Many procedures leading to the production of crystalline aluminium hydroxides have been described (e.g. Fricke and Jockers, 1947; Watson *et al.*, 1955; Lippens, 1961; Aldcroft and Bye, 1967). Mackenzie *et al.* (1962) found gels to crystallize rapidly at high pH values, but only extremely slowly at pH 5. Lippens (1961) also observed that precipitates obtained from aluminium salt solutions at pH values below 7.4 were amorphous to X-rays but noted that these invariably contained a large amount of anions, removal of which led to crystallization. Acting on the conclusions of Marboe and Bentur (1961) that the impurities are important in the crystallization of metal hydroxides in general and of aluminium hydroxides in particular, Gastuche and Herbillon (1962) studied the ageing of gels in deionized media. From their results they concluded that the elimination of contaminating ions (achieved by dialysis) was more important in determining the rate of crystallization than was the pH value.

The work described here is concerned with some morphological aspects of aluminium hydroxides and the factors influencing the manner in which alumina gels crystallize. Particular emphasis is placed on the conditions necessary for the production of pure gibbsite.

*Preparation of hydroxides*

*Hydrolysis method.* Aluminium foil was degreased in acetone, etched for one minute in 6*N* HCl, washed free of HCl with water, then amalgamated by dipping it for 5 to 10 seconds in a 1 % solution of HgCl<sub>2</sub> in acetone. The excess HgCl<sub>2</sub> solution was washed off with acetone and the foil was placed in 100 ml degassed conductivity water in a polyethylene beaker. Hydrolysis was very rapid and within half an hour all the metallic foil had reacted. The product was black at first, due to finely dispersed Hg, but it rapidly lightened in colour. The amount of material in suspension was controlled by varying the weight of amalgamated foil used and the suspensions studied contained 0.017, 0.05, and 0.2 moles aluminium per litre. Hydrolysis of amalgamated aluminium was also carried out in various solutions as indicated below.

*Anion-exchange method.* 200 ml 0.008*M* AlCl<sub>3</sub> solution was placed in a 250-ml beaker with 5 g Deacidite FF(OH) 1.5-2.0 WR anion exchange resin in a container of fine nylon mesh. The solution was stirred continuously by a magnetic stirrer until the removal of anions was complete. This procedure was repeated using 0.008*M* Al(NO<sub>3</sub>)<sub>3</sub> and 0.008*M* Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solutions. When precipitation began, at about pH 4.0, it was found necessary to add a further 2 g of resin in order to compensate for the reduced exchange efficiency of the resin caused by gel clogging. At pH 6.5-7.0 deionization was complete; the resin was then removed and the suspensions were aged in polythene bottles.

*Methods*

X-ray powder photographs were obtained using precision 9-cm powder cameras with Co-*K*<sub>α</sub> radiation from a Raymax diffraction unit. Samples dispersed in water to give a dilute suspension were dried on a carbon-coated grid for electron microscopy or on an aluminium-carbon coated grid for electron diffraction studies. In order to obtain more information on the morphology of certain preparations, carbon replicas were preshadowed with Pt/C at tan<sup>-1</sup> ½ (Kay, 1961). All specimens were examined in an A.E.I. EM6 electron microscope. Surface area measurements were made using the nitrogen adsorption method of Brunauer *et al.* (1938).

*Results*

*Products of hydrolysis in water and dilute alkali solutions.* The products obtained from the hydrolysis experiments were examined by X-ray diffraction after short periods of ageing (table I). All the initial precipitates gave an X-ray pattern similar to that of boehmite but the X-ray reflections were very diffuse indicating only short-range ordering. This material has been variously called microcrystalline boehmite, gelatinous boehmite, fibrous boehmite, and pseudoboehmite (Papée *et al.*, 1958), and the last name will be used here. From table I it is clear that the pseudoboehmite is only a transitory phase and alters rapidly to bayerite with some gibbsite.

The end-product from the 0.2*M* alkali-free suspension showed a weight loss consistent with the formula Al(OH)<sub>3</sub> and gave an X-ray diffraction pattern identical with that of bayerite, in agreement with the results of Fricke and Jockers (1947) and Watson

*et al.* (1955). Under the electron microscope this product appeared to consist almost entirely of well-developed triangular-shaped particles occasionally joined at their apices to give hour-glass shaped particles approaching  $10\ \mu\text{m}$  in length (fig. 1*a*). In addition, a few smaller laths, some of which were tapered, were observed.

