

THE NATURE OF POLYNUCLEAR OH-AL COMPLEXES IN LABORATORY-HYDROLYZED AND COMMERCIAL HYDROXYALUMINUM SOLUTIONS¹

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Abstract—Laboratory-hydrolyzed and commercial OH-Al solutions were characterized using kinetics of Al–ferron color development, kinetics of structural OH neutralization with H⁺, ²⁷Al NMR spectroscopy, and sulfate precipitation. The results showed that the Al₁₃ complexes having the Keggin structure were dominant only in fresh, laboratory-hydrolyzed OH-Al solutions of OH/Al molar ratio = 1.8 and above. These species gradually converted to other polynuclear forms that reacted with ferron slowly, were not detectable by ²⁷Al NMR spectroscopy, and yielded different basic Al sulfates following Na₂SO₄ addition. These more stable complexes can best be interpreted to have a Al(OH)₃-fragment structure. In the three commercial aluminum chlorohydrate (ACH) solutions studied, Al₁₃ complexes accounted for a small portion of the total Al present. More than 80% of the Al was present as species that were not detectable with NMR spectroscopy and resembled the slow-reacting complexes in aged, laboratory-hydrolyzed OH-Al solutions. Small portions of the slow-reacting complexes appeared to be submicron particulates that acted as nuclei for gibbsite formation or aggregates of Al₁₃ complexes that dispersed to Al₁₃ upon dilution. Polyaluminum chloride (PA) solution resembled the moderately aged laboratory-hydrolyzed OH-Al solutions.

Key Words—Al₁₃ complexes, Aluminum chlorohydrate, Polyaluminum chloride, Polynuclear OH-Al complexes.

INTRODUCTION

Hydroxyaluminum solutions have many industrial applications, e.g., as clay stabilizing agents in oilfields (Reed, 1972; Hesterberg and Reed, 1991); as catalyst supports in pillared clay (Pinnavaia, 1983); as antacid and antiperspirant agents (Teagarden *et al.*, 1981); and as coagulants in potable and waste water treatments (Buffle *et al.*, 1985). A thorough understanding of the nature and properties of the polynuclear OH-Al complexes in solution should be of great help in the improvement of manufacturing OH-Al solutions and in the development of future applications.

Much of our present understanding about the nature of polynuclear OH-Al complexes in solution has been derived from the study of laboratory-hydrolyzed solutions prepared by adding a base to Al salt solutions. At present, the Al₁₃ species of Keggin structure has frequently been assumed to be the dominant polynuclear OH-Al complex in solution (Bertsch, 1989). This complex, thus, has commonly been considered as the active component in many studies of the industrial applications of OH-Al solutions. Nevertheless, the polynuclear OH-Al complexes in commercial OH-Al solutions applied in industries may be different from those in laboratory-hydrolyzed OH-Al solutions be-

cause they are prepared under different conditions. Furthermore, it has been reported that the Al₁₃ complexes are artifacts in solution preparation, developed through localized high alkalinity (Akitt and Farthing, 1981; Teagarden *et al.*, 1981; Bertsch, 1987). They are dominant only in fresh, laboratory-hydrolyzed OH-Al solutions, but slowly convert with time to more stable and less reactive species (Tsai and Hsu, 1984, 1985) that are not detectable with NMR spectroscopy (Akitt and Farthing, 1981; Denney and Hsu, 1986). The objective of this study was to compare the polynuclear OH-Al complexes in commercial and laboratory-hydrolyzed OH-Al solutions. The results show that commercial aluminum chlorohydrate (ACH) solutions are dominated by complexes that resemble the slow-reacting OH-Al complexes in aged laboratory-hydrolyzed OH-Al solutions. Al₁₃ complexes account for only a small portion of the total polynuclear OH-Al complexes. Polyaluminum chloride (PA) solution resembles the moderately aged laboratory-hydrolyzed OH-Al solutions.

MATERIALS AND METHODS

Hydroxyaluminum solutions

All laboratory-hydrolyzed OH-Al solutions were prepared by adding appropriate amounts of 0.1 M NaOH to 400 ml of 0.1 M AlCl₃, drop by drop, at a rate of 1 ml min⁻¹, with constant stirring, and then diluting to 2000 ml. The prepared solutions had a

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NaOH/Al molar ratio ranging from 1 to 2.5 and were aged for various durations. Gibbsite precipitate developed in some solutions after prolonged aging. The gibbsite precipitate was removed by filtering the sample aliquot through a Millipore filter paper of 0.025 μm pore size before analysis.

Five commercial OH-Al solutions were studied. They included three aluminum chlorohydrate (ACH) solutions provided by Reheis Inc., Summit Research Lab, and Courtney Industries Inc.; one polyaluminum chloride (PA) provided by Courtney Industries; and another product with the trade name WAC-HB obtained from ATO Chemicals, France. It is not known if the last product has a common commercial name. The compositions of these commercial solutions are shown in Table 1. All solutions were diluted with H_2O to approximately 0.02 M in Al and analyzed periodically.

Kinetics of Al-ferron color development

An appropriate sample aliquot containing 0.002–0.012 mmol Al was added to a polyethylene bottle containing a predetermined amount of H_2O and 80 ml of color-developing reagent and mixed rapidly. The color-developing reagent was 2.85 mM in ferron, 1 M in Na acetate, 0.25 M in acetic acid, and pH 5.2 (Hsu and Cao, 1991). The total volume of sample aliquot and H_2O was 120 ml for all samples. The absorbance at 366 nm was monitored with time until the color fully developed. The distribution of rapid- and slow-reacting polynuclear Al complexes was calculated by assuming that they both reacted with ferron following pseudo-first-order kinetics (Tsai and Hsu, 1984; Hsu, 1992). The concentration of mononuclear Al ions was determined by subtracting the total polynuclear species from the total Al recovered. In principle, the concentration of total polynuclear OH-Al complexes should equal the sum of rapid- and slow-reacting complexes. For solutions containing high concentrations of rapid-reacting complexes and low concentrations of monomeric ions, however, the uncertainty in the concentration of monomeric ions so calculated was frequently large. To minimize this difficulty, the total polynuclear species was empirically determined by extrapolating $\log(\text{Al}_\infty - \text{Al}_t)$ against t for $t = 40\text{--}70$ s to zero time. The concentrations of polynuclear OH-Al complexes so determined were close to but more reproducible than the sum of rapid- and slow-reacting OH-Al complexes. For solutions of low concentration of rapid-reacting OH-Al complexes, the increase in the Al recovered during the first several minutes are frequently not noticeable. Therefore, the Al recovered in 40 s was taken as the concentration of mononuclear Al ions.

Kinetics of structural OH neutralization with HCl

One hundred milliliters of sample aliquot were pipetted into a 110-ml, wide mouthed glass bottle. Predetermined amounts of 1.0 M HCl and H_2O were added

Table 1. Composition of commercial OH-Al solutions.

Solution ¹	Al, M	Cl/Al	OH/Al	SO ₄ /Al	pH
		Molar ratio			
ACH (RH)	6.1	0.5	2.5	nil	3.5
PA	2.4	1.7	1.5	nil	2.5
WAC-HB	2.0	1.1	2.0	0.05	3.3

¹ ACH (RH) refers to aluminum chlorohydrate (Reheis). PA refers to polyaluminum chloride. WAC-HB was obtained from ATO Chemicals, France.

to each bottle, and the change in pH was monitored with time until 90% or more of the H^+ added was neutralized. The amount of H^+ added was adjusted to be equal to the total OH^- content in the sample aliquot. The total OH^- content in sample aliquot was either calculated from solution preparation or determined by titrating an acidified aliquot with 0.1 M NaOH to pH 7.5 in the presence of KF (see below). The total volume of HCl and H_2O was 5 ml. The composition of the structural OH^- was calculated by plotting $1/[\text{H}^+]$ against time. To minimize the effect of Al ions on $\text{pH}\text{--}[\text{H}^+]$ conversion, a series of AlCl_3 reference solutions, all 100 ml in volume and 0.02 M in Al, were prepared. Various amounts of HCl and H_2O were added, and the pH was read. The $\text{pH}\text{--}[\text{H}^+]$ relationship for these reference solutions was used to convert the measured sample pH to the concentration of H^+ in solution. Edge OH^- was determined by adding 0.1 M HCl to a sample aliquot to pH 3.6, which is the pH of a 0.02 M AlCl_3 solution. The amount of H^+ consumed was taken as the edge OH^- content. It was assumed that the edge OH^- reacted with H^+ instantaneously. Therefore, sample pH was read as soon as H^+ was added in the edge OH^- determination.

