

## *Formation of X-ray amorphous and crystalline aluminium hydroxides<sup>1</sup>*

By PA HO HSU, Ph.D., and THOMAS F. BATES, Ph.D.

Department of Geochemistry and Mineralogy, The Pennsylvania State University, University Park, Pennsylvania, U.S.A.

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*Summary.* Various crystalline and X-ray amorphous forms of aluminium hydroxide prepared from sulphate and chloride solutions by varying the mole ratio of NaOH to Al<sup>3+</sup> have been characterized by chemical analysis and X-ray diffraction. When the NaOH/Al ratio is 3 or 3.3, crystalline Al(OH)<sub>3</sub> in the form of bayerite, nordstrandite, gibbsite, or mixtures is obtained in several hours. When the ratio is 2.75 or below, no Al(OH)<sub>3</sub> is evident and the products are X-ray amorphous and remain so even after ageing for six months. Chemical analysis indicates that the amorphous precipitates are basic aluminium sulphates or chlorides. In the 0 to 2.1 range of NaOH/Al, the composition of the products is constant, being approximately Al(OH)<sub>2.2</sub>X<sub>0.8</sub>. In the 2.1 to 2.75 range, a continuous series of basic salts, of composition ranging from Al(OH)<sub>2.2</sub>X<sub>0.8</sub> to Al(OH)<sub>2.75</sub>X<sub>0.25</sub>, is obtained.

The following hypothesis is proposed to account for the occurrence of X-ray amorphous versus crystalline forms: When NaOH is added to an aluminium salt solution, the initial reaction yields Al(OH)<sub>2</sub><sup>+</sup> ions, which polymerize into stable 6-membered ring units of composition Al<sub>6</sub>(OH)<sub>12</sub><sup>6+</sup> or multiples thereof (double and triple rings of composition Al<sub>10</sub>(OH)<sub>22</sub><sup>8+</sup> and Al<sub>13</sub>(OH)<sub>30</sub><sup>9+</sup>), all with H<sub>2</sub>O molecules on the surface. At NaOH/Al = 2 or nearly so, the inclusion of Al<sup>3+</sup> in the basic ring units is complete; still further OH<sup>-</sup> then transforms these ring units to larger polymers, giving rise to a continuous series of species. At NaOH/Al = 2.75 and below, the positively charged hydroxy-aluminium polymers repel one another unless joined together by the counter-anions to form basic aluminium salts, which are usually X-ray amorphous because of their highly hydrated state. At NaOH/Al = 3, the net positive charge per aluminium disappears and consequently the repulsion among polymers as well as their water of hydration becomes negligible; therefore, all the polymers cluster together and form crystalline Al(OH)<sub>3</sub> in a matter of hours or days, depending on the conditions of crystal growth.

**P**RECIPITATION occurs when an aluminium salt solution is mixed with a base if both reagents are of the proper concentration. The precipitate is sometimes X-ray amorphous, sometimes crystalline. As shown in the literature and reviewed by Newsome *et al.* (1960), many workers have attempted to describe and characterize these precipitates.

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However, little attention has been paid to the mechanism of their formation and the reasons for the amorphous character of some and the crystallinity of others. Marboe and Bentur (1961) recently described the mechanism of aluminium hydroxide formation as a consequence of the removal of protons from the hydration shell of aluminium ions. According to their concepts, foreign ions hasten or retard the formation of aluminium hydroxide by their positive or negative effect on the removal of the protons.

The main objective of the present study is to provide additional experimental data and to further consider possible mechanisms of aluminium hydroxide formation in the light of the available evidence.

In most earlier work, various products were formed by controlling the pH of solutions during preparation or ageing (Weiser *et al.*, 1940 and 1941; Harris and Sing, 1955 and 1957; Papée, Tertian, and Biaï, 1958; Bale and Schmidt, 1958 and 1959; Marboe and Bentur, 1961; MacKenzie *et al.*, 1962). However, according to the preliminary work in this study, pH is closely related to the product only under restricted experimental conditions. By varying the conditions of preparation, quite different products can be produced at the same pH (e.g. Herbillon and Gastuche, 1962). The reason for this variation is not clearly known, but the kinetics of reaction and the presence of anions may play important roles. Preliminary experiments indicate that some precipitates formed as a result of locally high alkalinity are not readily, or are never, redissolved in a weakly acidic medium. It has long been known that the kind and amount of anions present are important to the product; the mechanism involved, however, is far from thoroughly understood.

In this study, in order to minimize localized high alkalinity, all the samples were prepared by adding dilute NaOH to a relatively concentrated aluminium chloride or sulphate solution. The amounts of NaOH and aluminium salts were critically controlled to provide a series of preparations with various ratios of NaOH/Al in order to understand more easily both the nature of the reaction between  $\text{OH}^-$  and  $\text{Al}^{3+}$  ions and the composition of the products.

The 'equilibrium' pH of these specimens was reached immediately after mixing. Upon ageing, some samples maintained their 'equilibrium' pH for one year, the limit of observation, while others maintained their pH for several months, after which time it dropped appreciably, accompanied by a change in the nature of the product. Emphasis in the present study is on the initial reaction. Investigation of the subsequent changes is still in progress.

*Preparation of aluminium hydroxides*

Most of the aluminium hydroxides used in this study were prepared by adding various amounts of 0.1 *N* NaOH to 500 ml of 0.2 *N* Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution or to 200 ml of 0.5 *N* AlCl<sub>3</sub> solution dropwise with vigorous stirring, then diluting to 2000 ml. The amounts of NaOH were adjusted to give a NaOH/Al ratio of 0.0 to 3.3 in the final suspension. The rate of addition of NaOH was kept at 50 ml in 30 minutes. The concentrations of aluminium, chloride, or sulphate in the final suspension were all 0.05 eq/litre.

Eight additional samples were prepared as follows: Four samples in the AlCl<sub>3</sub>+NaOH system (NaOH/Al = 2.40, 2.55, 2.70, and 2.75) were prepared by adding 0.4 *N* NaOH to 125 ml of *N* AlCl<sub>3</sub> dropwise with vigorous stirring, then diluting to 500 ml; the concentration of chloride in two of these samples (NaOH/Al = 2.70 and 2.75) was 0.25 eq/litre, but NaCl was added to the other two samples (NaOH/Al = 2.40 and 2.55) to give a final concentration of 1.0 eq/litre of chloride. Four samples with NaOH/Al = 1.8 in the Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>+NaOH system were prepared by adding dropwise with vigorous stirring 600 ml of 0.1 *N* NaOH to 200 ml of 0.5 *N* AlCl<sub>3</sub> solution containing various amounts of Na<sub>2</sub>SO<sub>4</sub>, then diluting to 2000 ml; the sulphate contents in the final suspensions were 0.02, 0.05, 0.2, and 1.0 eq/litre, respectively.