TABLE I. *Effect of ageing on products of suspensions prepared by hydrolysis of amalgamated aluminium in water*

Ageing time in hours	Hydrolysis products Moles of Al hydrolysed in a litre of H <sub>2</sub> O		
	0.017	0.05	0.20
1	pseudoboehmite	pseudoboehmite	pseudoboehmite
3	"	"	"
5	"	"	pseudoboehmite + bayerite
9	—	pseudoboehmite + bayerite	—
24	predominantly bayerite with some gibbsite	bayerite with a few crystals of gibbsite	bayerite

From the electron micrograph of a replica of the same product freeze-dried on a glass slide (fig. 1*d*), it is obvious that the triangular particles are in fact pyramids layered parallel to their bases. One of the more elongated crystals (fig. 1*b*) gave an electron-diffraction pattern (fig. 1*c*) with rows of spots parallel to the long axis of the pyramid: the repeat distance along the row is  $4.70\ \text{\AA}$ , in good agreement with the *a* parameter of bayerite.

When the hydrolysis was carried out in  $0.01\ M$  NaOH solution, pronounced elongation of the pyramids was observed (fig. 1*e*). The X-ray reflections were still those of bayerite, but the intensity of the line at  $4.74\ \text{\AA}$  was weakened relative to that of the  $4.38\ \text{\AA}$ .

*Products of hydrolysis in carboxylic acid solutions.* The presence of carboxylic acid altered the end products of hydrolysis and slowed down the rate of crystallization. As the molar ratio of acid to aluminium increased the end-product became richer in gibbsite until at a ratio of 1:5 the end-product was pure gibbsite. The effect of increasing acetic acid concentration on the hydrolysis of a suspension containing 0.017 mole Al per litre is summarized in table II. Similar results were obtained with formic and butyric acids. The presence of acid converts the initial pseudoboehmite gel to what is termed by Gastuche and Herbillon (1962) pregibbsite gel, which subsequently crystallizes to gibbsite. X-ray diffraction data for the pseudoboehmite gave lines at  $6.5$  (10),  $3.20$  (8),  $2.35$  (9),  $1.85$  (10), and  $1.42$  (7)  $\text{\AA}$  (intensities in parentheses); the indices of these lines are, respectively, 020, 021,  $130+041$ , 002, and 200. Pregibbsite gel gave lines at  $1.85$  (10) and  $1.439$  (7)  $\text{\AA}$  only.

The change in pH with time for the hydrolysis of 0.017 mole Al in 1 litre of  $0.003\ M$  acetic acid is shown in fig. 6. Between A and B the gel acts as a base and a neutralizing reaction occurs, whereas between B and C the gel acts as an acid and returns protons