Determination of total OH⁻ content in OH-Al solutions

Ten milliliters of the sample aliquot were pipetted into a 100 ml volumetric flask. Ten milliliters of 0.10 M HCl were added and heated at 70°C for 16 h until the structural OH^- completely decomposed. The contents were cooled to room temperature and diluted to 100 ml. A 25 ml aliquot was pipetted into a beaker, 5 ml of 0.5 M KF were added, and the mixture was titrated with 0.1 M NaOH to pH 7.5 immediately after KF addition. The amount of NaOH required to reach pH 7.5 was taken as the excess H^+ remaining in solution. The amount of H^+ consumed was taken as the total OH^- in OH-Al complexes.

NMR spectra

²⁷Al NMR spectra were obtained on a Varian 360 XL NMR spectrometer operating at 78.2 MHz. All five commercial OH-Al solutions were diluted with H_2O to approximately 0.02 M in Al before the acquisition of NMR spectra. To estimate the distribution of various species in solution, selected sample and stan-

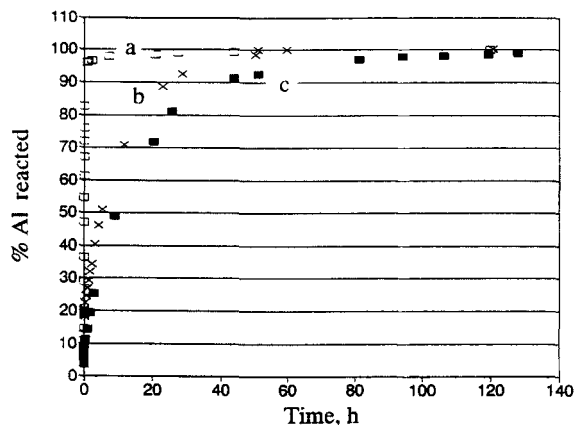


Figure 1. Percentage of Al reacted with ferron as a function of time: a) laboratory-hydrolyzed OH-Al solution, 0.02 M in Al, $R = 2.5$, 3 days; b) laboratory-hydrolyzed OH-Al solution, 0.016 M in Al, $R = 2.2$, 3925 days (gibbsite precipitate was observed and removed through filtration 2 years after preparation; this solution remained clear thereafter); and c) ACH (RH) diluted to 0.02 M in Al immediately before analysis.

standard solutions of known monomeric Al concentration were run using a coaxial sample tube, with a 0.02 M Na aluminate solution in the inner insert as reference. The intensities for ^{27}Al signals relative to the aluminate reference were used for calculating the Al concentrations for corresponding signals. The concentration for the 63 ppm signal was multiplied by 13 to obtain the concentration of Al_{13} (Buffle *et al.*, 1985; Bertsch *et al.*, 1986). It has been generally accepted that for the Al_{13} complex, only the tetrahedrally coordinated Al at the center of the structure yields the signal at 63 ppm.

Precipitation of basic Al sulfate

Two hundred milliliters of 0.5 M Na_2SO_4 were added to 800 ml of OH-Al solutions and mixed thoroughly. The precipitate was separated from solution using decantation and centrifugation after appropriate durations. Amorphous basic Al sulfate precipitates were much smaller and fluffier than the crystalline ones. Therefore, they can be separated using repeated decantation. Also, much of the precipitate was stuck on the wall of the glass container. In separation, the contents were first shaken by hand and allowed to stand for a few minutes until the coarse crystals settled. The suspension was decanted into a centrifuge tube and centrifuged to separate the solution from the precipitate. The centrifugate was analyzed for total Al, distribution of different Al species, and pH. Then an appropriate amount of water was added to the sample container. The precipitate stuck on the glass wall was loosened up using an ultrasonic vibrator. The fine amorphous precipitates were separated from crystalline ones by repeated decantation. All precipitates were washed twice with 70% methanol, filtered through a Millipore filter paper, and dried for further analyses.

Chemical composition of basic Al sulfates

Twenty milligrams of precipitate were weighed into a 100 ml volumetric flask. Ten milliliters of 0.1 M HCl were added and heated at approximately 70°C until the precipitate was completely dissolved. The content was diluted to 100 ml and analyzed for Al, Na, and sulfate concentrations. The OH^- content was calculated by subtracting the sulfate content from the sum of Al and Na, all on an equivalent basis.

General analyses

Aluminum was determined spectrophotometrically with ferron (Hsu and Cao, 1991). Sulfate was determined as BaSO_4 nephelometrically using a Hach Model 2100 meter. Solution pH was determined with a Fisher 825 Accumet meter. Morphology of basic Al sulfates was examined using a Nikon Apophot light microscope. Mineralogical composition of basic Al sulfate was determined with a Siemens X-ray diffractometer, using $\text{CrK}\alpha$ radiation.

RESULTS AND DISCUSSION

Kinetics of Al-ferron color development

With a fresh (3 days), laboratory-hydrolyzed OH-Al solution of $R = 2.5$ and 0.02 M in Al, nearly 97% of the Al was recovered in less than 30 min (Figure 1, Curve a). R refers to the NaOH/Al molar ratio in solution preparation. The Al in a 3925-day solution ($R = 2.2$; 0.016 M Al) reacted with ferron at a much slower rate (Figure 1, Curve b), with 22% of the total Al reacted in 30 min. It took more than 48 h for the Al-ferron color to develop fully. The distribution of different Al species can be calculated by plotting $\log(\text{Al}_\infty - \text{Al}_t)$ against time (Figure 2), assuming that the polynuclear complexes react with ferron following pseudo-first-order kinetics and that mononuclear Al ions react with ferron at a rate too rapid to be measured (Tsai and Hsu, 1984; Hsu, 1992). Table 2 shows that the Al in all laboratory-hydrolyzed OH-Al solutions can be grouped into three categories: mononuclear ions and rapid- and slow-reacting OH-Al complexes. It has been suggested that the rapid-reacting complexes were Al_{13} of Keggin structure and the slow-reacting complexes were of relatively stable $\text{Al}(\text{OH})_3$ -fragment structure (Tsai and Hsu, 1984, 1985; Hsu, 1989). All fresh, laboratory-hydrolyzed solutions are dominated by mononuclear ions and rapid-reacting complexes with less than 4% of the Al present as slow-reacting complexes. With each R ratio in preparation, the concentration of rapid-reacting complexes slowly decreased, while that of slow-reacting complexes slowly increased with increased duration of aging. Slow-reacting complexes became the dominant species in all solutions after prolonged aging. Despite the large variations in the R ratio in preparation and the duration of aging, the rate constants varied within a narrow range from 0.018–0.072

h^{-1} for slow-reacting complexes and from 3.83–12.1 h^{-1} for rapid-reacting complexes. The average rate constant for rapid-reacting polynuclear complexes (5.87 h^{-1}) was 150 times that of slow-reacting ones (0.0392 h^{-1}). To ascertain that the slow-reacting complexes are soluble macro-ions, 20 ml of each solution were shaken with 2 g of a Na-saturated cation exchange resin (AG50 X8) for 1 h. It was observed that the Al in solution completely entered the resin. Therefore, the slow-reacting species are likely soluble macro-ions.