*Methods of characterization*

*Chemical analysis of the precipitate product.* A 50-ml suspension aliquot was taken from each sample and centrifuged (the length of centrifuge time and the speed were not found to be critical). The pH of the centrifugate was measured with a Beckman pH meter, Model G. The precipitate was washed once with water and once with 70 % alcohol, then 10 ml of *N* HCl were added, and the precipitate was dispersed and maintained for exactly 20 minutes with frequent stirring; the suspension was centrifuged again. The precipitate remaining undissolved, if any, was brought into solution with 10 ml 6 *N* HCl while immersed in a boiling water bath. In some cases, when the aluminium content in the precipitate was of interest, the precipitate was dried at 100° C and weighed. The aluminium content in both HCl extracts was determined with aluminon (Hsu, 1963). In those samples containing sulphate, the sulphate content in the HCl extracts was determined. The sulphate was precipitated as barium sulphate and weighed according to the procedure of the U.S. Salinity Laboratories (1954). A control of known sulphate content was run along with the unknowns; the acidity, sulphate content, volume of sample, and amount of reagent used for the control were kept as close to that of the unknowns as possible.

The OH<sup>-</sup> in the precipitate was determined as follows: a separate 50-ml aliquot was taken from each sample, centrifuged, and washed with water and alcohol as before. Then the precipitate was dissolved in 50 ml of 0.5 *N* NaF solution. The OH<sup>-</sup> released was titrated with 0.1 *N* HCl, using phenolphthalein as the indicator. Then the sample was heated at 90° C for two hours and titrated with HCl again. This heat-and-titration procedure was repeated several times until the pink colour developed after heating was very faint; at this point one or two drops of 0.1 *N* HCl

sufficed to turn the solution colourless. The total  $\text{OH}^-$  titrated is referred to as the  $\text{OH}^-$  bound in the precipitate. If the number of 'heat-and-titrations' is more than three, it is desirable to repeat the determination by adding the approximate titre in the first titration in order to reduce the error due to blank and titrations. This procedure works satisfactorily for the amorphous products, but is not suitable for crystalline  $\text{Al}(\text{OH})_3$ , as the rate of reaction is too slow in this case.

*Chemical analysis of the hydroxy-aluminium solution.* The nature of the hydroxy-aluminium species in the solution was studied by treating the latter with sodium saturated Dowex-50 (X8, 20-50 mesh) in the following two ways:

A one-tenth gram portion of sodium-saturated Dowex-50 was allowed to equilibrate with 100 ml of hydroxy-aluminium solution by letting the mixture stand in an Erlenmeyer flask for several hours (with occasional shaking), replacing the spent solution with fresh, and repeating the process—the complete experiment involving 10 changes of solution over a period of 48 hours. The resin was then washed three times with alcohol, and shaken five times with *N* KCl solution (using 20 ml and 15 minutes for each extraction) to replace any exchangeable  $\text{Al}^{3+}$ . The resin was then washed with alcohol and shaken five times with *N*  $\text{CaCl}_2$  solution in the same manner as for the *N* KCl extraction. The amount of potassium in the  $\text{CaCl}_2$  extract indicated the cation exchange capacity after the treatment with the hydroxy-aluminium solution. The aluminium not exchangeable with neutral salt was extracted with 3 *N* HCl on a steam hot plate for 2 hours and determined. The difference between the original cation exchange capacity of the resin and that after the hydroxy-aluminium treatments represents the exchange charge on the resin inactivated by the non-exchangeable aluminium.

Secondly, a one-gram portion of the Na-resin was equilibrated with 50 ml of the hydroxy-aluminium solution for 24 hours with frequent shaking; the solution was then decanted and the pH and concentration of aluminium were determined. The resin was washed three times with alcohol, then extracted five times with *N* KCl as before. The aluminium that was not exchangeable with KCl was extracted with 3 *N* HCl on a steam hot plate for about 2 hours, and determined.

The pH and aluminium were determined in the same manner as for the precipitate product. The potassium was determined with a Beckman DU flame photometer.

*X-ray diffraction.* A suitable aliquot of product suspension (10 ml for most samples) was transferred to a 15 ml test-tube and centrifuged. The precipitate was washed once with water, dispersed in 1 ml of water, pured on to a glass slide, and dried at room temperature. In those samples containing sulphate, an additional 10 ml aliquot of suspension was transferred to a 15 ml test-tube and centrifuged. Ten ml of *N* HCl was added and the sample dispersed. This acid treatment was maintained for exactly 20 minutes, then the sample was centrifuged, washed, and mounted on a glass slide as before. In some cases, a randomly mounted specimen was desirable in order to obtain a more complete diffraction pattern. Then a 200 ml aliquot was taken and treated as before, but an additional acetone washing was made and the precipitate was dried under vacuum. The dried specimen was lightly ground to a fine powder and mounted in a special aluminium holder with a hole in the centre to obtain as random an orientation of particles as possible. The X-ray diffraction patterns were taken with a Norelco unit, using copper radiation.

### *Results and discussion*

The products can be separated into two categories according to the NaOH/Al ratio involved in their preparation. When NaOH/Al = 3 and 3.3, crystalline  $\text{Al}(\text{OH})_3$  in the form of bayerite, nordstrandite, or gibbsite

or mixtures was the main constituent of the precipitate. When the ratio was 2.75 or below, the products were basic aluminium sulphates or chlorides, and were amorphous to X-ray diffraction even after 6 months of ageing.

*Products in the  $\text{Al}_2(\text{SO}_4)_3 + \text{NaOH}$  system*

*X-ray crystalline material.* Crystalline  $\text{Al}(\text{OH})_3$  formed rapidly in the two precipitates prepared at  $\text{NaOH}/\text{Al} = 3.0$  (Product 13) and 3.3 (Product 14). The physical appearance, rate of solution in acid, and X-ray diffraction patterns of these two products changed rapidly in the first

TABLE I. Percentage of aluminium extracted by *N* HCl in 20 minutes at room temperature from representative crystalline precipitates

Time of ageing	$\text{AlCl}_3 + \text{NaOH}$		$\text{Al}_2(\text{SO}_4)_3 + \text{NaOH}$	
	Prod. 1 ( $R = 3.0$ )*	Prod. 2 ( $R = 2.93$ )*	Prod. 13 ( $R = 3.0$ )*	Prod. 14 ( $R = 3.3$ )*
2 hr.	88.6	100.0	85.0	—
4 hr.	69.5	86.3	46.2	16.7
8 hr.	50.0	77.8	—	—
1 day	32.1	39.2	11.9	5.3
2 days	23.3	31.8	6.6	4.8
1 week	14.6	17.8	—	—
2 weeks	—	14.8	2.8	1.9
3 weeks	—	—	2.8	1.7
1 month	13.7	—	2.2	1.1
2 months	11.4	11.8	2.1	1.0
4 months	—	12.0	2.2	0.8

\*  $R = \text{NaOH}/\text{Al}$  mole ratio.

two days, then continued changing at a slower rate. It is believed that the rapid-changing stage is far from equilibrium and therefore not significant in this study; hence most of the results and discussion presented here concern characterizations made two or more days after preparation.