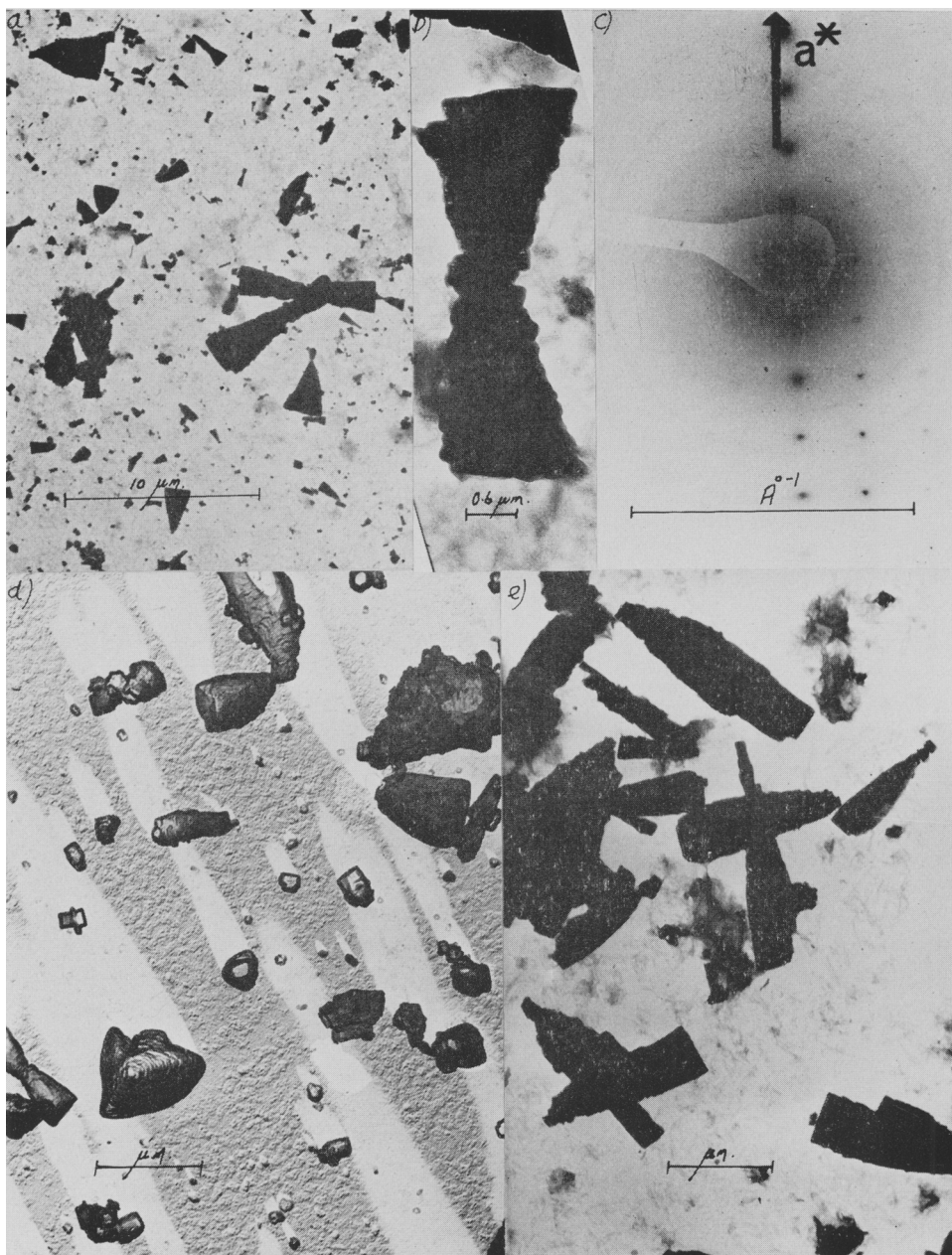


FIG. 1. *a* (top left).  $\text{Al}(\text{OH})_3$  prepared by hydrolysis of amalgamated Al in water.  $\times 2600$ . *b* (top centre). Electron micrograph of crystal, giving pattern in *1c*.  $\times 11000$ . *c* (top right). Electron diffraction pattern obtained from crystal in *1b*;  $3.8 \text{ cm} = 1 \text{ \AA}^{-1}$ . The faint rings are from pseudoboehmite surrounding the crystal. *d* (bottom left). A preshadowed (Pt/C at  $\tan^{-1} \frac{1}{2}$ ) carbon replica of the same preparation as *1a*.  $\times 14000$ . The material has been water washed several times and freeze dried from suspension on to a glass slide. *e* (bottom right).  $\text{Al}(\text{OH})_3$  prepared by hydrolysis of amalgamated Al in  $0.01 M$  NaOH.  $\times 14000$ .

to the solution. Stage AB of the process is reversible: thus, addition of alkali within 4 hours of the start of hydrolysis in acid was effective in regenerating pseudoboehmite, which crystallized rapidly to bayerite, and addition of the requisite amount of acid to a pseudoboehmite gel within four hours of its formation produced a pregibbsite gel. The surface area of a pregibbsite gel was found to be 540 m<sup>2</sup>/g compared with 320 m<sup>2</sup>/g for the parent pseudoboehmite gel.