The reaction of ACH with ferron was complex. All three ACH solutions from Reheis (RH), Summit (SU), and Courtney (CN) have an overall OH/Al molar ratio of 2.5 (Table 1). They are similar in their reactions with ferron, and the data for Reheis are presented in Figures 1 and 2. With a freshly diluted solution, only 10%–12% of the Al reacted with ferron in 30 min, and it took 120–240 h for the Al in solution to react completely (Figure 1, Curve c). The $\log(\text{Al}_\infty - \text{Al}_t)$ vs. time plot was linear ($r^2 = 0.999$ in most cases) for the data between 30 min and 12 h, but the data points after 24 h deviated from this straight line (Figure 2, Curve c). This suggests that the slow-reacting complexes in this solution consist of more than one species, but attempts to determine the concentrations of the individual components of the slow-reacting OH-Al complexes have not been satisfactory. In this report, therefore, the data between 30 min and 12 h were used to estimate the total slow-reacting complexes. The rate constants thus calculated represent only the more rapid-reacting fraction of the slow-reacting complexes.

Table 3 shows that the freshly diluted (<5 min) ACH (RH) solution consisted of 3.9%, 1.1%, and 94.9% of monomeric ions and rapid- and slow-reacting OH-Al complexes, respectively. The concentration of the rapid-reacting species increased to 12.1% 1 day after dilution, to 15.4% after 7 days, and decreased thereafter. This species completely disappeared after 159 days. The concentrations of monomeric ions and slow-reacting complexes decreased continuously, although only slightly, until 49 days. After that, the concentration of monomeric ions increased with time, whereas that of slow-reacting complexes remained around 16 mmol Al/liter up to the end of this experiment. The rate constants for both the rapid- and the slow-reacting complexes indicated little change with time and were comparable to the corresponding constants for the laboratory-hydrolyzed OH-Al solutions.

Although the original ACH solution remained clear for years, the diluted ones became turbid 10 days after dilution, and gibbsite was detected with XRD after 14 days. The amount of gibbsite increased with time until rapid-reacting complexes completely disappeared (Table 3). In contrast, it usually took at least 6 months for a laboratory-hydrolyzed OH-Al solution 0.02 M in Al and $R = 2.5$ to develop gibbsite. It is evident from these results that ACH is different from laboratory-

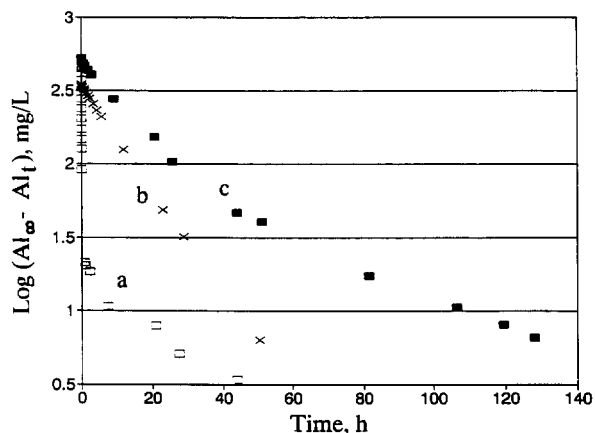


Figure 2. Kinetic analysis of Al-ferron reactions. Same solutions as in Figure 1.

hydrolyzed OH-Al solutions. A working hypothesis is proposed to assume that the major portion of the slow-reacting complexes in ACH solutions were of $\text{Al}(\text{OH})_3$ -fragment structure resembling the slow-reacting complexes in laboratory-hydrolyzed solutions. A small portion of the slow-reacting complexes were aggregates of Al_{13} complexes that dispersed upon dilution. Therefore, the concentration of rapid-reacting complexes increased during the first several days after dilution. Another small portion of the slow-reacting complexes were submicron particulates that acted as nuclei for gibbsite crystallization. During aging, the polynuclear OH-Al complexes dissociated to monomeric ions that then deposited onto nuclei to form gibbsite (Hsu, 1988). The rapid-reacting Al_{13} complexes were easy to dissociate and, therefore, their disappearance was closely related to gibbsite formation. To test the presence of aggregates and their subsequent dispersion to soluble macro-ions, 20 ml portions of diluted ACH (RH) solution were each shaken with 2 g of Na-resin (AG50 \times 8) for 1 h. With a freshly diluted solution, only about 20% of the total Al entered the resin. In contrast, with an aged ACH solution, after gibbsite was removed through filtration, 96% of the Al solution entered the resin. Table 3 also shows that solution pH increased immediately after dilution and began to decrease after 7 days. The increase in pH probably was related to the dissociation of Al_{13} aggregates to individual complexes, whereas the later pH decrease was attributed to gibbsite crystallization. Further investigation to examine this postulate is in progress.

The PA solution from Courtney (CN) has an overall OH/Al molar ratio of 1.5 (Table 1). The slow-reacting complexes slowly increased with time, whereas the rapid-reacting complexes slowly decreased. The variation in the concentration of mononuclear Al ions was within the experimental uncertainty. The solution pH and turbidity remained unchanged up to at least 1 year (Table

Table 2. Distribution of various Al species in laboratory-hydrolyzed OH-Al solutions analyzed using kinetics of Al-ferrous color development.

R ¹	Aging, day	pH	Total Al, mM	Mono ²		Rapid ²		Slow ²				
				mmol/liter	%	mmol/liter	%	mmol/liter	%	k, h ⁻¹	k, h ⁻¹	
1.0	3	4.00	20.00	13.27	66.37	6.32	31.58	0.41	2.05	7.57	0.0180	
1.0	489	4.04	21.03	12.14	57.72	5.64	26.82	2.99	14.20	4.92	0.0347	
1.0	1073	3.96	19.62	10.89	55.49	2.04	10.18	6.14	30.72	3.83	0.0238	
1.5	3	4.07	20.00	7.61	38.03	11.05	55.27	0.47	2.35	9.59	0.0720	
1.5	121	4.11	19.18	6.71	34.99	11.54	60.18	1.26	6.55	4.59	0.0314	
1.5	540	4.12	20.76	7.34	35.36	9.21	44.36	4.10	19.73	5.24	0.0377	
1.5	2716 ³	3.83	15.70	8.69	55.31	0.45	2.86	6.45	41.10	12.10	0.0353	
2.0	6	4.22	20.62	4.18	20.28	16.54	80.23	0.49	2.37	4.03	0.0557	
2.0	272	4.22	21.24	4.48	21.08	14.79	69.65	3.10	14.60	4.59	0.0418	
2.0	1642	4.15	20.63	4.38	21.25	4.40	21.34	11.84	57.40	4.69	0.0405	
2.2	3	4.28	20.00	3.72	18.61	15.59	77.96	0.45	2.25	8.48	0.0300	
2.2	3925 ³	4.17	16.05	2.74	17.06	0.50	3.11	12.86	80.11	4.63	0.0346	
2.5	3	4.69	19.53	0.61	3.12	17.79	91.09	0.86	4.41	4.21	0.0453	
2.5	93	4.44	20.89	0.58	2.78	19.03	92.40	1.33	6.39	4.82	0.0465	
2.5	347 ³	4.38	13.13	1.57	11.99	9.15	69.69	2.79	21.27	4.82	0.0400	
AV												0.0392

¹ R refers to the OH/Al molar ratio in the original solution.

² Mono refers to monomeric ions; rapid and slow refer to rapid- and slow-reacting polynuclear OH-Al complexes, respectively.

³ Gibbsite precipitate was observed and removed through filtration before speciation.

