MECHANISMS OF GIBBSITE CRYSTALLIZATION FROM PARTIALLY NEUTRALIZED ALUMINUM CHLORIDE SOLUTIONS[1]

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Abstract—To interpret the erratic conditions, rates, and extent of gibbsite crystallization from partially neutralized $AlCl_3$ solution, the following hypothesis is proposed: The initial OH-Al polymers in the freshly prepared solutions were probably unstable and transformed into either gibbsite or stable OH-Al polymers via two different reaction paths. In the presence of nuclei, the OH-Al polymers dissociated into monomeric ions, which then deposited onto nuclei to form gibbsite. In the absence of nuclei, the unstable polymers slowly converted to stable polymers. The erratic stability of OH-Al solutions and gibbsite crystallization are therefore attributed to the relative magnitudes of these two reaction paths which, in turn, are attributed to two key factors: (1) the distribution of unstable vs. stable OH-Al polymers; and (2) the presence or absence of nuclei. The duration of aging of the parent solution governed the distribution of unstable vs. stable polymers. The rate of neutralization resulted in varying localized high alkalinity in OH-Al solution preparation and thus varying development of nuclei.

Key Words—Aluminum hydroxide, Crystallization, Gibbsite, OH-Al polymer, Nucleation.

INTRODUCTION

By adding a dilute base to an Al salt solution, clear solutions may be obtained at OH/Al molar ratios as high as 2.5, or even 2.7 if the neutralization is carried out slowly (Hsu, 1977). The presence of OH-Al polymers in such partially neutralized Al solutions has long been recognized. Many of these solutions, however, become turbid, and aluminum hydroxide develops after prolonged aging (Hsu, 1966, 1977; Turner and Ross, 1970; Smith, 1971; Smith and Hem, 1972; Turner, 1976a; Tsai and Hsu, 1985). Nevertheless, the reported conditions, rates, and extent of gibbsite crystallization from partly neutralized Al solutions are highly variable. For example, some solutions of NaOH/Al molar ratio = 1 prepared by this investigator remained clear to the naked eye, having a turbidity reading of <1 FTU (Formazin turbidity unit) for more than 10 yr (Tsai and Hsu, 1984). Occasionally, however, some solutions became turbid and developed gibbsite after a few months of aging. For solutions of NaOH/Al molar ratio = 2.2, gibbsite developed from all preparations, but the amount of gibbsite developed varied from 2.7% in 34 mo in one sample to 47% in 18 mo in another (Tsai and Hsu, 1985). The OH-Al polymers initially formed in freshly prepared solutions were probably unstable and converted to either stable OH-Al polymers or gibbsite via two different reaction paths. The erratic crystallization of gibbsite was likely governed by the relative magnitude of these two reaction paths. The objective of the present study was to test this interpretation.

MATERIALS AND METHODS

Preparation of OH-Al solutions

Partially neutralized aluminum chloride solutions having OH-Al molar ratios of 0 to 2.5 were prepared by dropwise addition of appropriate amounts of 0.1 M NaOH to 400 ml of a freshly prepared 0.1 M $AlCl_3$ solution and then diluted to 2000 ml. In most preparations, NaOH was added at a rate of 1 ml/min. To study the effect of neutralization rates, NaOH was added at different rates as described below. To study the effect of seed addition, 5 ml of a seeding solution was added to 500 ml of partially neutralized OH-Al solutions. According to Tsai and Hsu (1984, 1985), polymeric OH-Al complexes in a partly neutralized solution slowly change with time. To compare the different OH-Al polymers in their rates of gibbsite crystallization, the parent solutions, aged for various durations, were used in this study. Gibbsite crystallites prepared in previous studies were used to seed solutions of either OH/Al = 1 or 2.2.

Analysis of samples

Solutions were periodically analyzed for changes in pH, turbidity, and the concentration and nature of Al ions in solution. The Al ions in solution were speciated using the kinetics of Al-Ferron color development (Tsai and Hsu, 1984). The solution $p(Al^{3+})(OH^-)^3$ activity product was calculated from the solution pH and the concentration of monomeric Al ions using $pK_1 = 5.01$ for Al^{3+} hydrolysis (Frink and Peech, 1963) and the Davis equation for the activity coefficient. Samples that became turbid during aging were centrifuged through Millipore filter papers of appropriate pore size, using