TABLE II. *Effect of acetic acid concentration on products of suspensions prepared by hydrolysis of 0.017 mole Al in 1 litre of solution*

Molar concentration of CH <sub>3</sub> COOH solution	pH change during first 24 hours	Products after 1 month ageing at 23 °C
1.7 × 10 <sup>-4</sup>	4.3-5.3	gibbsite + bayerite
1.7 × 10 <sup>-3</sup>	3.6-5.2	increased gibbsite + bayerite
2.4 × 10 <sup>-3</sup>	3.6-5.1	mostly gibbsite
3.3 × 10 <sup>-3</sup>	3.5-5.1	gibbsite
8.3 × 10 <sup>-3</sup>	3.4-5.1	amorphous gel + gibbsite
1.7 × 10 <sup>-2</sup>	3.3-4.9	amorphous gel

From an electron micrograph of the hydrolysis product of 0.017 mole Al in 1 litre 0.003*M* acetic acid after ten days' ageing (fig. 2*a*) it is clear that the gibbsite crystals have already begun to form. After five months ageing (fig. 2*b*) the hexagonal particles in the same product are sharply defined, being 0.1-0.2 μm in diameter and 0.02-0.08 μm thick. The laths observed in this photograph are hexagonal particles sitting on a prism face.

*Products of the anion-exchange method.* X-ray diffraction results for the products obtained on ageing the precipitates obtained from aluminium salt solutions at pH 6.5-7.0 using anion-exchange resin showed that after one day the product was pseudoboehmite with weakened 020 reflection, after three days pseudoboehmite and bayerite, after seven days pseudoboehmite, bayerite, and gibbsite, and after twenty-eight days approximately equal amounts of bayerite and gibbsite. X-ray patterns of the end-products from the AlCl<sub>3</sub> and Al(NO<sub>3</sub>)<sub>3</sub> solutions were similar to those from the hydrolysis of 0.017 mole Al in 1 litre 1.7 × 10<sup>-4</sup>*M* acetic acid but morphologically the two products differed in that the cone-shaped bayerite crystals obtained from the exchange-method suspension were less serrated than those from the hydrolysis suspension. No crystalline product was obtained from Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solutions even after six months' ageing.

From a comparison of the electron micrographs of the products obtained from AlCl<sub>3</sub> solution by the exchange-resin method after ageing for ten days (fig. 2*c*) and six months (fig. 2*d*) it is clear that a greater proportion of the material has crystallized after six months, even although the sizes of the crystals formed are very similar. Furthermore, the laths are better developed and probably more numerous than the triangles. Fibrous material is still present but is much less plentiful than after only ten days. Four different particle shapes can be distinguished in fig. 2*d*: triangles,