Table 3. Distribution of various Al species in commercial OH-Al solutions analyzed using kinetics of Al-ferron color development.¹

Aging, day	pH	Turbidity, JTU ²	Total Al, mmol/liter		Mono ³		Rapid ³		Slow ³		Gibbsite ⁴ mmol/liter
			mmol/liter	%	mmol/liter	%	mmol/liter	%	mmol/liter	%	
0	4.78	0.20	21.8	0.85	3.9	0.24	1.1	2.94	20.70	94.9	0.0232
1	4.83	0.19	21.0	0.61	2.9	2.53	12.1	4.77	18.30	87.3	0.0397
7	4.82	0.35	21.6	0.25	1.2	3.32	15.4	3.44	18.11	83.9	0.0349
14	4.73	10	21.3	0.30	1.4	3.13	14.7	4.12	18.25	85.6	0.0371
21	4.57	48	19.2	0.29	1.5	2.56	13.4	3.90	16.67	87.0	0.0362
49	4.45	95	17.5	0.19	1.1	1.68	9.6	3.87	15.84	90.7	0.0373
114	4.22	130	16.5	0.42	2.5	0.34	2.1	3.49	15.87	95.9	0.0356
159	4.16	350	17.1	0.64	3.7	0.00	0.0		16.40	96.2	0.0402
206	4.12	280	17.0	0.64	3.8	0.00	0.0		16.32	96.1	0.0415
431	4.05	420	15.9	0.72	4.5	0.00	0.0		15.22	95.4	0.0418
Polyaluminum chloride (Courtney), R = 1.5											
1	4.06	0.20	20.1	7.42	36.9	8.19	40.7	4.45	4.47	22.2	0.0385
109	4.07	0.20	20.6	7.91	38.3	7.70	37.3	4.69	5.03	24.4	0.0333
217	4.09	0.11	21.0	7.80	37.2	7.52	35.9	5.36	5.46	26.1	0.0358
392	4.10	0.11	20.9	8.20	39.4	6.42	30.8	5.01	6.01	28.8	0.0408
WAC-HB (ATO Chemicals, France), R = 2.0											
0	4.33	0.31	19.3	3.08	16.0	1.40	7.3	2.20	14.50	75.3	0.0268
2	4.31	0.30	19.3	2.54	13.1	2.38	12.3	3.76	14.21	73.6	0.0260
48	4.21	0.35	19.4	2.65	13.5	3.73	19.3	3.73	12.99	67.1	0.0261
115	4.25	0.31	19.4	2.62	13.6	3.94	20.3	4.31	12.79	66.0	0.0255
363	4.23	0.40	19.1	2.58	13.5	3.96	20.7	4.48	12.50	65.4	0.0252

¹ All commercial OH-Al solutions were diluted to approximately 0.02 M in Al before analysis.² JTU refers to Jackson turbidity unit.³ Mono refers to monomeric ions; rapid and slow refer to rapid- and slow-reacting polynuclear OH-Al complexes, respectively.⁴ Gibbsite precipitate was removed through filtration before speciation.

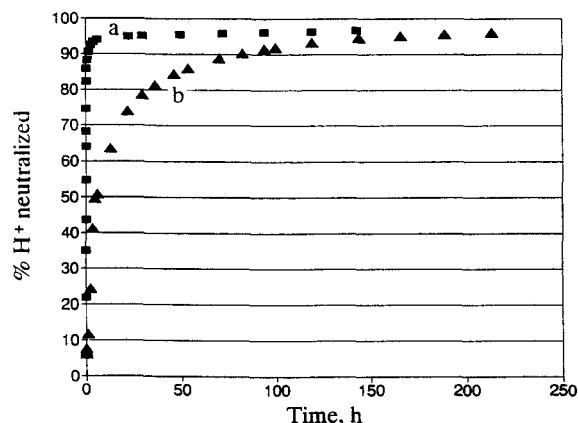


Figure 3. Percentage of solution H^+ neutralized by structural OH as a function of time: a) laboratory-hydrolyzed OH-Al solution, 0.02 M in Al, $R = 2.5$, 90 days; and b) ACH (RH) diluted to 0.02 M in Al immediately before analysis.

3). Gibbsite precipitate, however, developed from this solution approximately two years after it was received. This solution seems to resemble moderately aged, laboratory-hydrolyzed OH-Al solutions in Al species distribution.

With a freshly diluted WAC-HB solution, the concentrations of the monomeric ions and rapid- and slow-reacting complexes accounted for 16.0%, 7.3%, and 75.3%, respectively, of the total Al in solution. The rapid-reacting polynuclear complexes increased, whereas the slow-reacting complexes decreased shortly after dilution, but showed little change from 48 days to at least 1 year (Table 3). Solution pH and turbidity also showed little change during aging up to 1 year. The initial increase in rapid-reacting complexes suggests that a small number of Al_{13} complexes was present as aggregates. The unusual stability of this solution probably was attributed to the small amount of SO_4 present.

The rate constants for rapid- and slow-reacting polynuclear OH-Al complexes in commercial solutions (Table 3) are comparable to the corresponding constants for laboratory-hydrolyzed OH-Al solutions (Table 2).

Kinetics of structural OH neutralization with HCl

Each OH in the polynuclear complex is bridged between two Al^{3+} ions. The reaction rate between the H^+ added to solution and the OH^- in structure should reflect the stability of the OH-Al complex. For every OH^- reacted, one H^+ ion in solution must be consumed. Therefore, the neutralization process is likely to follow second-order reaction kinetics. By adjusting the amount of H^+ added to equal the amount of OH^- present in the polynuclear complexes, the concentrations of OH^- and H^+ in the system should always be equal during the reaction. Under this condition, a lin-

ear plot of $1/[H^+]$ vs. time should be expected. The rate constants and the concentration of the OH^- in structure can be calculated from the slopes and the intercept, respectively.

Figure 3 (Curve a) shows that with a 90-day, laboratory-hydrolyzed OH-Al solution of $R = 2.5$, 89% of the H^+ was consumed in 60 min, and the subsequent reaction progressed slowly. By plotting $1/[H^+]$ against time, two nearly straight lines were observed (Figure 4, Curve a). The reaction can be interpreted as indicating that two types of structural OH groups were present and reacted with solution H^+ at different rates. The rate constants corresponding to the rapid- and slow-reacting structural OH were 323.0 and 1.89 liter $mole^{-1} h^{-1}$, respectively (Table 4). The concentrations of the rapid- and slow-reacting structural OH account for 87% and 6%, respectively, of the total structural OH. In addition, this solution also contains 0.92% of edge OH, which was assumed to react with solution H^+ instantaneously. Table 4 shows that all laboratory-hydrolyzed OH-Al solutions consisted of two types of structural OH groups of very different reaction rates with H^+ . All fresh, laboratory-hydrolyzed Al solutions were dominated by rapid-reacting OH groups. With each R ratio in preparation, the concentrations of rapid-reacting OH decreased, whereas those of slow-reacting OH increased with increased solution aging. Slow-reacting OH dominated all aged solutions. The rate constants for the slow-reacting OH among different solutions were close to one another. The gradual increase in the resistance to reaction with H^+ provides additional evidence that the polynuclear OH-Al complexes in solution gradually converted to more stable structure during aging. The edge-OH constitutes only a small fraction of the total OH present in all solutions.

With a freshly diluted (< 5 min) ACH (RH) solution, the rate of structural OH neutralization was much slower (Figure 3, Curve b). It took 82 h for 90% of the H^+ to be consumed, with only 11% of the H^+ consumed in 60 min. When $1/[H^+]$ was plotted against time, a nearly straight line was observed (Figure 4, Curve b). This line, however, can be split into two straight lines by expanding the initial portion of the line. This solution consisted of 5% rapid-reacting OH and 89% slow-reacting OH. The rate constants were 533 and 2.46 liter $mole^{-1} h^{-1}$, respectively. In addition, this solution contains 3.8% of edge OH. It is evident from the comparison that commercial ACH solutions are very different from the fresh, laboratory-hydrolyzed OH-Al solutions, but close to the aged, laboratory-hydrolyzed OH-Al solutions in their structural OH distribution. PA solution contains many more rapid-reacting and many fewer slow-reacting OH groups than the ACH solutions.