The pH values of Products 13 and 14 were 9.6 and 11.0, respectively, measured two days after preparation, and there was no noticeable change in pH during the entire ageing period of one year.

The precipitates became highly resistant to the *N* HCl treatment shortly after preparation, as shown by the data in table I. The resistance of the crystalline fraction to the acid treatment employed herein is useful in fractionating and identifying the product. In 6 *N* HCl in a boiling water-bath, it required about two hours to dissolve the residual precipitate completely after the previous *N* HCl treatment.

In Product 13 ( $\text{NaOH}/\text{Al} = 3.0$ ), aluminium was completely removed from the solution. The free  $\text{OH}^-$  remaining in solution was negligible

(0.04 meq/l, pH 9.6) as compared with the total  $\text{OH}^-$  added (50 meq/l), indicating that this  $\text{OH}^-$  was practically completely precipitated with aluminium, thereby presumably resulting in a product of composition  $\text{Al}(\text{OH})_3$ . Chemical analysis showed that this product, when dried at  $100^\circ\text{C}$ , contained trace sulphate and that its aluminium content was  $34.6 \pm 2.0\%$ , which corresponds to the composition of  $\text{Al}(\text{OH})_3$ . A  $N$  HCl wash (20 minutes) removed the trace sulphate together with a small portion of aluminium (table I), and reduced the precipitate to about  $\frac{1}{5}$  to  $\frac{1}{2}$  of its former volume. This suggests that the original precipitate was a mixture of  $\text{Al}(\text{OH})_3$  and a highly hydrated component containing aluminium and sulphate. Product 14 contained trace sulphate in the fresh precipitate, but this disappeared a few days after preparation. The precipitate, dried at  $100^\circ\text{C}$ , contained  $34.6 \pm 2.0\%$  aluminium, characteristic of  $\text{Al}(\text{OH})_3$ . In this product, the concentration of aluminium in solution amounted to about 100 ppm, presumably in the form of aluminate.

X-ray diffraction patterns showed that bayerite ( $4.36 \text{ \AA}$ ;  $4.72 \text{ \AA}$ ), with nordstrandite ( $4.15 \text{ \AA}$ ;  $4.37 \text{ \AA}$ ;  $4.79 \text{ \AA}$ ) or gibbsite ( $4.34 \text{ \AA}$ ;  $4.82 \text{ \AA}$ ) or both, started to develop in both products shortly after preparation, the X-ray peaks becoming sharper and larger as the period of ageing increased up to one month with no further noticeable change after this period (fig. 1). A broad peak with its diffraction maximum representing a spacing of approximately  $6.5 \text{ \AA}$  was also observed, and in a randomly packed, freeze-dried, sample of Product 13, additional broad peaks with diffraction maxima at  $3.20 \text{ \AA}$ ,  $2.33 \text{ \AA}$ , and  $1.86 \text{ \AA}$  were also present. In Product 13, this broad  $6.5 \text{ \AA}$  peak persisted without change in height or breadth during the entire ageing process of one year, whereas in Product 14 it decreased in intensity with increased age and disappeared in three weeks. These broad peaks correspond to those of the material referred to by Calvet *et al.* (1953) as pseudoboehmite because the X-ray diffraction pattern is close to but distinctly different from that of boehmite. Papée, Tertian, and Biais (1958, p. 1304) postulated that the broad diffraction peaks result from a poorly ordered arrangement of elementary sheet-like units. A 20-minute  $N$  HCl wash completely removed this  $6.5 \text{ \AA}$  peak, while the  $\text{Al}(\text{OH})_3$  peaks remained unchanged (fig. 2). Since the  $N$  HCl wash also caused a large reduction in the volume of precipitate together with the removal of trace sulphate and a small portion of aluminium (table I), it is believed that this broad peak is in some way related to the aforementioned highly hydrated component containing aluminium and sulphate.

The characteristics of products like No. 13, formed at an  $\text{NaOH}/\text{Al}$

ratio of 3.0, varied considerably with a slight deviation of the ratio from this value. In the case of Product 14 ( $\text{NaOH}/\text{Al} = 3.3$ ) and the X-ray amorphous products discussed in the next section formed at ratios of

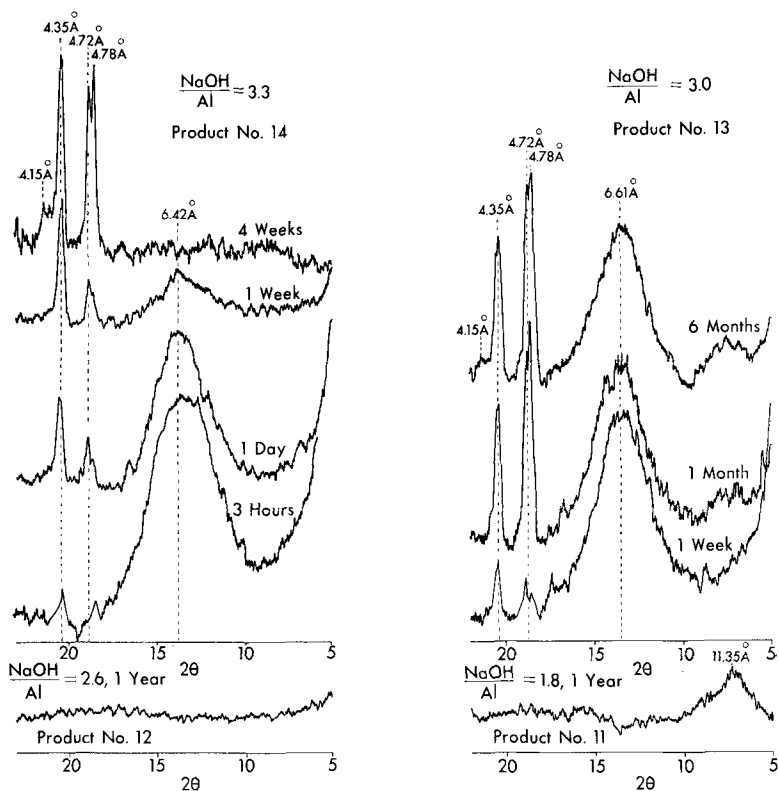


FIG. 1. X-ray diffraction patterns of representative crystalline and amorphous aluminium hydroxides prepared from  $\text{Al}_2(\text{SO}_4)_3 + \text{NaOH}$ .

2.7 or less, a slight deviation from the given ratio does not have a similarly drastic effect on the nature of the product.

*X-ray amorphous material.* The products prepared at  $\text{NaOH}/\text{Al} = 2.7$  and below were amorphous to X-ray diffraction. Electron micrographs taken of material prepared by freeze-drying revealed lacy aggregates of roughly equidimensional particles 50 to 250 Å in diameter and having rounded to irregular outlines. Electron diffraction did not reveal the presence of any crystalline components.