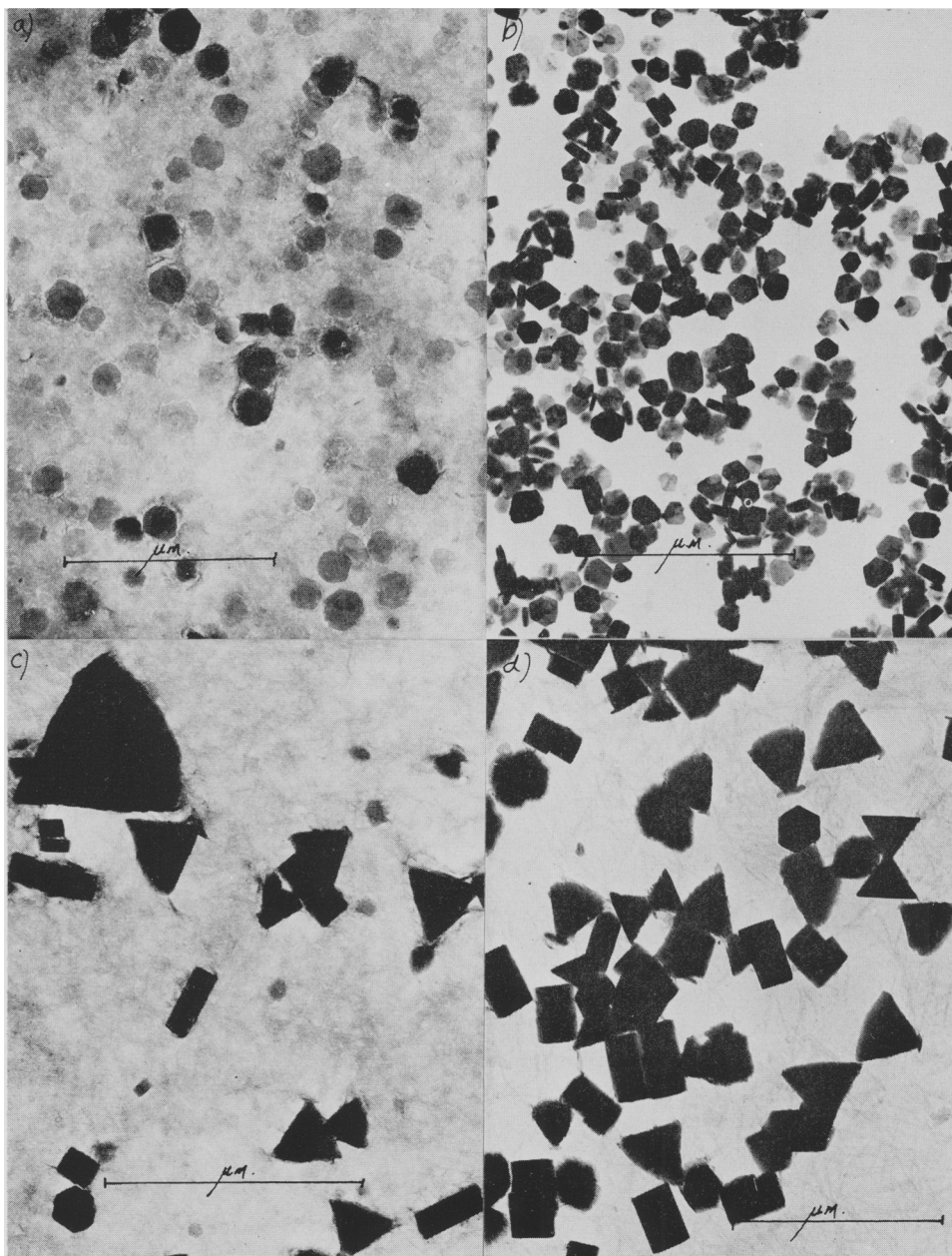


FIG. 2. *a* (top left).  $\text{Al}(\text{OH})_3$  prepared by hydrolysis of amalgamated Al (0.017 mole) in 1 litre  $\text{CH}_3\text{COOH}$  (0.003M); aged ten days. *b* (top right). Same preparation as *2a*; aged five months. *c* (bottom left).  $\text{Al}(\text{OH})_3$  precipitated from  $\text{AlCl}_3$  solution with Deacidite FF(OH) anion exchange resin; aged ten days at pH 7.0–7.5. *d* (bottom right). Same preparations as *2c* aged for six months at pH 7. *a, b, d*  $\times 28\,000$ ; *c*  $\times 34\,000$ .

frequently with one side rounded (these are the largest and most obvious of the particles present and sometimes two are joined at their tips forming hour-glass shapes); rounded particles diffuse in outline; rectangular laths; and hexagonal plates.

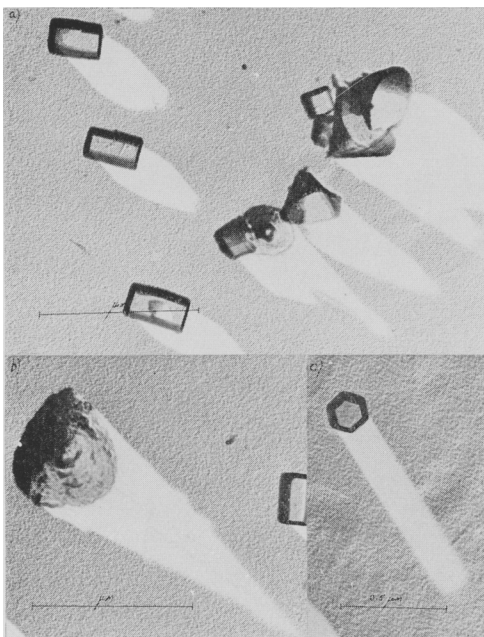


FIG. 3. *a*, top; *b*, bottom left; *c*, bottom right. Preshadowed ( $\text{Pt/C}$  at  $\tan^{-1} \frac{1}{3}$ ) carbon replicas of the same preparation as in *2d*. The material was air dried from suspension on to a glass slide. *a*, *b*  $\times 20\ 000$ ; *c*  $\times 28\ 000$ .