The distribution of rapid- and slow-reacting structural OH was in general parallel to that of rapid- and slow-reacting OH-Al complexes, but the comparison

Table 4. Distribution of edge and rapid- and slow-reacting structural OH in polynuclear OH-Al complexes.

R	Aging, day	OH ⁻¹ , mmol/liter	Edge			Rapid ¹			Slow ¹		
			mmol/liter	%	mmol/liter	%	L/mol/h	mmol/liter	%	L/mol/h	Rec. %
Laboratory-hydrolyzed OH-Al solutions											
1.0	1	20.0	1.06	5.4	15.80	80.6	181.4	0.80	4.1	0.84	90.1
1.0	385	20.0	0.97	4.8	13.01	62.0	283.0	4.41	23.2	2.22	89.9
1.0	646	20.0	n.d.	n.d.	9.65	48.3	420.0	9.51	47.5	2.18	95.8
1.0	1080	20.0	n.d.	n.d.	7.80	39.0	107.1	11.02	55.1	2.02	94.1
1.5	23	30.0	0.93	3.1	24.35	81.2	234.5	2.44	8.1	0.34	92.4
1.5	555	30.0	0.94	3.1	19.78	65.9	332.5	7.18	23.9	2.15	93.0
1.5	2730 ²	16.7	0.25	1.5	1.69	10.1	250.9	14.79	88.6	1.70	100.2
2.0	20	40.0	0.78	2.0	34.74	86.9	313.7	3.17	7.9	0.98	96.7
2.0	1642	40.0	0.70	1.8	10.10	25.3	340.1	24.78	62.0	2.89	89.0
2.5	90	50.0	0.46	0.9	43.55	87.1	323.0	2.98	6.0	1.89	94.0
Aluminum chlorohydrate (Reheis) ³											
2.5	0	50.0	2.09	3.8	2.52	5.1	533.0	44.52	89.1	2.46	98.0
Polyaluminum chloride (Courtney) ³											
1.5	0	30.7	1.32	4.4	15.30	53.6	286.8	10.10	35.4	1.33	93.4

¹ OH-t, rapid, and slow refer to total, rapid- and slow-reacting structural OH, respectively.² Gibbsite precipitate was removed through filtration before analysis.³ Both solutions were diluted to approximately 0.02 M in Al before analysis.

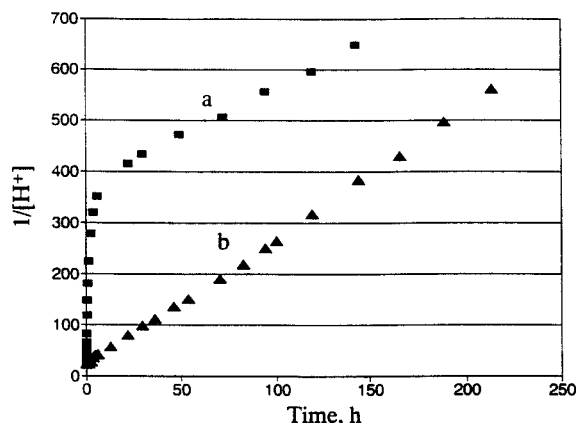


Figure 4. Kinetic analysis of H-neutralization. Same solutions as in Figure 3.

was only qualitative. The determination of structural OH was only semiquantitative, and the recovery was frequently poor (Table 4). The inclusion or exclusion of a few data points frequently resulted in a large difference in the concentrations of the rapid- and slow-reacting structural OHs calculated. Also, in some solutions, the curve leveled off when the solution was near complete neutralization. In such cases, it is difficult to conclude whether the later level-out portion is due to another species or experimental uncertainty. Nevertheless, such semiquantitative calculation indicates the existence of at least two very different structural OH groups.

NMR spectra

Hydroxyaluminum solutions commonly show two signals in ^{27}Al NMR spectra. One is attributed to monomeric Al^{3+} and the other to Al_{13} , which is 63 ppm downfield from Al^{3+} . The signal for Al_{13} , however, has been shown to convert slowly to a nondetectable species with increased solution aging (Akitt and Farthing,

Table 5. Effect of aging on the distribution of various Al species in OH-Al solutions determined with NMR spectroscopy.

R ¹	Aging, day	Total Al		Al recovered			% Nondetected
		Mono	Al ₁₃	Mono	Al ₁₃	Sum	
Laboratory-hydrolyzed OH-Al solutions							
2.5	3	19.53	0.71	19.10	19.81	—	1.43
2.2	13	20.90	2.38	15.30	17.68	15.41	
2.2	2953	16.05	3.17	0.00	3.17	80.25	
Aluminum chlorohydrate (Reheis)							
2.5	0	21.80	0.58	2.38	2.96	86.42	
2.5	14	21.30	0.17	3.10	3.27	84.65	
2.5	114	16.50	0.50	0.96	1.46	91.15	
2.5	206	17.10	0.68	0.00	0.68	96.02	

¹ R refers to OH/Al molar ratio in solutions.

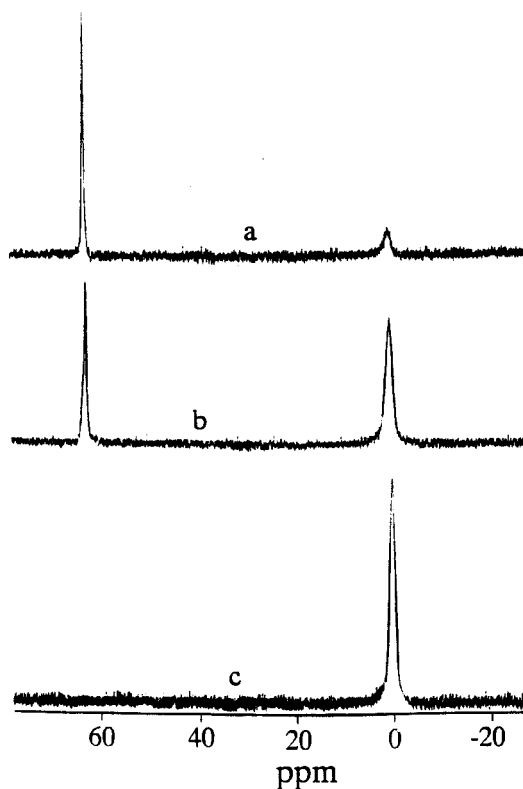


Figure 5. ^{27}Al NMR spectra of laboratory-hydrolyzed OH-Al solutions: a) R = 2.5, 0.02 M Al, 3 days; b) R = 2.2, 0.02 M Al, 3 days; and c) R = 2.2, 0.016 M Al, 3925 days. Gibbsite was removed through filtration 2 years after preparation. This solution remained clear thereafter.

1981; Denney and Hsu, 1986). To further ascertain this conclusion, the ^{27}Al NMR spectra for three laboratory-hydrolyzed OH-Al solutions are presented in Figure 5. The two upper spectra were obtained from fresh, laboratory-hydrolyzed OH-Al solutions, both 0.02 M in Al, having R = 2.5 (a) or 2.2 (b). Each shows two signals, with their chemical shifts 63 ppm apart. The concentrations of monomeric Al (0 ppm) and Al_{13} complexes (63 ppm) calculated from the NMR signal intensities for these two solutions (Table 5) were close to those determined from the kinetics of Al-ferron color reactions (Table 2). Spectrum c, which was obtained from a 3925-day solution of R = 2.2, yielded only the signal for monomeric Al ions at 0 ppm. The concentration of monomeric Al calculated from this signal was 3.17 mmol Al/liter (Table 5), which is comparable to the monomeric Al concentration (2.74 mmol Al/liter) determined from Al-ferron reactions (Table 2). It is evident that the slow-reacting OH-Al complexes that account for 80% of the total Al in this solution were not detectable in the NMR spectrum and were not of Al_{13} structure.

