



## Hydrolyzed Al(III) clusters: Speciation stability of nano- $\text{Al}_{13}$

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### Abstract

Pure nano- $\text{Al}_{13}$  and aggregates at various concentrations were prepared to examine the particle size effect of coagulation with inorganic polymer flocculant. The property and stability of various species formed were characterized using Infrared,  $^{27}\text{Al}$ -NMR, photo correlation spectroscopy (PCS), and Ferron assay. Results showed that concentration and temperature exhibited different roles on the stability of  $\text{Al}_{13}$ . The quantity of  $\text{Al}_b$  species analyzed by ferron assay in the initial aging period corresponded well with that of  $\text{Al}_{13}$ , which has been confirmed in a dimension range of 1–2 nm by PCS.  $\text{Al}_{13}$  solutions at high concentrations (0.5–2.11 mol/L) were observed to undergo further aggregation with aging. The aggregates with a wide particle size distribution would contribute to the disappeared/decreased  $\text{Al}_{13}$  basis on the  $^{27}\text{Al}$ -NMR spectrum, whereas a part of  $\text{Al}_{13}$  would still remain as  $\text{Al}_b$ . At low concentrations,  $\text{Al}_{13}$  solution was quite stable at normal temperature, but lost its stability quickly when heating to 90°C.

**Key words:** nano- $\text{Al}_{13}$ ; clusters; inorganic polymer flocculant; speciation stability

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### Introduction

Inorganic polymer flocculants (IPFs) are widely applied as special chemical reagents in water and wastewater treatment processes. Compared with the traditional coagulants, IPFs can give markedly improved coagulation effects, and show many advantages such as low dosage, efficient sedimentation, low sludge volume and flexibility to various water quality conditions (Gray et al., 1995; Tang, 1998; Solomentseva et al., 1999; Wang and Tang, 2001; Wang et al., 2002). Therefore, IPFs have the potential to become the main reagents for water and wastewater treatment. Among the IPFs, polyaluminum chloride (PACl) is the most efficient, widely applied coagulant.

PACl is an intermediate product during the hydrolysis-polymerization-precipitation process of Al(III) ions under specific conditions. A large amount of investigation and practical application show that  $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}^{7+}$  (simplified as  $\text{Al}_{13}$ ) is the most efficient species in PACl coagulant (Gray et al., 1995; Tang, 1998; Solomentseva et al., 1999; Wang and Tang, 2001; Parthasarathy and Buffle, 1985; Benschoten and Edzwald, 1990; Furrer, 1993; Matsui et al., 1998; Xu et al., 2003; Wang et al., 2004). The content of  $\text{Al}_{13}$  is therefore the main quality index in PACl products besides the basicity, i.e., OH/Al mole ratio. In current

industrial PACl products,  $\text{Al}_{13}$  content shown as  $\text{Al}_b$  with ferron assay is normally less than 40% (Wang et al., 2004). In some cases, it remains a minor component in the products (Tang, 1998).

To prepare PACl with high content  $\text{Al}_{13}$ -nanoflocculant (containing more than 70%  $\text{Al}_{13}$ ) or pure  $\text{Al}_{13}$  have become recently the target in the research of IPFs. This is also of interest in several other fields such as catalysis, pharmaceuticals, paper industry (Teagarden et al., 1981; Pinnavia, 1983). However, due to the quite complicated nature of Al(III) hydrolysis, the properties of  $\text{Al}_{13}$ -nanoflocculant need further exploration.

The objective of this study is to investigate the stability of  $\text{Al}_{13}$  at various concentrations using IR,  $^{27}\text{Al}$ -NMR, photo correlation spectroscopy (PCS), and Ferron assay in combination. The pathway of species transformation is also proposed.

## 1 Materials and methods

### 1.1 Preparation of $\text{Al}_{13}$

The separation and preparation of pure  $\text{Al}_{13}$  was carried out as shown in a previous publication (Xu et al., 2003). Batches of purified  $\text{Al}_{13}$  samples were mixed together and freeze-dried to white solid powder. Different purified  $\text{Al}_{13}$  solutions were then prepared by dissolving a certain

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amount of the powder into distilled water to desired concentrations, i.e., 0.01–2.1 mol/L. The total aluminum concentration, and speciation distribution were further characterized by IR, Ferron assay,  $^{27}\text{Al}$ -NMR, and PCS.

Samples with different concentrations were aged at room temperature and analyzed at certain period during aging process. To examine the effect of temperature, 20 mL of the newly prepared 0.11 mol/L solution was transferred into three 50 mL conical flasks and aged at room temperature (22–25°C), and 55 and 90°C with a constant temperature water-bath. After certain times, samples were taken out for analysis.