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a Millipore centrifugation apparatus to separate any suspended particles from solution. The filtration usually started with filter paper of 0.22-μm pore size. If the filtrate was not clear, it was refiltered with a smaller pore size until the filtrate had a turbidity of <1 FTU. The filtrates were analyzed for the concentration and nature of Al ions present. The amount of aluminum in precipitate was estimated from the reduction of Al concentration in solution. The precipitate was analyzed with Siemens X-ray powder diffraction (XRD) equipment for its mineralogical composition and with a JEM 100 CX transmission electron microscope for particle size and morphology. The specimen for XRD was prepared by centrifuging a suitable aliquot through a Millipore filter paper. The filter paper containing the precipitate was pasted onto a glass slide and X-rayed. The specimen for electron microscopy was prepared by placing one drop of suspension onto a copper grid and drying it.

Reaction of OH-Al solutions with acid

Two milliliters of 1.0 M HCl were added to 100 ml of OH-Al solution (0.02 M Al, OH/Al = 1), and the change in pH with time was recorded continuously during the first 3 hr and then periodically afterwards until equilibrium was attained. Three solutions that had been aged for 1 day, 1 year, and 3 years were studied to compare the reaction rates of the different OH-Al polymers with acid. A series of standard $AlCl_3$-HCl solutions was prepared by adding various amounts of 1.0 M HCl and H_2O to 100 ml of 0.02 M $AlCl_3$. The sum of HCl and H_2O was also 2 ml, so that the final Al concentration of all samples and standards was 0.0196 M. A calibration curve was constructed from these standard $AlCl_3$-HCl solutions to calculate the amounts of H^+ consumed during reaction.

General chemical analysis

Solution pH was determined with a Fisher 825 Accumet pH meter. Turbidity was measured with a Hach Model 2100 turbidity meter. Total Al in solution was determined with Ferron after acid decomposition of the polymeric species similar to the Aluminon procedure (Hsu, 1963). The detailed procedures were described in an earlier report (Tsai and Hsu, 1984).

RESULTS AND DISCUSSION

Solution $(Al^{3+})(OH^-)^3$ activity product

The $p(Al^{3+})(OH^-)^3$ activity products for a series of freshly prepared OH-Al solutions are calculated from their concentrations of monomeric Al species and pH (Figure 1). The results show that all solutions were supersaturated with respect to gibbsite, the negative logarithm of the solubility product of gibbsite being 34.03 (Kittrick, 1966) or 33.96 (Singh, 1974).
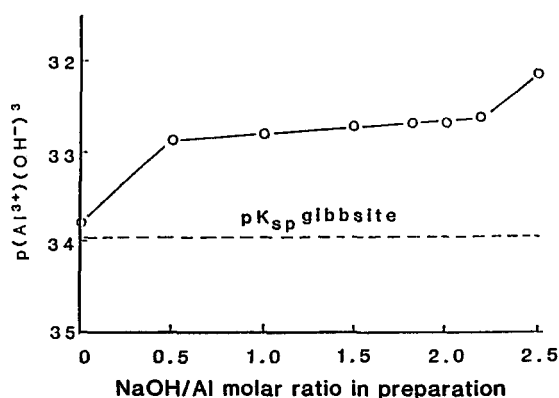

Figure 1.   Solution $p(Al^{3+})(OH^-)^3$ activity product for partially neutralized 0.02 M $AlCl_3$ solutions.

Effect of seed addition

A precipitate was formed in all OH/Al = 1 solutions after they had been seeded with aluminum hydroxide crystallites. The precipitate was identified as gibbsite by XRD. The initial precipitate showed a broad peak corresponding to the basal spacing of 4.84 Å, but the crystallinity rapidly improved with time. A complete series of XRD peaks characteristic of gibbsite was observed in all samples shortly after the solutions became turbid. The rates and extent of gibbsite crystallization, however, greatly decreased with increased duration of aging of the parent OH-Al solutions (Table 1). Gibbsite precipitation was accompanied by decreases in pH and in unstable polymers and an increase in the concentration of monomeric Al species. The amount of stable polymer increased slightly at the early stage of aging. Once gibbsite crystallization was noticeable, the amount of stable OH-Al polymers practically remained unchanged. The 12-yr-old parent solution contained only a very small amount of unstable polymer, and only a trace of gibbsite was observed 564 days after seeding. The amount of stable polymer remained practically unchanged during the entire period of the experiment. In contrast, all controls (parent OH-Al solutions) remained clear for as long as 348 days after the experimentation began. The concentrations of unstable polymers slowly decreased, whereas those of stable polymers increased with time, similar to the results reported by Tsai and Hsu (1984). Table 1 also shows that the concentration of unstable polymers decreased at a much faster rate in seeded solutions in which a large amount of gibbsite had developed than in the controls, which remained clear throughout the experimentation.