The hexagonal particle in fig. 3*c* is  $0.2\ \mu\text{m}$  wide, and, from the shadow length,  $0.4\ \mu\text{m}$  high. These dimensions are identical with those of the prisms in fig. 3*a* so that there is little doubt they are the same material. The shape of the prisms is such that only a small proportion would be expected to settle on their ends. Although the prisms and cones are similar in size, the prisms are more sharply defined.

The replica method has thus resolved the four apparently different morphologies in fig. 2*d* into two:  $60^\circ$  cones sometimes tending towards pyramids, and hexagonal prisms with length roughly twice the width. Comparison of electron microscope observations with X-ray diffraction results for aged gels indicates that the cones are bayerite and the prisms gibbsite.

The hexagonal prisms gave good electron-diffraction patterns, consisting of rows of closely spaced spots, the rows being parallel to the length of the crystals. Several patterns were recorded and at first sight these appeared identical. However, closer examination revealed that there were two types of pattern: in one the spots can be referred to two perpendicular axes (fig. 4*a*) whereas in the other, which is the more

The true morphology of the triangular particles is revealed by replicas (compare figs. 3*a*, *b*, and *c* with fig. 2*d*). The sample examined was centrifuged and washed several times with distilled water to free it from fibrous material before replicas were prepared. The triangular particles are now clearly revealed as cones lying on their sides so that they present the triangular outlines observed in figs. 2*c* and 2*d*. Occasionally they lie on their bases thus accounting for the rounded particles observed. The cone shown in fig. 3*b* is not perfect but has a tendency towards a pyramidal shape; the diameter of the base is  $0.75\ \mu\text{m}$  and the height  $0.65\ \mu\text{m}$ , giving an apical angle of about  $60^\circ$ . Layering parallel to the base of the cone can just be discerned and the sloping edges appear to be rough.

Replicas of the rectangular crystals have a wider electron-dense layer along their long edges than at their ends, and this, together with the shape of the shadows, indicates hexagonal prisms.

common, the two axes are a few degrees away from perpendicularity (fig. 4*b*). The two patterns have been indexed and using the unit-cell dimensions given by Lippens (1961),  $a$  8.67,  $b$  5.07,  $c$  9.72 Å,  $\beta$  94°34', the rows of reflections recorded on fig. 4*a* have been indexed  $00l$ ,  $02l$ ,  $04l$ , etc., and on fig. 4*b*  $00l$ ,  $31l$ ,  $62l$ , etc. Agreement between the observed and calculated spacing is good.

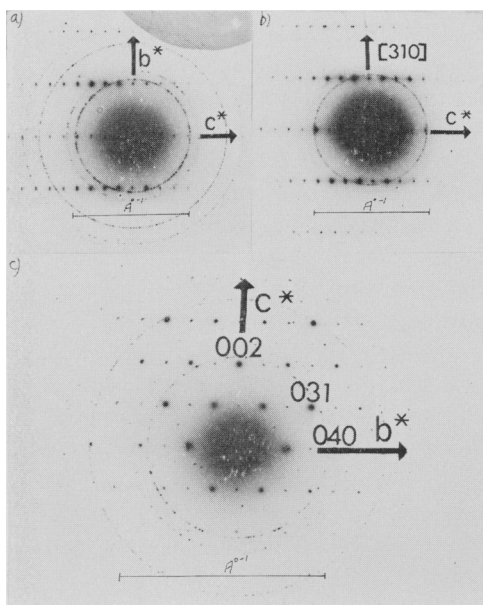


FIG. 4

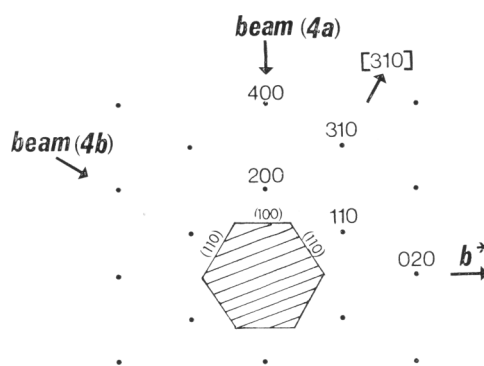


FIG. 5

FIG. 4. *a* (top left). Electron diffraction pattern from a hexagonal prism lying with (100) parallel to the substrate. Inner ring is the 2.338 Å reflection from evaporated Al used for calibration. *b* (top right). Electron diffraction pattern from prism lying with (110) parallel to the substrate. Inner ring is the 2.338 Å reflection from evaporated Al used for calibration. *c* (bottom). Electron diffraction pattern from a cone-shaped crystal lying with cone axis parallel to the beam. Rings are from evaporated Al used for calibration.