## 1.2 Al-ferron assay

The basic procedure of Ferron assay has been described elsewhere (Wang et al., 2004). The pre-mixed ferron solution of 5.5 mL was pipetted into a 25-mL graduated glass tube and then diluted with distilled water. After homogeneous mixing, the reacting sample was added quickly to a 1-cm glass cuvette. The timed absorbance measurements (at 366 nm), using a DU650 Beckman UV-Visible spectrophotometer (USA), were carried out after 1 min and recorded for further 2 hr. Operationally, 1 min absorbance was defined as  $\text{Al}_a$ , while the consequently developed from 1 min to 2 hr was defined as  $\text{Al}_b$ . Then  $\text{Al}_c$  was calculated as the difference between total Al ( $\text{Al}_t$ ) and  $\text{Al}_a + \text{Al}_b$ .

## 1.3 $^{27}\text{Al}$ -NMR analysis

The solution was examined using 500 MHz  $^{27}\text{Al}$  NMR spectroscopy (Advance Drx 500 Bruker, Germany). The experimental conditions are: NS = 128, P1 = 14.00 s, PL<sub>1</sub> = -3.00 dB, O<sub>1</sub>P: 47.38; DW: 19.20, solvent: D<sub>2</sub>O, and temperature 298 K. The external standard used is 0.05 mol/L NaAlO<sub>2</sub> (with 75% D<sub>2</sub>O).

## 1.4 PCS characterization

The basic procedure of PCS analysis was addressed by Xu et al. (2003). Samples were filtered twice using 0.45 μm Millipore membrane and then put into the clean sample bottle. The samples were measured at an angle of 90° by using BIC 9000SM laser light scattering instrument (BIC Company, USA).

## 1.5 IR characterization

The IR characterization was carried out by using NEXUS 670X. Samples (1–2 mg) were mixed with 100 mg KBr as carrier. Under the pressure of 10 atm, the samples were made into transparent slices. It should be noted that the samples and KBr must be dried before preparation.

# 2 Results and discussion

## 2.1 Characterization of $\text{Al}_{13}$

Speciation of prepared  $\text{Al}_{13}$  solutions was analyzed by Ferron assay and  $^{27}\text{Al}$  NMR as shown in Table 1 and Fig. 1. It can be seen that the samples prepared at

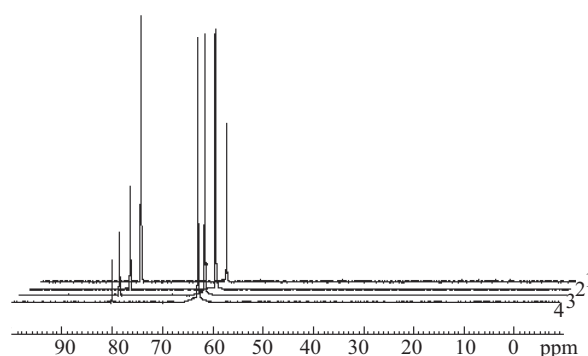
concentrations of 0.10–2.1 mol Al/L contain mainly  $\text{Al}_b$  species.  $\text{Al}_c$  fraction does not exist significantly as the ferron method has the typical analytical errors of around 1%. It seems also that  $\text{Al}_a$  fraction could be contributed from surface Al of  $\text{Al}_{13}$ , i.e., as the results of the rapid dissolution/dissociation of surface Al by ferron. It needs to be noted that the speciation characterization by ferron method is operationally defined, i.e.,  $\text{Al}_a$  is the fraction reacted suddenly in 1 min. Some researchers define the  $\text{Al}_a$  fraction reacted in 30 sec (Parker and Bertsch, 1992). Therefore, the  $\text{Al}_a$  calculated here is significantly high. Samples obtained contain therefore mainly  $\text{Al}_{13}$  species. It indicates that the  $\text{Al}_{13}$  samples prepared can be diluted into various concentrations. High concentration  $\text{Al}_{13}$  solutions are relatively stable and become therefore the valid proof for a commercial preparation. From the  $^{27}\text{Al}$ -NMR results in Fig. 1, it can be seen that only sharp single response at 63.0 ppm. No peak of  $\text{Al}_m$  (monomer) at 0 ppm or other species can be observed for all the samples. And the peak area at 63.0 ppm increases rapidly with increasing  $\text{Al}_t$  concentration. A very good linear equation with  $R^2$  of 0.9996 can be yield, i.e.,  $y = 4.085x + 0.0231$ , where  $y$  is the peak area, and  $x$  is the concentration. It indicates that the only one species observed in the above samples is  $\text{Al}_{13}$ . The results show that the  $\text{Al}_{13}$  detected by  $^{27}\text{Al}$ -NMR has good relation with  $\text{Al}_b$  under these conditions.