The pH values of these products, plotted against the NaOH/Al mole ratio in their preparation, showed a break at the ratio of 2 (fig. 3). Below this inflection point, the pH value changed smoothly and only slightly with the increased NaOH/Al ratio; this suggests that the OH<sup>-</sup> added is strongly held in a product with little dissociation. The OH<sup>-</sup>

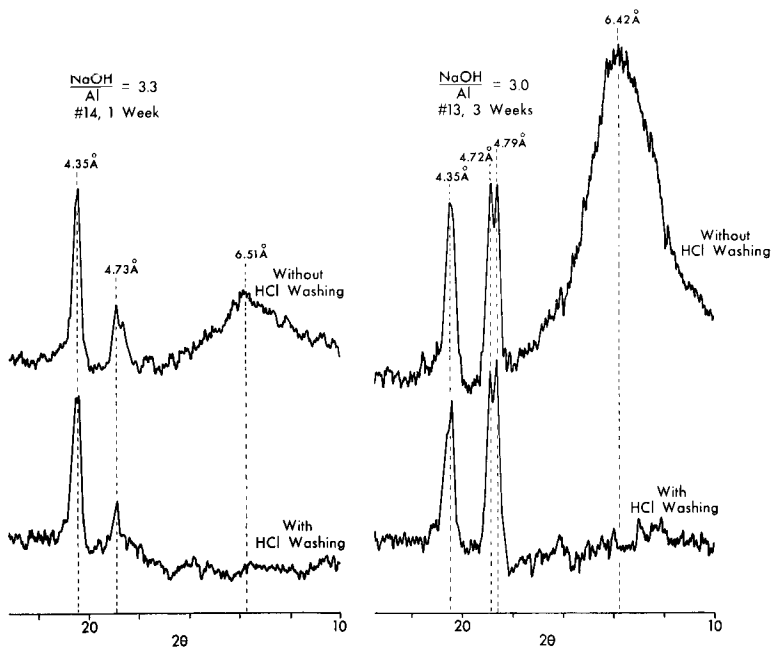


FIG. 2. Removal of the pseudoboehmite X-ray peak with *N* HCl washing.

in the products above this point was relatively more dissociable; however, the OH<sup>-</sup> added was still nearly completely combined with aluminium, as shown by the free OH<sup>-</sup> in solution and the total OH<sup>-</sup> added in the preparation.

The time required for solution in *N* HCl gradually increased with an increase in NaOH/Al ratio, but complete solution took place in 20 minutes even at NaOH/Al = 2.7. This behaviour is significant when compared with the high resistance to acid of those products prepared at NaOH/Al = 3 and 3.3.

Chemical analysis of these products indicated that they were basic aluminium sulphate (fig. 4). In the range of NaOH/Al = 0.3 to 2.1, the



amount of precipitate increased with increased ratio, but the composition of the precipitates was approximately constant, averaging at  $\text{Al}(\text{OH})_{2.2}(\text{SO}_4)_{0.4}$ . Four specimens prepared at  $\text{NaOH}/\text{Al} = 1.8$  deserve particular

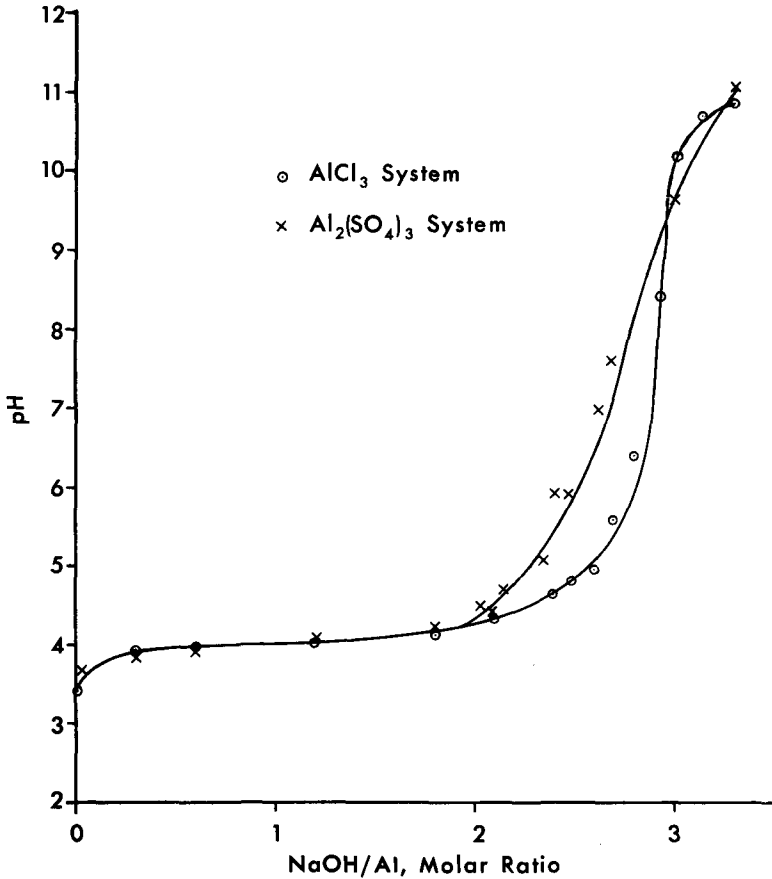


FIG. 3. The pH values of aluminium hydroxide suspensions or solutions prepared at various  $\text{NaOH}/\text{Al}$  mole ratios.

mention for, although the sulphate content in the original preparation was adjusted with  $\text{Na}_2\text{SO}_4$  to cover the range from 0.02 to 1 *N*, the composition of the precipitates did not change. It is believed, therefore, that the precipitate is a chemical compound of definite composition,  $\text{Al}(\text{OH})_{2.2}(\text{SO}_4)_{0.4}$ , which should be unusually stable. The formation of basic

aluminium sulphate of definite composition under similar conditions has also been reported by Weiser *et al.* (1941) and Williamson (1923); the compositions they found were  $\text{Al}_2\text{O}_3 \cdot \text{SO}_3 \cdot 1.5\text{H}_2\text{O}$  and  $(\text{Al}_2\text{O}_3)_5 \cdot (\text{SO}_3)_3 \cdot 15\text{H}_2\text{O}$ , respectively.