The fresh and aged solutions were also very different in their rates of reaction with acid (Figure 2). With a 1-day-old solution, 74% of H^+ was consumed in the first hour and 91% in 5 hr. The neutralization practically reached equilibrium in 24 hr. In contrast, the 1-yr-old and 3-yr-old OH-Al solutions took more than

Table 1. Effect of seed addition on the crystallization of gibbsite and accompanying changes in soluble Al species (mg Al/liter) from OH/Al = 1 solutions during prolonged aging.

Reaction time[1] (days)	Control (mg Al/liter)						Seed added[2] (mg Al/liter)					
	pH	Mono[3]	USP[3]	SP[3]	Al(OH)₃ ppt	p(Al³⁺)(OH⁻)³	pH	Mono[3]	USP[3]	SP[3]	Al(OH)₃ ppt	p(Al³⁺)(OH⁻)³
					Age of parent solution (B422) = 4 days							
2	4.04	292	212	nil	nil	32.59	4.04	292	212	nil	nil	32.59
33							4.06	269	215	49	nil	32.56
68							3.98	314	178	22	tr	32.77
158							3.97	327	87	37	83	32.76
221							3.85	348	46	40	135	33.10
293	3.89	303	155	72	nil	33.02	3.64	329	31	43	139	33.74
348	3.93	306	129	80	nil	32.90	3.63	324	30	37	145	33.74
585	3.99	297	102	109	nil	32.73	3.65	319	38	36	154	33.72
					Age of parent solution (B306) = 219 days							
2	4.05	280	178	58	nil	32.57	4.05	280	178	58	nil	32.57
33							3.99	284	153	75	nil	32.74
68							4.00	298	146	70	tr	32.70
108							3.97	310	114	76	35	32.78
158							3.95	324	68	76	75	32.82
221							3.84	315	32	73	114	32.16
293	3.87	308	123	104	nil	33.08	3.64	313	33	84	113	33.76
348	3.93	295	78	143	nil	32.91	3.65	306	42	86	108	33.73
585	3.98	298	65	130	25	32.76	3.70	308	40	78	110	33.58
					Age of parent solution (B304) = 484 days							
2	4.02	297	118	106	nil	32.64	4.02	297	118	106	nil	32.64
33							4.03	288	120	102	nil	32.62
68							3.97	306	106	114	14	32.78
108							3.97	324	72	118	34	32.76
158							3.95	325	39	116	63	32.82
221							3.82	307	27	114	84	33.23
348	3.92	284	76	151	nil	32.95	3.67	309	20	110	91	33.67
585	3.96	298	61	153	nil	32.82	3.69	309	30	110	87	33.61
					Age of parent solution (B302) = 604 days							
2	4.02	287	110	112	nil	32.66	4.02	287	110	112	nil	32.66
33							4.03	296	101	123	nil	32.62
68							3.97	305	81	123	tr	32.78
108							3.96	333	58	132	35	32.78
158							3.93	337	34	130	62	32.87
221							3.80	305	24	125	74	33.29
293	3.89	308	70	150	nil	33.02	3.64	317	37	137	45	33.75
348	3.92	293	67	160	nil	32.94	3.69	306	20	121	80	33.61
585	3.95	300	54	150	tr	32.85	3.70	307	40	121	78	33.58
					Parent solution, 12 yr (Z1)							
564	3.82	292	20	209	nil	33.24	3.78	295	18	202	tr	33.36

[1] After seed addition.

[2] Seeded with submicrometer gibbsite crystallite suspension, 5 ml/500 ml.

[3] Mono = monomeric Al; USP = unstable OH-Al polymers; SP = stable OH-Al polymers.

30 days to reach a neutral pH, providing additional evidence that the OH-Al polymers in solution gradually increased in stability during aging.

For OH/Al = 2.2 solutions, gibbsite was observed in all preparations after prolonged aging (Tsai and Hsu, 1985), but the precipitation of gibbsite accelerated markedly with seeding (Table 2). The results listed in Table 2 also show that, prior to the start of gibbsite crystallization, the unstable polymers slowly converted to stable polymers with time. Once the solution condition favored gibbsite crystallization, the concentration of unstable polymers decreased at a much faster rate, whereas that of stable polymers indicated little change with time. The final $p(Al^{3+})(OH^-)^3$ activity products for all OH/Al = 1 or 2.2 solutions seem to reach a constant value of 33.72, slightly higher than the reported pK_{sp} of gibbsite (34.03, Kittrick, 1966; 33.96, Singh, 1974).