The spectra for four diluted ACH (RH) solutions after different durations of aging (Figure 6) indicate

that the signal at 0 ppm (monomeric Al ions) decreased initially and then increased with time of aging. In contrast, the signal at 63 ppm (Al_{13}) increased initially, then decreased with aging, and eventually disappeared. The change in the distribution of various Al species from this NMR study (Table 5) was comparable to the data determined from the kinetics of Al-ferron color development (Table 3). The sum of the concentrations of mononuclear Al ions and Al_{13} complexes calculated from the NMR signal intensities accounts for only a minor fraction of the total Al present (Table 5). It is evident that the slow-reacting complexes determined using ferron were not detected in the NMR spectra. Because some signals are very broad, the concentrations calculated from NMR spectra are semiquantitative. The existence of NMR-nondetectable species is unmistakable, however.

Some earlier studies of ACH solutions (Pinnavaia *et al.*, 1984; Teagarden *et al.*, 1981) emphasized the existence of Al_{13} complexes and overlooked the existence of this nondetectable form. Probably because of the weak signals, more concentrated ACH solutions were used in their NMR studies (0.23 M Al by Pinnavaia *et al.*, 1984; 1.0 M Al, by Teagarden *et al.*, 1981).

Precipitation of basic Al sulfates

The origin of the Al_{13} structure was based on the structure of basic Al salts obtained by adding sulfate to partially neutralized Al solutions of $R = 2.5$ (Johansson, 1960, 1963). The nature of basic Al sulfates varied, however, with the R ratio in preparation and the duration of solution aging (Bersillon *et al.*, 1980; Tsai and Hsu, 1984, 1985). Crystalline basic Al sulfates of tetrahedral (Figure 7a), elongated prismatic (Figure 7b), and irregular (Figure 7c) habits were observed in both earlier (Bersillon *et al.*, 1980; Tsai and Hsu, 1984, 1985) and present studies of laboratory-hydrolyzed OH-Al solutions following sulfate addition. The X-ray diffraction patterns for these three crystalline basic Al sulfates are different from one another (Figure 8, Curves a–c). In addition, X-ray-amorphous basic Al sulfates were also observed from a variety of OH-Al solutions. Table 6 summarizes the effects of the R ratio in preparation and the duration of solution aging on the nature of the basic Al sulfates obtained from laboratory-hydrolyzed Al solutions. With a 3-day, laboratory-hydrolyzed solution of $R = 1$, only 5% of the basic Al sulfates were of tetrahedral crystals, and 95% of the precipitate was fine particles amorphous to X-ray diffraction. The amount of the precipitate and the crystalline fraction of the precipitate increased with increased R ratio. At $R = 2.5$, the precipitates were almost exclusively crystals of tetrahedral or prismatic habit. The precipitation began usually after a brief induction period (1–8 h). With aged solutions, however, only irregular crystals were observed, regardless of the R ratio in preparation. Long induction periods (4–7 days)

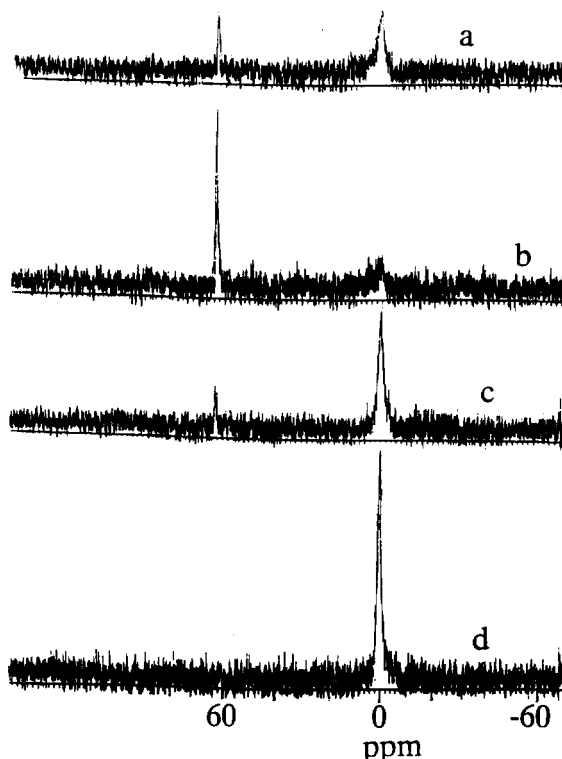


Figure 6. ^{27}Al NMR spectra of diluted ACH (RH) after different durations of aging: a) fresh; b) 14 days; c) 114 days; and d) 206 days. Gibbsite was removed from all aged solutions through filtration before analysis.

prior to the start of precipitation were always observed. The chemical compositions of tetrahedral, prismatic, and irregular crystals were $\text{Na}_{0.07}\text{Al}(\text{OH})_{2.43}(\text{SO}_4)_{0.31}$, $\text{Al}(\text{OH})_{2.52}(\text{SO}_4)_{0.24}$, and $\text{Al}(\text{OH})_{2.43}(\text{SO}_4)_{0.29}$, respectively. Although these three types of crystals are not much different in basicity, they are different in two aspects:

- 1) Na was found in all tetrahedral crystals. The analysis of 11 specimens yielded a Na/Al molar ratio = 0.07 ± 0.01 . The presence of Na in the tetrahedral crystals was also reported earlier (Johansson, 1963; Bersillon *et al.*, 1980; Tsai and Hsu, 1984, 1985), but the position of Na in the structure was not located in Johansson's structural analysis.
- 2) These crystals showed distinctly different resistance to acid. Tetrahedral crystals dissolved in 0.1 M HCl in <20 min at 70°C. Prismatic crystals dissolved in 0.1 M HCl almost instantaneously. In contrast, it took at least 6 h for the irregular crystals to dissolve completely. The irregular crystals (Figure 7c) were generally smaller than the tetrahedral ones (Figure 7a). Therefore, surface area was not the factor contributing to the difference in dissolution rates. The change in the nature of basic Al sulfates provides additional evidence that the nature of the OH-Al species in solutions changed with time.