Aluminium was completely removed from solution at  $\text{NaOH}/\text{Al} = 2.1$ . Chemical analysis of precipitates at higher ratios (2.1 to 2.7) indicated

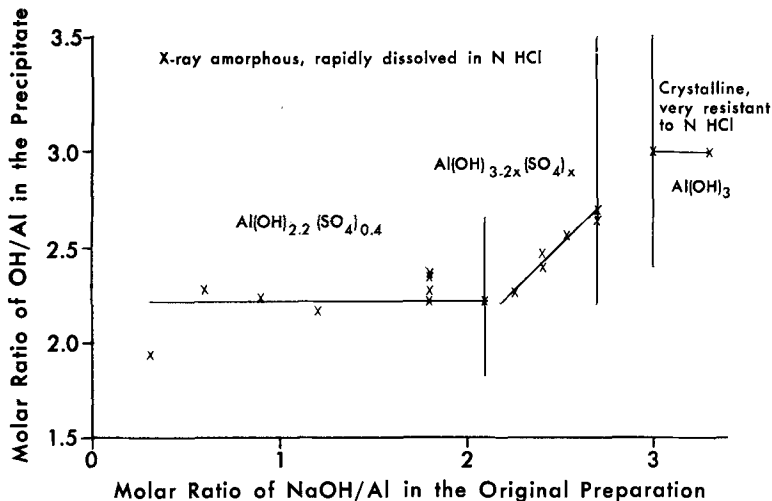


FIG. 4. The chemical composition of aluminium hydroxides prepared from  $\text{Al}_2(\text{SO}_4)_3 + \text{NaOH}$ .

the formation of basic aluminium sulphates of continuous variability in composition (fig. 4) and increasing basicity. The authors do not believe that these products can be considered mixtures of X-ray crystalline  $\text{Al}(\text{OH})_3$  and amorphous  $\text{Al}(\text{OH})_{2.2}(\text{SO}_4)_{0.4}$ . If this were true, 63 % of the aluminium should be present as  $\text{Al}(\text{OH})_3$  and 37 % as  $\text{Al}(\text{OH})_{2.2}(\text{SO}_4)_{0.4}$  at  $\text{NaOH}/\text{Al} = 2.7$ . Under this condition, it should be possible to fractionate the crystalline  $\text{Al}(\text{OH})_3$  from the amorphous  $\text{Al}(\text{OH})_{2.2}(\text{SO}_4)_{0.4}$  with *N* HCl washing, and to detect  $\text{Al}(\text{OH})_3$  by X-ray diffraction, infrared absorption, or electron microscopic observation. However, none of these techniques indicates the presence of crystalline  $\text{Al}(\text{OH})_3$ .

Most of the samples were studied during a period of two days to two weeks after preparation. Two products (No. 11,  $\text{NaOH}/\text{Al} = 1.8$ ; and No. 12,  $\text{NaOH}/\text{Al} = 2.6$ ) were aged for one year, and periodic investigation of these two samples was made in order to study any possible

change in their nature and properties. The study revealed that these products did not show any significant change in pH, chemical composition, or X-ray diffraction pattern up to six months. The time required for solution of the precipitate in *N* HCl gradually increased with increased ageing, but the precipitate of NaOH/Al = 2.6 (Product 12), even after six months of ageing, was still completely dissolved in *N* HCl in 20 minutes.

After one year, however, only 50.2 % of the aluminium in Product 11 was extracted by *N* HCl in 20 minutes. The chemical analysis showed

TABLE II. X-ray diffraction data for Product 11 after one year of ageing, compared with data for hydrobasaluminite (Hollingworth and Bannister, 1950)

Hydrobasaluminite		Product 11*		Hydrobasaluminite		Product 11*	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
12.6 Å	vvs			3.73 Å	s		
		11.33 Å	s	3.43	m	3.40 Å	m
8.08	m			3.21	w	3.19	w
6.18	s			3.07	s		
		5.72	m			2.92	w
5.29	s	5.28	m	2.83	mw	2.85	w
4.70	s	4.65	m	2.57	m	2.59	m
4.23	ms			2.25	m	2.34	w
4.00	ms			2.22	w	2.18	w
		3.90	vvs				

\* All X-ray diffraction peaks are broad. The relative intensities are estimated from the height of the peaks.

that the portion of the product dissolved in the *N* HCl was of the composition  $\text{Al}(\text{OH})_{2.35}(\text{SO}_4)_{0.33}$  which was close to that of the original precipitate, whereas the residual precipitate after *N* HCl treatment was of the composition  $\text{Al}(\text{OH})_{2.58}(\text{SO}_4)_{0.21}$ . An X-ray diffraction pattern showed development of a broad peak representing a spacing of 11.35 Å (fig. 1). A randomly packed sample of Product 11 was X-rayed and the pattern showed additional broad peaks (table II) which are close to but not identical with hydrobasaluminite,  $\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot 36\text{H}_2\text{O}$  (Hollingworth and Bannister, 1950). Product 12, after the same one-year period of ageing, remained amorphous to X-ray diffraction (fig. 1) and 87 % of aluminium in the precipitate was dissolved in *N* HCl in 20 minutes. These facts suggest that under certain conditions, basic aluminium sulphate can be crystallized out, but that the sulphate content is important in determining the process and result of crystallization.

*Products in the AlCl<sub>3</sub> + NaOH system.* In this system, crystalline components were formed at NaOH/Al ratios of 2.93 (Product 2), 3.0 (Product 1), and 3.3. The properties of these products are similar to those of

the crystalline products formed in the  $\text{Al}_2(\text{SO}_4)_3 + \text{NaOH}$  system. The pH values were 8.4, 10.2, and 10.8, respectively. All the products became highly resistant to acid shortly after preparation (table I). In Products 1 and 2, aluminium was completely removed from the solution. The free  $\text{OH}^-$  remaining in solution was negligible (0.16 meq/l in Product 1, pH 10.2; 0.003 meq/l in Product 2, pH 8.4) as compared with the total  $\text{OH}^-$  added (50 meq/l in Product 1 and 49 meq/l in Product 2) indicating that this  $\text{OH}^-$  was practically completely precipitated with aluminium thereby presumably resulting in a product of a composition close to  $\text{Al}(\text{OH})_3$ . The dry precipitate ( $100^\circ \text{C}$ ) contained  $34.6 \pm 2.0\%$  aluminium which corresponds to this composition. The X-ray diffraction patterns for Product 1 showed that bayerite started to appear in 2 hours after preparation, and the X-ray peaks became sharper and larger with ageing (fig. 5). These products in the chloride system differed slightly from those of the sulphate system in that bayerite was the only crystalline  $\text{Al}(\text{OH})_3$  found and no gibbsite, nordstrandite, or pseudoboehmite appeared in any of the specimens. Also, bayerite formed at a slightly lower  $\text{NaOH}/\text{Al}$  ratio (2.93). The fact that Weiser *et al.* (1940), Papée *et al.* (1958), Bale and Schmidt (1958 and 1959), and MacKenzie *et al.* (1962) found boehmite or pseudoboehmite in the  $\text{AlCl}_3 + \text{NaOH}$  system can only be attributed to differences in the preparation and characterization methods.