The results may be interpreted by assuming that the initial polymers present in freshly prepared solutions were unstable and converted to either gibbsite or stable polymers via two different reaction paths. The relative magnitudes of these two reaction paths were governed by: (1) the distribution of unstable and stable OH-Al
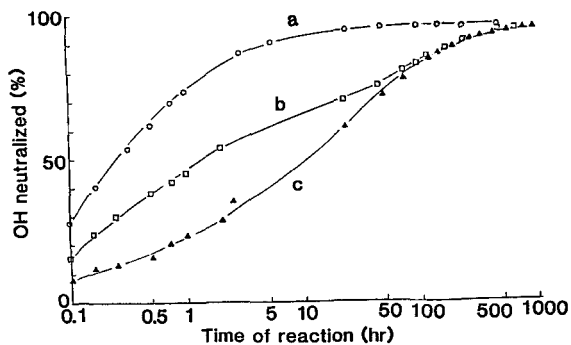
Figure 2. Neutralization of polymer-OH in three partially neutralized 0.02 M $AlCl_3$ solutions (OH/Al = 1) with HCl: (a) 1 day old; (b) 1 yr old; (c) 3 yr old. (2 meq HCl added to 100 ml OH-Al solution containing 2 meq of OH^- in preparation.)

Table 2. Effect of seed addition on the crystallization of gibbsite and accompanying changes in soluble Al species from a OH/Al = 2.2 solution during prolonged aging.

Reaction time,[1] (days)	pH	Distribution of Al (mg Al/liter)				$p(Al^{3+})(OH^-)^3$ [3]
		Mono[2]	USP[2]	SP[2]	Al(OH)$_3$ ppt	
Control[3]						
1	4.20	77	426	64	nil	32.44
272	4.19	67	366	112	nil	32.73
375	4.25	56	329	156	tr	32.62
706	4.16	100	47	193	209	32.66
Seed added[3]						
1	4.20	77	420	64	nil	32.44
87	4.23	75	339	60	62	32.56
195	4.09	124	65	86	284	32.78
272	3.76	119	tr	78	321	33.77
375	3.78	114	tr	82	329	33.73
706	3.80	110	tr	115	309	33.68

[1] After seed addition.
[2] Mono = monomeric Al ions; USP = unstable OH-Al polymers; SP = stable OH-Al polymers.
[3] The parent solution was aged for 30 days prior to seed addition.

polymers; and (2) the presence or absence of nuclei. The crystallization of gibbsite probably started by the deposition of monomeric species, most likely monomeric $Al(OH)_3$, onto the seeds added. This precipitation then prompted further dissociation of OH-Al polymers. Because the concentrations of unstable OH-Al polymers decreased at a much faster rate in seeded solutions than the controls, the rate-determining step for gibbsite crystallization seems to have been the dissociation of polymers into monomeric species. In the absence of nuclei, gibbsite crystallization cannot take place, and thus the unstable polymers converted to stable polymers. Because solution pH only slightly decreased, whereas the concentration of monomeric Al remained nearly the same, the basicities and the thermodynamic dissociation constants for the unstable and stable polymers should have been similar. That the unstable and stable OH-Al polymers were similar in basicity was reported earlier (Turner, 1976a, 1976b; Tsai and Hsu, 1984, 1985). An exact mechanism for the unstable-stable polymer transformation cannot be proposed on the basis of the results currently available, but this mechanism most likely involves internal structural arrangement.

Hsu and Bates (1964) and Hsu (1966) postulated that OH-Al polymers progressively hydrolyzed to larger polymers and eventually to gibbsite. This hypothesis is not consistent with the results in the present report and should now be disregarded. Based on that earlier hypothesis, the addition of gibbsite crystallite should not have affected the rate of gibbsite crystallization. The transformation of unstable to stable polymers should have been accompanied by an increase in basicity prior to the development of gibbsite. The stable polymers should have been even more likely to form gibbsite than the unstable polymers. These requirements are not consistent with the results in this report. For the same reason, the coalescence of OH-Al polymers into gibbsite or direct deposition of OH-Al poly-

mers onto nuclei to form gibbsite should also be ruled out.