FIG. 5. Diagrammatic representation of the reciprocal lattice section in relation to the hexagonal cross section of the gibbsite crystal in real space.

The presence of two types of pattern is consistent with the fact that gibbsite is monoclinic and that in only one of three possible positions will the hexagonal prism lie with the  $a$  axis parallel to the beam. It can readily be understood from fig. 5 that a crystal lying with (100) normal to the beam will give rows of spots  $00l$ ,  $02l$ ,  $04l$ , etc., whereas if the crystal lies with (110) perpendicular to the beam the pattern will consist of rows of spots of index  $\bar{6}2l$ ,  $\bar{3}\bar{1}l$ ,  $00l$ ,  $31l$ ,  $62l$ .

It will be noted that many of the reflections are strictly forbidden from space-group considerations ( $P2_1/n$ ). For example, on the zero layer the reflections with  $l$  odd appear although they are of reduced intensity compared with the reflections with  $l$  even. Their appearance can be explained by the phenomenon of double diffraction—i.e. by diffracted beams within the crystal being themselves further diffracted (Hirsch *et al.*,



1965). The extra spots that can result from this process are obtained by translating the primary diffraction pattern so that its origin coincides successively with all the strong spots of the primary pattern. Such a treatment accounts for the presence of all points of successive rows in figs. 4*a* and 4*b*.

The cone-shaped bayerite crystals were unstable in the electron beam and patterns faded quickly unless the beam intensity was kept at a minimum. Fig. 4*c* shows a typical electron diffraction pattern obtained from a cone lying on its base—i.e. with the beam parallel to the axis of the cone. The main spots lie on a rectangular net of spacings 8.73 Å and 5.06 Å—figures that agree with the *b* and *c* parameters of bayerite. Values given in the literature for the unit-cell dimensions of bayerite vary slightly, e.g. Unmack (quoted by Lippens, 1961) gives *b* = 8.68 Å, Montoro (1942) *b* = 8.70 Å, and Yamaguchi and Sakamoto (1960) *b* = 8.73 Å. Although the *a* parameter of gibbsite is also very close to this value—Megaw (1934) quotes *a* = 8.641 Å and Saalfeld (1960) and Lippens (1961) obtained values close to 8.67 Å—the conical particles must be bayerite since X-ray diffraction patterns indicate that bayerite and gibbsite are both present and the hexagonal prisms have already been positively identified as gibbsite.

On the diffraction pattern in fig. 4*c* spots with *k*+*l* even are much stronger than spots with *k*+*l* odd—a fact that explains why the strong spots appear in a hexagonal array. However, there are also additional weak spots that can only be accounted for by the presence of a second identical reciprocal lattice section at an angle of 60° to the first. There must, therefore, be discontinuity in the stacking of the aluminium hydroxide layers that make up the crystal: some layers, or more probably sequences of layers, must be at an angle of 60° or 120° to the others. If the crystal were truly hexagonal all such positions would be equivalent.

#### Discussion

Watson *et al.* (1955) and Mackenzie *et al.* (1962) have published electron micrographs of alumina gels that show particles of morphology similar to that on fig. 2*c* and the latter authors concluded that bayerite normally forms readily on the ageing of alumina gels, the process being more rapid at high pH values. They attributed the two main particle shapes observed (hexagonal prisms and triangular somatoids) to bayerite, basing their conclusions on a comparison of morphological and X-ray evidence; they did not have the advantage of single-crystal electron diffraction. Watson *et al.* (1955), on the other hand, considered that these two shapes represent gibbsite and bayerite respectively. To the triangular particles they attributed a roughly conical or pyramidal shape. The replicas and diffraction patterns in figs. 3 and 4 strongly support the conclusions of Watson *et al.*

Some variation in the intensities of the first two X-ray reflections of bayerite at 4.74 Å and 4.38 Å has been noted in this study; this may be due to differences in degree of preferred orientation in specimens, which is understandable when it is considered how the size and shape of the crystals of bayerite vary with the conditions of preparation. Nevertheless, the crystals are all cone or pyramid shaped, varying from the narrow darts produced by hydrolysis of amalgamated aluminium in dilute alkali (fig. 1*e*) to the regular cones with apical angle 60° (fig. 2*c, d*) produced by the anion-

exchange procedure. There is no evidence in this study for the hexagonal-plate habit encountered by Yamaguchi and Sakamoto (1960) during examination of the *a* and *b* forms of bayerite.