At a 0.05 *N* concentration of aluminium in the final solution and  $\text{NaOH}/\text{Al}$  ratios of from 0 to 2.7, no precipitate was observed; the solutions appearing clear to the naked eye. Tyndell effect was observed only in the two solutions of  $\text{NaOH}/\text{Al} = 2.55$  and 2.70. No product could be separated out with a Spinco ultra-centrifuge Model E at a velocity of 67 000 r.p.m. As noted in previous sections, amorphous aluminium hydroxides were precipitated out in the corresponding  $\text{Al}_2(\text{SO}_4)_3 + \text{NaOH}$  system, and it is probably for this reason that many investigators believe that these two systems differ. However, the analysis of the 'chloride' solutions with the Dowex-50 treatment indicated that the reaction product in the range of  $\text{NaOH}/\text{Al} = 0$  to 2 was approximately  $[\text{Al}(\text{OH})_{2.2}]^{0.8+}$  (tables III and IV, and fig. 6), which is the same as that in the sulphate system in the same range of  $\text{NaOH}/\text{Al}$  ratio (fig. 4). The pH curve of these solutions coincides with that of the sulphate system in the same range of  $\text{NaOH}/\text{Al}$  ratio (fig. 3). The curves suggest that the reaction mechanism between  $\text{Al}^{3+}$  and  $\text{NaOH}$  is basically the same in these two systems. In table III, the basicity of the hydroxy-aluminium species was estimated by dividing the cation exchange charge inactivated by the

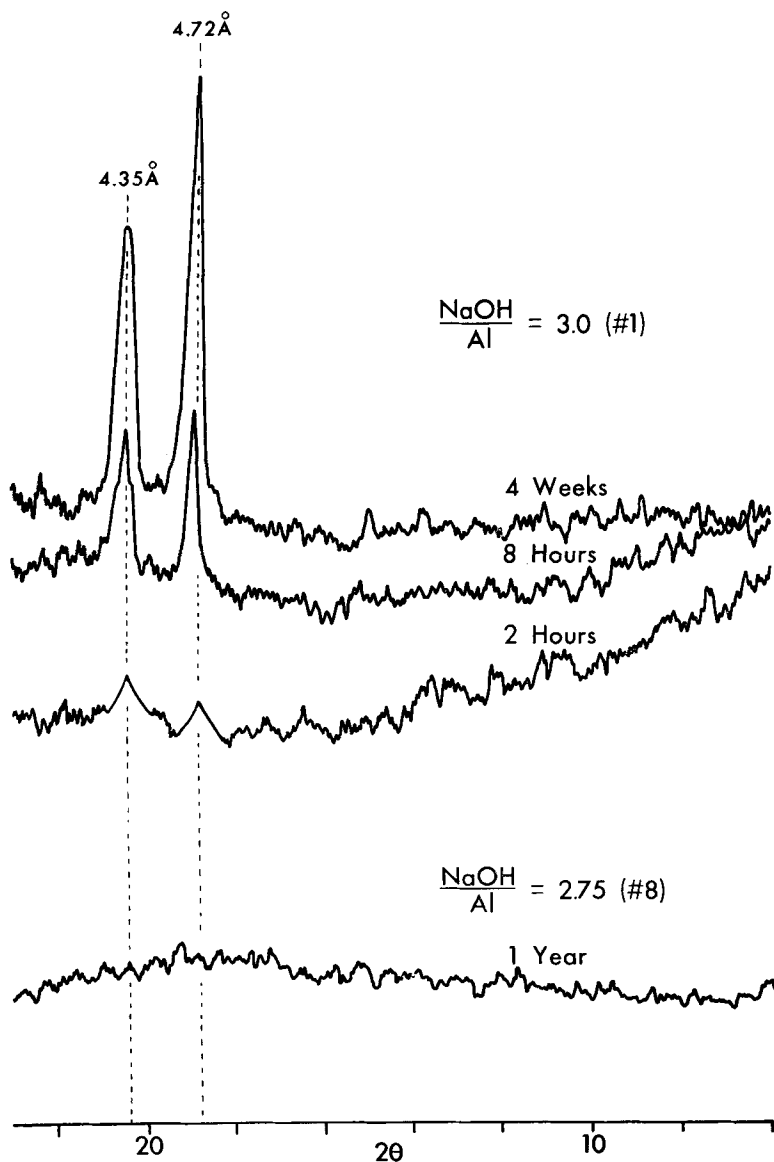


FIG. 5. X-ray diffraction patterns of representative crystalline and amorphous aluminium hydroxides prepared from  $\text{AlCl}_3 + \text{NaOH}$ .

non-exchangeable aluminium to obtain the net positive charge per atom of aluminium. In table IV, the composition of the hydroxy-aluminium species in the first seven solutions was estimated by assuming

TABLE III. Data obtained by repeated saturation of 0.1 g sodium saturated Dowex-50 with 1000 ml of hydroxy-aluminium solution

Hydroxy-aluminium solution, NaOH/Al, molar ratio	Non-exch. Al, millimoles/g	Exch. charge inact., meq/g	Basicity of† non-exch. Al
0.00*	1.08	0.86	Al(OH) <sub>2.20</sub> <sup>3.80+</sup>
0.48	2.40	1.92	Al(OH) <sub>2.20</sub> <sup>0.80+</sup>
0.96	2.41	1.99	Al(OH) <sub>2.17</sub> <sup>3.83+</sup>
1.48	2.33	2.05	Al(OH) <sub>2.12</sub> <sup>0.88+</sup>
			Average Al(OH) <sub>2.17</sub> <sup>0.83+</sup>

\* Aged 0.05 N AlCl<sub>3</sub> solution.

† The basicity of the non-exchangeable aluminium was estimated by dividing the exchange charge inactivated by the non-exchangeable aluminium to obtain the net positive charge per millimole of aluminium.

TABLE IV. Data obtained by equilibration of 1 g sodium saturated Dowex-50 with 50 ml of hydroxy-aluminium solution

Hydroxy-aluminium solution, NaOH/Al, molar ratio	NaOH added, mM/g resin	Al in solution after treatment mM/l	Non-exch. aluminium mM/g resin	Basicity of non-exch. Al*
0.48	0.40	nil	0.167	Al(OH) <sub>2.35</sub> <sup>0.65+</sup>
0.96	0.80	nil	0.400	Al(OH) <sub>2.00</sub> <sup>1.00+</sup>
1.44	1.20	nil	0.552	Al(OH) <sub>2.18</sub> <sup>0.82+</sup>
1.68	1.40	nil	0.618	Al(OH) <sub>2.26</sub> <sup>0.74+</sup>
1.74	1.45	nil	0.704	Al(OH) <sub>2.06</sub> <sup>0.94+</sup>
1.92	1.60	nil	0.682	Al(OH) <sub>2.35</sub> <sup>0.85+</sup>
2.10	1.75	nil	0.778	Al(OH) <sub>2.25</sub> <sup>0.75+</sup>
				Average Al(OH) <sub>2.31</sub> <sup>0.79+</sup>
2.40	2.00	2.6	n.d.	
2.50	2.08	8.2	0.368	
2.60	2.16	10.2	0.269	
2.70	2.25	11.1	0.092	

\* The basicity of the non-exchangeable aluminium was estimated by dividing the NaOH added by the non-exchangeable aluminium.

that the total NaOH added was bound to the total non-exchangeable aluminium. This assumption was based on the following facts: aluminium completely entered the resin; the exchangeable aluminium was trivalent (Hsu and Rich, 1960); and the OH<sup>-</sup> activity in these solutions was negligible as estimated from their pH values (fig. 3). The detailed

procedure and interpretation has been described in an earlier report by Hsu and Rich (1960).