Two polymer models have been proposed. One has a composition $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (Al-13 polymer); the other is a fragment of gibbsite. The Al-13 polymer consists of a four-coordinated AlO_4 tetrahedron surrounded by four trioctahedral OH-Al units at the corners of a truncated tetrahedron (Johansson, 1960, 1963). ^{27}Al nuclear magnetic resonance (NMR) studies demonstrated the existence of four-coordinated Al in OH-Al solutions (Akitt et al., 1972; Akitt and Farthing, 1978, 1981; Teagarden et al., 1981; Bertsch et al., 1986a, 1986b). Such a structure, however, should not be stable in aqueous solutions because of the following reasons (Denney and Hsu, 1986): (1) Al-O is unstable in aqueous solution and tends to hydrate to Al-OH or Al-H_2O. (2) A trioctahedral OH-Al configuration has not been observed in any stable compound. (3) In the Al-13 configuration, 13 Al^{3+} ions are packed within 40 oxygen atoms (4 O^{2-}, 24 OH^-, and 12 H_2O). The charge density of this configuration is much higher than that in gibbsite, in which 13 Al^{3+} ions are packed within 48 OH^-, and gibbsite is known to be stable in the Earth's surface environment. Denney and Hsu (1986) also indicated that only the unstable OH-Al polymers were NMR-detectable, not the stable polymeric OH-Al species. Bertsch (1987) suggested that the formation of Al-13 complexes could be attributed to localized high alkalinity. The gibbsite fragment structure is based on the reasoning that the forces that hold Al^{3+} and OH^- in soluble complexes are similar to those in crystalline aluminum hydroxide solids (Hsu and Rich, 1960). This model, if valid, probably represents the stable polymers developed later during aging (Denney and Hsu, 1986).

Table 3. Effect of rate of neutralization on the crystallization of aluminum hydroxide (mg Al/liter) from four OH/Al = 2.2 solutions.

Duration of aging (days)	Rate of NaOH addition (ml/min)			
	1	2.5	10	Rapid neutralization[1]
6	nil	nil	nil	nil
104	nil	nil	78	341
153	nil	85	335	370
237	23	357	N.D.[2]	367
358	110	350	N.D.	349
679	301	367	N.D.	381
1182	330	367	N.D.	399

[1] NaOH was added to $AlCl_3$ solution rapidly through a buret without controlling the rate of addition.

[2] N.D. = not determined.

Furthermore, the method of sulfate precipitation suggest that the unstable polymers initially formed consist of more than one species, but cannot be distinguished with the kinetics of Al-Ferron reactions (Tsai and Hsu, 1984, 1985).

Effect of neutralization rate

Our interpretation suggests that the polymers that initially formed slowly converted to either stable polymers or gibbsite through two different reaction paths, depending on the presence or absence of nuclei. To examine this interpretation further, it is necessary to trace the origin of nuclei.

During solution preparation, localized high alkalinity at the point of NaOH introduction was unavoidable. The localized high alkalinity could have helped to pull Al^{3+} and OH^- ions together, giving rise to the formation of "clusters." Most "clusters," however, are unstable and rapidly dissociate into constituent ions upon rapid stirring, but traces of them might have reached the critical size and structure of nuclei for subsequent crystallization of aluminum hydroxide. The number of nuclei developed from such localized high alkalinity should have been related to the rate of neutralization. The faster NaOH was added, the greater was the chance for localized high alkalinity. The peristaltic pump used in this study was not of high quality and did not pump at a constant rate. The rate of stirring was also not precisely controlled. Such variations in preparation conditions might have produced variations in local regions of high alkalinity, which, in turn, might have given rise to different numbers of nuclei and thus caused erratic aluminum hydroxide precipitation. Tsai and Hsu (1985) proposed this hypothesis to interpret the erratic gibbsite crystallization from OH/Al = 2.2 solutions.

To examine this hypothesis experimentally, four OH/Al = 2.2 solutions and two OH/Al = 1 solutions were prepared by adding 0.1 NaOH to 0.1 M $AlCl_3$ solutions at different rates. For OH/Al = 2.2, the rates of NaOH

Table 4. Effect of rate of neutralization on the crystallization of aluminum hydroxide and accompanying changes in soluble Al species from two NaOH/Al molar ratio = 1 solutions.