Lippens (1961), in a study on the structure and texture of aluminas, published an electron diffraction pattern from a rod-shaped crystal with six-sided cross section, which is very similar to that in fig. 4*a*, consisting of a number of parallel rows of spots showing two mutually perpendicular axes. The repeat distance between rows was 5.00 Å and the distance between adjacent spots 9.56 Å (cf. 9.68 Å in fig. 4*a*). From the length of the *c*-axis and from the sequence of intensities of the *oo**l* reflections he concluded that the crystal was nordstrandite. Although one of his criteria (that reflections with *l* odd would be absent) is not necessarily correct if double diffraction takes place, the difference in the *c*-spacing is sufficient proof that two distinct species are involved. It is interesting to note that in the present investigation no evidence of nordstrandite was found.

From their studies on the crystallization of alumina gels Gastuche and Herbillon (1962) concluded that, irrespective of the pH of precipitation, alumina gels will crystallize provided all foreign ions are removed from the suspension medium. They found that an alumina gel precipitated at pH 4.6 had crystallized to pure gibbsite after dialysis against distilled water for one month. While largely confirming their results the present study shows that their conclusions require some modification. Alumina gels will crystallize at low pH values in the presence of acids

such as formic, acetic, and butyric (in the ratio of one mole acid to five moles of aluminium) to give gibbsite as the end-product, but acids weaker than butyric, e.g. carbonic acid or phenol, do not completely inhibit the formation of bayerite.

It is interesting to speculate on the reaction occurring during the formation of pregibbsite gel represented by the portion AB of the curve in fig. 6. Electrolysis of a pregibbsite gel caused the migration of colloidal material towards the cathode chamber and of a soluble component into the anode chamber. The latter gave a distinctly acid solution and this, when dried and ignited, gave the X-ray diffraction pattern of corundum. Similar experiments with pseudoboehmite gel showed that it was uncharged under both neutral and alkaline conditions.

Stage AB of the reaction depicted in fig. 6 may be regarded as the formation of pregibbsite gel, a positively charged colloid with, in acetic acid, a basic aluminium acetate counterion. The substitution of strong inorganic acids for weak carboxylic acids would produce very low pH's and favour the formation of insoluble basic aluminium salts, thus inhibiting crystallization of the alumina gel.

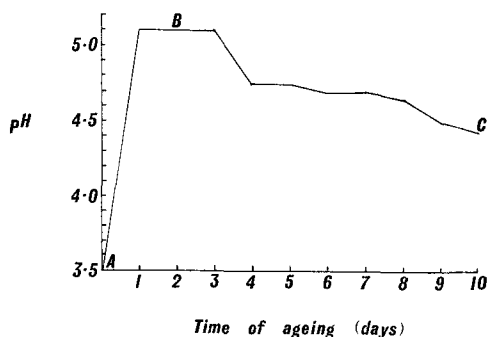


FIG. 6. Change in pH with time for the hydrolysis reaction of 0.017 mol Al in 1 litre of 0.003*M* acetic acid.

Stage BC in fig. 6 depicts the slow transformation of pregibbsite gel to gibbsite with the formation of an uncharged basic aluminium acetate and acetic acid: the former has not been checked, but the latter is consistent with the slow decrease of pH of the suspension during this period.

### Conclusions

When aluminium hydroxide is precipitated in aqueous suspension two different types of gel can be formed depending on the conditions. The first type, pseudoboehmite, occurs in the absence of acids, is uncharged, and crystallizes rapidly to bayerite. The second type, pregibbsite gel, occurs in acid solution, is positively charged, and in the absence of inorganic anions crystallizes slowly to gibbsite. The inhibiting effect of inorganic anions on gibbsite formation is attributed to the formation of insoluble amorphous basic aluminium salts. The fact that carboxyl anions at low concentrations do not interfere is explained by the formation of a soluble basic aluminium carboxyl ion.

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