In the range of  $\text{NaOH}/\text{Al} = 2.1$  to  $2.7$ , the fixation of aluminium by resin decreased rapidly with increasing  $\text{NaOH}/\text{Al}$  ratio (table IV). Apparently the product was too large to enter the resin, which has a pore size of  $8\text{--}12 \text{ \AA}$  (Kunin, 1958, p. 46). Two precipitated products

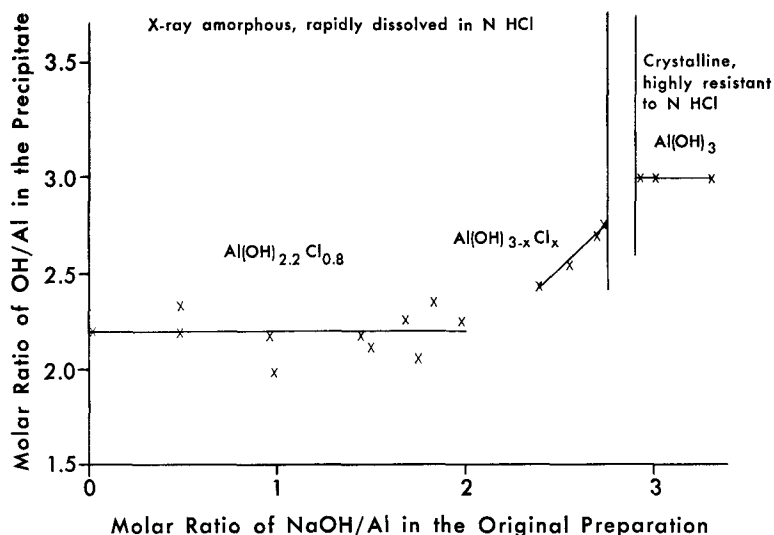


FIG. 6. The chemical composition of aluminium hydroxides prepared from  $\text{AlCl}_3 + \text{NaOH}$ .

( $\text{NaOH}/\text{Al} = 2.7$  and  $2.75$ ) in this group were prepared at an  $0.25 \text{ N}$  concentration of aluminium; whereas two other precipitated products ( $\text{NaOH}/\text{Al} = 2.40$  and  $2.55$ ) were also prepared at an  $0.25 \text{ N}$  aluminium concentration, the chloride concentration for these two was adjusted to  $1 \text{ N}$  with  $\text{NaCl}$ , since the product would otherwise remain in solution. Chemical analyses in which both the aluminium and  $\text{OH}^-$  contents were directly determined indicated that these four products are members of a continuous series of basic salts (fig. 6). The chloride content was not directly determined because of the difficulty involved in washing out the excess chloride. At the  $\text{NaOH}/\text{Al} = 2.75$  ratio, both aluminium and  $\text{OH}^-$  precipitated completely giving, therefore, a product of the composition  $\text{Al}(\text{OH})_{2.75}^{0.25+}$ . All these products were dissolved in  $\text{N HCl}$  in a matter of seconds and gave amorphous X-ray diffraction patterns even after one year of ageing. The pattern for Product 8 ( $\text{NaOH}/\text{Al} = 2.75$ )

is given in fig. 5 as an example. Because bayerite is highly resistant to  $N$  HCl and is detectable with X-ray within a few hours after preparation, it is reasonable to conclude that none was present in these precipitates. In addition, 50 ml suspensions of Products 8 (NaOH/Al = 2.75) and 24 (NaOH/Al = 2.55), after being aged one year, were each seeded with 1 ml of Product 1 for another two months, but no crystallization of bayerite or gibbsite was observed.

It should be mentioned here that some hydroxy-aluminium solutions of NaOH/Al = 1.2 to 2.7 and 0.05  $N$  aluminium remained clear for about three to six months but became turbid afterwards. Probably the concentration of chloride in the system is an important factor in determining the stability of the product and it is hoped that a detailed study, now in progress, of the effect of anions on the formation of aluminium hydroxides may help to explain this development.

#### *A theory of the development of aluminium hydroxides*

In an attempt to understand why some aluminium hydroxides are amorphous and others are crystalline, two concepts may be considered:

Each  $Al^{3+}$  ion in solution is co-ordinated with six molecules of  $H_2O$  and contributes half a positive charge to each; when a hydroxyl ion is attached to an  $Al^{3+}$  ion, half of its negative charge will be used to neutralize half a positive charge contributed by the  $Al^{3+}$  ion, leaving another half negative charge on the OH unsatisfied and available to balance half a positive from another  $Al^{3+}$  ion. The  $OH^-$  is thus shared equally by the two  $Al^{3+}$  ions and functions as a bridge between them. The authors consider this to be the fundamental principle underlying polymerization of hydroxy-aluminium ions in solution.

In order to test this hypothesis, several hydroxy-aluminium solutions were prepared by adding NaOH to  $AlCl_3$  solutions with the ratio of NaOH to aluminium varying from 0.3 to 2.7; the preparation procedure was the same as that described heretofore. A 100 ml aliquot of each solution was back-titrated with 0.1  $N$  HCl to pH 3.7, the pH of the control (a 0.05  $N$   $AlCl_3$  solution to which no NaOH had been added); if the  $OH^-$  does not exist as a bridge, it should immediately be neutralized. The results (last column of table V) show that the  $OH^-$  in all the solutions was largely in bridge form: in all cases, the pH of the solution rapidly decreased when HCl was added, then slowly increased, apparently due to the breakdown of the  $OH^-$  bridge. The experiment showed that in the first nine solutions (NaOH/Al = 0.3 to 2.4), the pH stayed at 3.7 for at least several minutes; this indicates that the  $OH^-$  bridge is stable and not easily broken down. In the last two solutions (NaOH/Al = 2.55 and 2.70) a few drops of 0.1  $N$  HCl rapidly lowered the pH, but later it slightly and slowly increased. The readings reported here were taken at the point at which the pH values varied little during a period of 30 seconds.