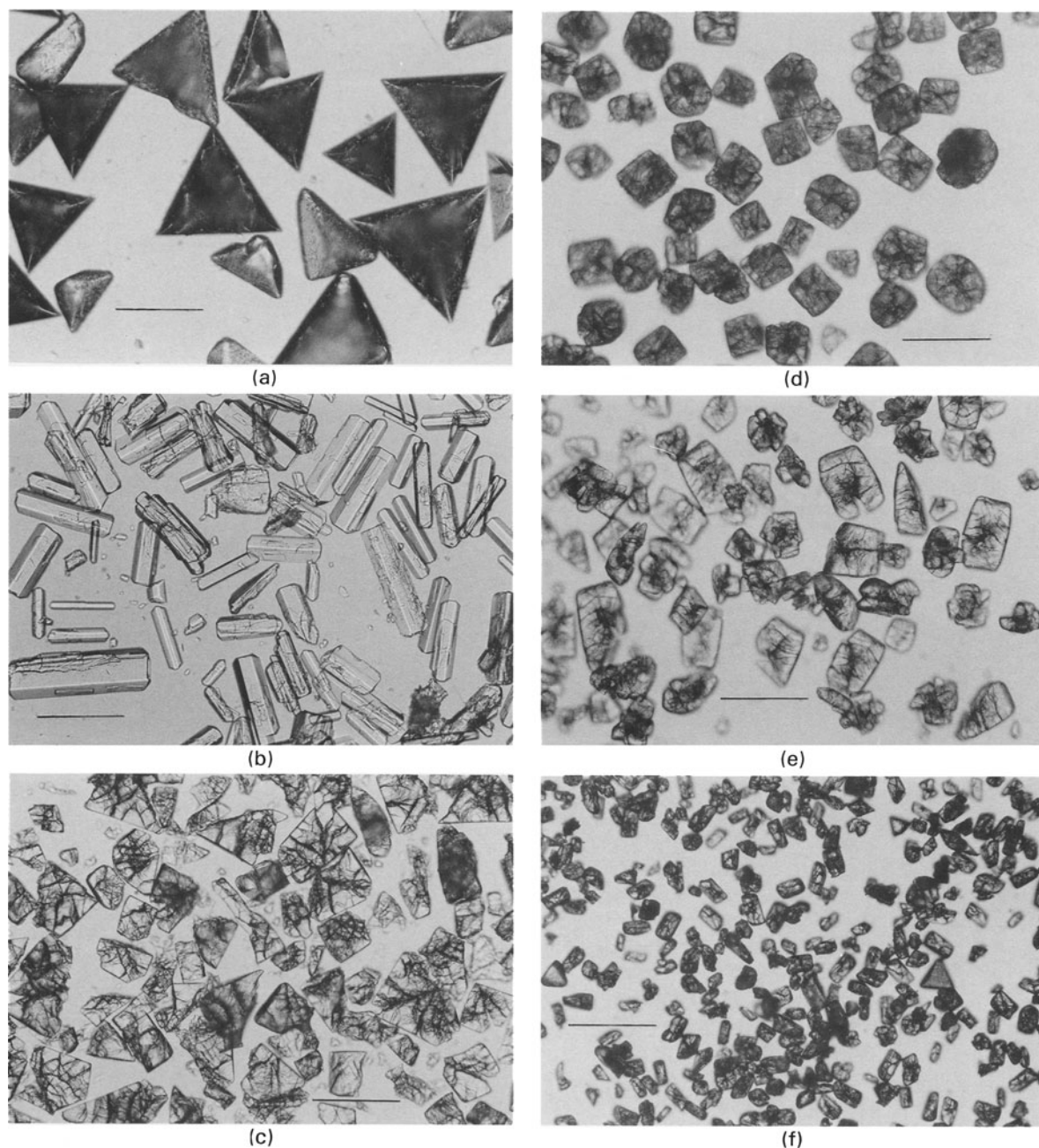


Figure 7. Morphology of crystalline basic Al sulfates prepared from laboratory-hydrolyzed (a–c) and commercial (d–f) OH-Al solutions: a) tetrahedral (0.02 M Al, $R = 2.2$, 3 days); b) elongated prismatic (0.02 M Al, $R = 2.5$, 3 days); c) irregular (0.012 M Al, $R = 1.8$, 2730 days; gibbsite was removed using filtration before the addition of Na_2SO_4); d) irregular from aged (93 days) aluminum chlorohydrate (Reheis); e) irregular from aged (240 days) aluminum chlorohydrate (Summit); and f) irregular from aged (267 days) polyaluminum chloride (Courtney). The length of bar in the figure corresponds to 0.2 mm.

The precipitation of basic Al sulfates from commercial ACH solution was complex. Precipitation of basic Al sulfate occurred almost immediately after the addition of Na_2SO_4 to freshly diluted ACH (approximately 0.02 M in Al) solutions, with 70% of the Al precipitated in 1 h. The precipitates appeared as loose,

hydrated, and voluminous mass and were amorphous to X-ray diffraction (Figure 8, Curve g). The kinetics of Al-feron color development showed that the rapid-reacting OH-Al complexes were completely precipitated in 1 h. A considerable portion of the slow-reacting complexes was also precipitated. The remaining so-

Table 6. Distribution of various basic Al sulfates obtained by adding Na sulfate to OH-Al solutions.

R	Aging, day	Induct ¹	Pptn ²	mg Al/liter		Precipitate ³			Distribution of crystals ⁴			
				Init	Final	Tot mg	Cryst %	Amp %	Tet	Prism	Irreg	
Laboratory-hydrolyzed OH-Al solutions												
1.0	3	8 h	14 d	540	323	464	5.2	94.8	+++	—	—	
1.5	3	4 h	14 d	540	227	780	67.9	32.1	+++	—	—	
1.8	3	4 h	14 d	540	167	1151	79.9	20.1	+++	—	—	
2.2	3	2 h	14 d	540	97	1377	90.8	9.2	+++	—	—	
2.4	3	2 h	14 d	540	85	1271	95.3	5.0	++	+	—	
2.5	3	1 h	14 d	540	65	1550	98.7	1.3	+	++	—	
1.0	3417	6 d	32 d	490	276	420	100	0	—	—	+++	
1.8	2730	7 d	27 d	336	179	410	100	0	—	—	+++	
2.0	1642	4 d	14 d	557	142	1300	100	0	—	—	+++	
Aluminum chlorohydrate (RH)												
2.5	0	0 d	1 h	448	126	1210	0	100	—	—	—	
2.5	93 ⁵	0 d	1 h	448	397	not collected ⁶			—	—	—	
2.5	93	7 d	43 d	397	221	960	100	0	—	—	+++	
Polyaluminum chloride (CN)												
1.5	0	n.d.	5 d	449	n.d.	n.d.	0	100				
1.5	267 ⁵	n.d.	5 d	449	325	n.d.	0	100				
1.5	267	n.d.	104 d	325	230	380	100	0	—	—	+++	

¹ Induct refers to induction period, the time elapsed before precipitation started.

² Pptn refers to the duration during which basic Al sulfates were allowed to accumulate.

³ Tot, crys, and amp refer to total, crystalline, and amorphous precipitates, respectively.

⁴ Tet, Prism, and irreg refer to tetrahedral, prismatic, and irregular crystals, respectively.

⁵ The precipitate was first separated from solution 1 h (RH) or 5 days (CN) after addition of sulfate. The remaining solutions were allowed to further age for 43 (ACH) or 104 (PA) days.

⁶ The amount of precipitate was small, stuck to the filter paper, and could not be quantitatively collected.

lution consisted mainly of slow-reacting complexes and monomeric ions. Probably because of the low concentration of OH-Al complexes remaining in solution, the subsequent precipitation of basic Al sulfate from the remaining solution was very slow. Only a trace amount of precipitate, which was identified as irregular crystals (data not shown), was collected after 160 days.

With the addition of Na₂SO₄ to a 93-day, diluted ACH (RH) solution, only about 10% of the total Al was precipitated, mainly gibbsite, in 1 h. Crystalline basic Al sulfate started to develop in the remaining solution after a subsequent 7-day induction period. The precipitate was exclusively crystals of irregular habit (Figure 7d). Same crystals were obtained by adding Na₂SO₄ to a 240-day aged ACH from Summit Research Lab (Figure 7e). They showed the same XRD patterns (Figure 8), chemical composition, and resistance to HCl dissolution as the irregularly shaped crystals obtained from aged laboratory-hydrolyzed OH-Al solutions. These results and the results for laboratory-hydrolyzed solutions suggest that the major portion of the polynuclear OH-Al complexes in diluted ACH solution resemble the slow-reacting OH-Al complexes of Al(OH)₃-fragment structure in aged, laboratory-hydrolyzed OH-Al solutions.

Adding sulfate to a freshly diluted PA solution, the turbidity increased slowly with time without a clear-cut induction period. A considerable portion of the suspended particles passed through a Millipore filter

paper of 0.025 μm pore size. The particles retained by the filter paper were X-ray amorphous without any tetrahedral crystals, although the solution contained 40% of the total Al as rapid-reacting complexes and showed a relatively strong signal at 63 ppm in its ²⁷Al NMR spectra (data not shown). These results and the results for laboratory-hydrolyzed OH-Al solutions suggest that not all the tetrahedrally coordinated Al are of the Al₁₃ Keggin structure. When sulfate was added to a 267-day PA solution, the precipitate was amorphous during the first 5 days, a mixture of amorphous particles and irregular crystals after 15 days (data not shown), and exclusively irregular crystals thereafter.