Duration of aging (days)	pH	Distribution of Al (mg Al/liter)				$p(Al^{3+})(OH^-)^3$
		Mono[1]	USP[1]	SP[1]	$Al(OH)_3$ ppt	
Rate of NaOH addition = 1 ml/min[2]						
5	4.05	299	197	tr	nil	32.55
358	4.01	298	148	87	nil	32.67
1292	3.88	287	35	202	nil	33.07
Rapid neutralization[3]						
3	4.02	302	223	tr	nil	32.64
70	4.00	303	204	17	nil	32.70
113	3.96	328	150	31	25	32.79
169	3.72	317	28	41	139	33.51
246	3.71	316	tr	32	173	33.54
301	3.66	324	17	38	145	33.69
358	3.63	310	33	33	157	33.79
592	3.62	315	20	29	161	33.81

[1] Mono = monomeric Al; USP = unstable OH-Al polymer; SP = stable OH-Al polymer.

[2] 400 ml of 0.1 M NaOH were added to 500 ml of 0.1 M $AlCl_3$ at a rate of 1 ml per min, then diluted to 2000 ml.

[3] 400 ml of 0.1 M NaOH were added to 400 ml 0.1 M $AlCl_3$ rapidly through a buret without controlling the rate of addition, then diluted to 2000 ml.

addition were 1 ml/min, 2.5 ml/min, 10 ml/min, and rapidly through a buret without rate control (rapid neutralization). For the 1 ml/min NaOH addition, gibbsite started to develop in about 8 months (Table 3). The minimum induction period prior to gibbsite formation was 8 months for all OH/Al = 2.2 solutions in previous studies prepared by adding 1 ml NaOH/min (Tsai and Hsu, 1985). For 2.5 ml and 10 ml NaOH/min additions, the solutions turned turbid after about 4 months and 80 days, respectively. With rapid neutralization, the solution was turbid immediately after preparation, but cleared up in less than 24 hr and became turbid again after about 30 days. The rate of aluminum hydroxide precipitation increased with increased rate of NaOH addition (Table 3). The precipitation of aluminum hydroxide was always associated with decreases in solution pH and increases in monomeric Al ions. The concentration of stable OH-Al polymers stopped increasing as soon as gibbsite started to form. These results are similar to the results of the seed-addition studies (Tables 1 and 2). Transmission electron micrographs showed that, at the end of experiment, the particle size distribution of the gibbsite precipitate in three of the four samples was homogeneous, about 0.5 μm, 0.2 μm, and 0.1 μm in diameter for solutions prepared with 1 ml/min, 2.5 ml/min, and rapid neutralization of NaOH addition, respectively. The sample prepared at the addition rate of 10 ml/min was not characterized with electron microscopy. Schoen and Roberson (1970) reported that gibbsite crystals have a thickness of about $1/10$ their diameter. Thus, the average volume of the precipitated particles can be

estimated at about 0.00982, 0.000628, and 0.0000785 μm^3, respectively. The amounts of aluminum hydroxide precipitate for these three samples account for 330, 365, and 390 mg/liter, respectively. The number of gibbsite particles in these three samples can then be calculated to be in the ratio of 1:17:148. The particle size of the aluminum hydroxide developed should have been inversely related to the number of nuclei present; i.e., the initial number of nuclei should have increased with an increased rate of neutralization. Therefore, localized high alkalinity could have accounted for the erratic rate and extent of gibbsite formation in those OH/Al = 2.2 solutions.

Experiments using OH/Al = 1 solutions gave similar results. One solution was prepared by adding 1 ml of 0.1 M NaOH/min. This solution remained clear to the naked eye and gave a turbidity reading of <1 FTU for as long as 1292 days. The reaction during aging was dominated by the conversion of unstable to stable polymers (Table 4), similar to that reported by Tsai and Hsu (1984). The other solution was prepared by rapidly adding NaOH through a buret without rate control (rapid neutralization). This solution was initially turbid, but cleared in 30 min. This solution then showed similar pH, turbidity, and monomeric Al concentration as the 1 ml NaOH/min solution for a period of 3 months, at which time aluminum hydroxide started to precipitate. The precipitation of gibbsite was accompanied by decreases in solution pH and unstable polymers and slight increases in monomeric Al ions. The concentration of stable polymers increased slightly during the early stage of reaction and then remained unchanged once gibbsite precipitation became noticeable (Table 4). Thus, a very rapid rate of neutralization could have produced a localized high alkalinity and triggered the development of gibbsite. Nevertheless, such rapid neutralization was much different from the routine preparations in our earlier studies, and therefore other factors contributing to the erratic observations in the stability of OH-Al solutions and the crystallization of gibbsite may have been present.

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