Secondly, it is believed that the hydroxy-aluminium ions tend to



polymerize in a 6-membered ring unit (fig. 7) or multiples of such units, similar to those found in gibbsite. This unit of structure was earlier proposed by Brosset *et al.* (1954) with a composition  $\text{Al}_6(\text{OH})_{15}^{3+}$  and

TABLE V. Percentage of bridged hydroxyl in hydroxy-aluminium solutions

NaOH/Al, molar ratio	pH	NaOH added in preparation, meq.	HCl added in* acidification, meq.	% OH <sup>-</sup> bridged
0.0	3.70	—	—	—
0.3	4.04	0.60	0.10	83.3
0.6	4.10	1.20	0.11	91.3
0.9	4.14	1.80	0.06	96.7
1.2	4.19	2.40	0.04	98.3
1.5	4.21	3.00	0.04	98.7
1.8	4.36	3.60	0.02	99.4
2.1	4.29	4.20	0.02	99.5
2.25	4.72	4.50	0.02	99.6
2.40	5.00	4.80	0.02	99.6
2.55	5.49	5.10	0.04	99.2
2.70	6.20	5.40	0.07	98.7

\* HCl added to acidify the hydroxy-aluminium solutions to pH 3.7, the pH of 0.05 N  $\text{AlCl}_3$ .

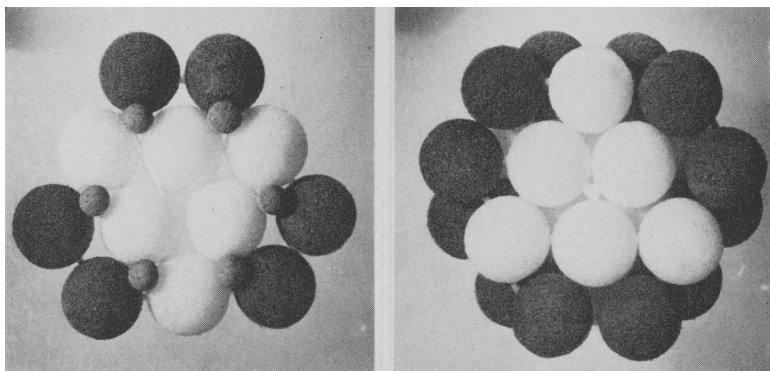


Fig. 7. Structural model of 6-member ring hydroxy-aluminium polymers. Left view has upper layer of  $\text{OH}^-$  and  $\text{H}_2\text{O}$  removed. (Large white balls =  $\text{OH}^-$ ; large black =  $\text{H}_2\text{O}$ .)

by Hsu and Rich (1960) with  $\text{Al}_6(\text{OH})_{12}^{6+}$ , and it seems to be a logical model for the hydroxy-aluminium polymers in solution.

Using these two concepts, it is possible to depict the development of amorphous and crystalline aluminium hydroxides as follows:

When NaOH is added to an aluminium salt solution, the initial reaction

should be as equations (1) and (2) below. According to the first concept, neither the  $\text{Al}(\text{OH})_2^+$  nor the  $\text{Al}(\text{OH})_2^+$  ion would be stable and therefore polymerization would occur immediately after the  $\text{OH}^-$  ion is attached to the  $\text{Al}^{3+}$  ion. According to the second concept, the polymerization of the hydroxy-aluminium species would start from a single ring unit composed of six  $\text{Al}(\text{OH})_2^+$  ions, or  $\text{Al}_6(\text{OH})_{12}^{6+}$  (eq. 3), and the initial reaction could be summarized as equation (4). Because  $\text{Al}^{3+}$  has a much higher

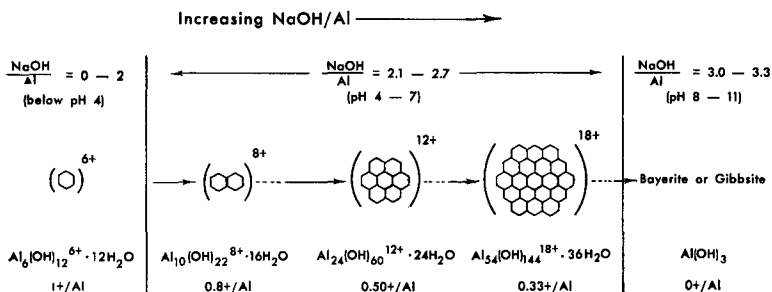
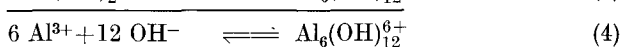
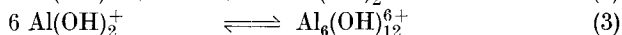
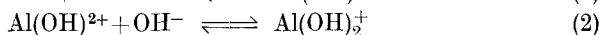
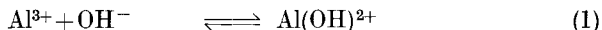


FIG. 8. Proposed development of aluminium hydroxides.

net positive charge per aluminium than the unit ring polymer, the additional  $\text{OH}^-$  would be taken by former and transform it to the latter.



At  $\text{NaOH}/\text{Al} = 2$  or nearly so, reaction 4 would be complete, and further  $\text{OH}^-$  would then go to the ring units. Based on the same reasoning, the  $\text{OH}^-$  attached to the unit ring would function as a bridge and foster the formation of polymers gradually increasing in size and basicity, such as double rings of the composition  $\text{Al}_{10}\text{OH}_{22}^{8+}$ , or triple rings of  $\text{Al}_{13}(\text{OH})_{30}^{9+}$ , &c. (fig. 8), rather than neutral  $\text{Al}(\text{OH})_3$  molecules. The difference in charge density between single and double, and between double and triple rings, is not very large, probably resulting in the co-existence of a variety of units in these products. However, because of the high charge-density difference between  $\text{Al}^{3+}$  and these ring units, the formation of polymers of still higher basicities would be limited until all the aluminium ions are included in the ring units. Thus, the reaction products in the range of  $\text{NaOH}/\text{Al} = 0$  to 2, would be a mixture of single and double, even

triple, rings, with units of higher basicities being rare. This is a possible explanation of the approximately constant composition  $\text{Al}(\text{OH})_{2.2}X_{0.8}$  obtained in the experimental work (see figs. 4 and 6).

The net positive charge per aluminium would decrease with increasing NaOH/Al ratio, but all the hydroxy-aluminium polymers would remain positively charged until the ratio reaches 3. Thus, up to this point the hydroxy-aluminium polymers would repel one another.

In order to maintain electro-neutrality, anions would occupy positions between the positively charged polymers, thereby giving rise to basic aluminium salts. The basic aluminium sulphate is not very soluble and precipitates even at NaOH/Al = 0.3. The basic aluminium chloride is highly soluble and can be precipitated only at a high NaOH/Al ratio and a high solution concentration of aluminium and chloride. Since the size and amount of hydration of the polymers and of the counter-anions generally are not uniform, the precipitate would tend to be disordered. However, this does not rule out the possible formation of a crystalline basic salt if conditions are favourable.

At NaOH/Al = 3 the net positive charge per aluminium would disappear and, consequently, the repulsion among polymers, as well as their hydration water, would become negligible. Therefore, at this ratio, it is to be expected that all the polymers would cluster together and form crystalline  $\text{Al}(\text{OH})_3$  in a matter of hours or days, depending on the conditions of crystal formation.

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