CONCLUSIONS

The authors reached the following conclusions:

- 1) Al₁₃, which contains a tetrahedrally coordinated Al at the center of the structure, is the dominant species only in fresh, laboratory-hydrolyzed OH-Al solutions of OH/Al molar ratio = 1.8 or above. This species slowly converts to a more stable one that is assumed to have a Al(OH)₃-fragment structure.
- 2) A comparison of the results from kinetics of Al-ferron reaction, NMR spectra and sulfate precipitation suggests that not all the rapid-reacting complexes are of Al₁₃ structure.
- 3) Al₁₃ constitutes only a small fraction of the polynuclear OH-Al complexes in commercial aluminum chlorohydrate solutions.

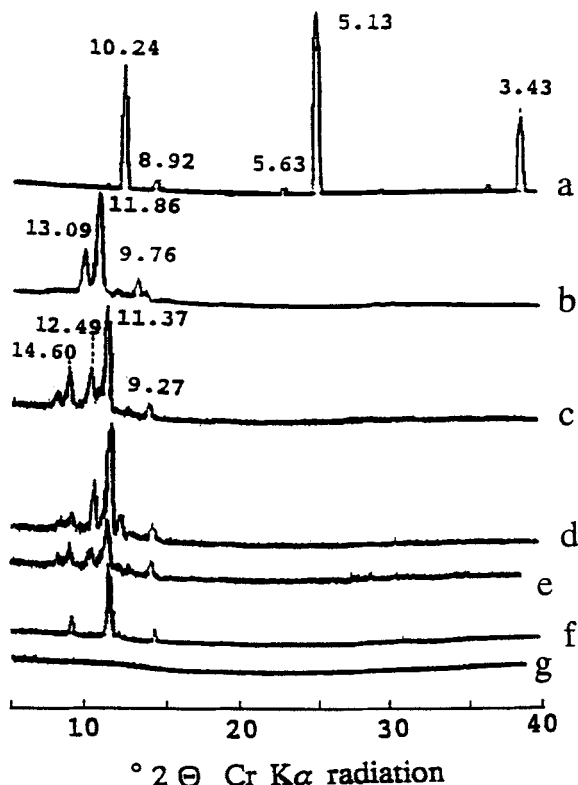


Figure 8. X-ray diffraction patterns of basic aluminum sulfates: a) tetrahedral (laboratory-hydrolyzed, $R = 2.2$, 3 days); b) elongated prismatic (laboratory-hydrolyzed, $R = 2.5$, 3 days); c) irregular (laboratory hydrolyzed, $R = 1.8$, 2730 days); d) irregular from aged (93 days) aluminum chlorohydrate (Reheis); e) irregular from aged (240 days) aluminum chlorohydrate (Summit); f) irregular from aged (267 days) polyaluminum chloride (Courtney); and g) amorphous from freshly diluted aluminum chlorohydrate (Reheis).

- 4) The slow-reacting OH-Al complexes in aluminum chlorohydrate solutions consisted of at least three species. The major portion was of slow-reacting $Al(OH)_3$ -fragment structure. A small portion of the slow-reacting complexes consisted of submicron particulates that act as nuclei for gibbsite formation. Another small portion of complexes were aggregates of Al_{13} that dispersed upon dilution.
- 5) The slow-reacting OH-Al complexes in aged laboratory-hydrolyzed and aged commercial OH-Al solutions are similar to one another. They do not contain tetrahedrally coordinated Al and are not Al_{13} .
- 6) Polyaluminum chloride resembles moderately aged, laboratory-hydrolyzed OH-Al solutions.

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REFERENCES

- Akitt, J. W. and Farthing, A. (1981) Aluminum-27 nuclear magnetic resonance studies of the hydrolysis of aluminum(III). Part 4. Hydrolysis using sodium carbonate: *J. Chem. Soc. Dalton Trans.* 1981, 1617-1623.
- Bersillon, J., Hsu, Pa Ho, and Fiessinger, F. (1980) Characterization of hydroxy-aluminum solutions: *Soil Sci. Soc. Amer. J.* **44**, 630-634.
- Bertsch, P. M. (1987) Conditions for Al_{13} polymer formation in partially neutralized Al solutions: *Soil Sci. Soc. Amer. J.* **51**, 825-828.
- Bertsch, P. M. (1989) Aqueous polynuclear aluminum species: in *The Environmental Chemistry of Aluminum*, G. Sposito, ed., CRC Press Inc., Boca Raton, Florida.
- Bertsch, P. M., Thomas, G. H., and Barnhisel, R. I. (1986) Characterization of hydroxy-aluminum solutions by aluminum-27 nuclear magnetic resonance spectroscopy: *Soil Sci. Soc. Amer. J.* **50**, 825-830.
- Buffle, J., Parthasarathy, N., and Haerdi, W. (1985) Importance of speciation methods in analytical control of water treatment processes with application to fluoride removal from waste waters: *Water Res.* **19**, 7-23.
- Denney, D. and Hsu, Pa Ho (1986) ^{27}Al nuclear magnetic resonance and ferron kinetic studies of partially neutralized $AlCl_3$ solutions: *Clays & Clay Minerals* **34**, 604-607.
- Hesterberg, D. and Reed, M. (1991) Volumetric treatment efficiencies of some commercial clay stabilizers: *SPE Prod. Eng.* **6**, 57-62.
- Hsu, Pa Ho (1988) Mechanism of gibbsite crystallization from partially neutralized aluminum chloride solutions: *Clays & Clay Minerals* **36**, 25-30.
- Hsu, Pa Ho (1989) Aluminum Hydroxides and Oxyhydroxides: in *Minerals in Soil Environments*: 2nd ed., J. B. Dixon and S. W. Weed, eds., Soil Science Society of America, Madison, Wisconsin, 331-378.
- Hsu, Pa Ho (1992) Reaction of OH-Al polymers with smectites and vermiculites: *Clays & Clay Minerals* **40**, 300-305.
- Hsu, Pa Ho and Cao, Dan-Xia (1991) Effects of acidity and hydroxylamine hydrochloride on the determination of aluminum with ferron: *Soil Sci.* **152**, 210-219.
- Johansson, G. (1960) On the crystal structures of some basic aluminum salts: *Acta Chem. Scand.* **14**, 771-773.
- Johansson, G. (1963) On the crystal structures of basic aluminum sulfate, $13Al_2O_3 \cdot 6SO_3 \cdot H_2O$: *Ark. Kemi.* **20**, 321-342.
- Pinnavaia, T. J. (1983) Intercalated clay catalysts: *Science* **220**, 365-371.
- Pinnavaia, T. J., Tzou, Ming-Shin, Landau, S. D., and Raythatha, R. H. (1984) On the pillaring and delamination of smectite clay catalysts by polyoxo cations of aluminum: *J. Mol. Catal.* **27**, 195-212.
- Reed, M. (1972) Stabilization of formation clays with hydroxy-aluminum solutions: *J. Pet. Tech.* **24**, 860-864.
- Teagarden, D. L., Kozlowski, J. F., White, J. L., and Hem, S. L. (1981) Aluminum chlorohydrate I. Structure studies: *J. Pharma. Sci.* **70**, 758-761.
- Tsai, Ping Ping and Hsu, Pa Ho (1984) Studies of aged OH-Al solutions using kinetics of Al-ferron reactions and sulfate precipitation: *Soil Sci. Soc. Amer. J.* **48**, 59-65.
- Tsai, Ping Ping and Hsu, Pa Ho. (1985) Aging of partially neutralized aluminum solutions of NaOH/Al molar ratio = 2.2: *Soil Sci. Soc. Amer. J.* **49**, 1060-1065.

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