In addition, the solid powder of purified  $\text{Al}_{13}$  sample and sulfate salts have been analyzed by IR, which is shown in Fig. 2. It can be seen that the frequency between 3500–3400  $\text{cm}^{-1}$  is the vibration of -OH group, reflecting the complexation of OH-Al. And the frequency at 2400  $\text{cm}^{-1}$  is the vibration of Al-O, and 1640  $\text{cm}^{-1}$  shown as the structure combined water. The frequencies between 1000–400  $\text{cm}^{-1}$  are the vibration of surface -OH group.

**Table 1** Speciation distribution of purified  $\text{Al}_{13}$  solutions by Ferron assay

$\text{Al}_t$ (mol Al/L)	$\text{Al}_a$ (%)	$\text{Al}_b$ (%)	$\text{Al}_c$ (%)
0.11	2.31	97.33	0.36
0.42	2.06	97.38	0.56
1.06	2.02	96.80	1.18
2.11	1.91	96.59	1.60

$\text{Al}_t$ : total aluminum concentration;  $\text{Al}_a$ : the fraction reacted suddenly within 1 min;  $\text{Al}_b$ : the fraction reacted quickly between 1 min and 2 hr;  $\text{Al}_c$ : the un-reacted fraction.



**Fig. 1** Characterization of pure  $\text{Al}_{13}$  by  $^{27}\text{Al}$ -NMR after one week aging.  $\text{Al}_t$  for the samples 1, 2, 3, 4 is 0.11, 0.42, 1.06, and 2.11 mol/L, respectively.

The spectra largely similar feature for the  $\text{Al}_{13}$  powder and its sulfate salts except that the latter shows a typical S–O vibration at  $1117\text{ cm}^{-1}$ .

## 2.2 Effect of concentration on the stability of $\text{Al}_{13}$

The effect of concentration on the stability of  $\text{Al}_{13}$  was also investigated at various  $\text{Al}_{13}$  solutions with ferron assay, as shown in Table 2. The speciation results from ferron assay show that  $\text{Al}_{13}$  is in a state of pseudo-stability and tends to aggregate with aging. Concentrations above 0.5 mol/L play a significant role on its stability. It explains partially the reason why  $\text{Al}_{13}$  sharply decreased during preparation of PACl at concentrations higher than 0.5 mol/L (Gray et al., 1995). Slow aggregation occurred for  $\text{Al}_{13}$  of 2.11 Al mol/L and the solution becomes turbid after one week. Moreover, there is only 86.79% of  $\text{Al}_b$  remaining after one month aging. However, the 0.11 mol/L  $\text{Al}_{13}$  shows quite stable feature and undergoes only minor change during one month aging. This has also been confirmed by NMR analysis as shown in Table 3. From the one week aging results in Fig. 1, it seems again that 0.11 mol/L solution exhibits quite good stability at ordinary temperatures. With increasing concentration, the speciation stability decreases gradually. The quantity of  $\text{Al}_{13}$  decreases 8% and 25% for solutions at 1.06 and 2.11 mol/L, respectively. While in ferron assay, the  $\text{Al}_b$  fractions are 95% and 87% after one week, i.e., decrease only 2% and 10%, respectively. This indicates that the decreased  $\text{Al}_{13}$  in  $^{27}\text{Al}$ -NMR spectrum corresponds only partially with the remaining  $\text{Al}_b$  fraction after aging.

The particle size distribution of  $\text{Al}_{13}$  solutions after aging was also characterized by PCS. The results are shown in Table 4 and Fig. 3. It is observed that the particle

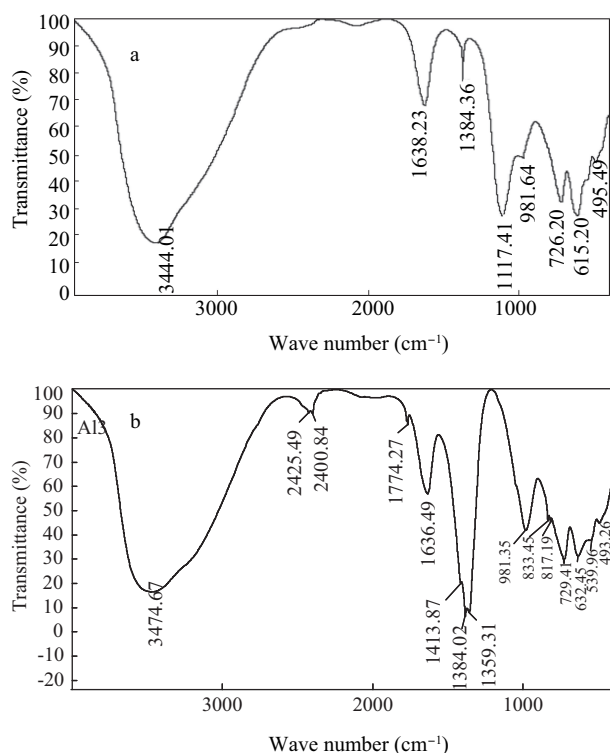


Fig. 2 IR spectra of solid  $\text{Al}_{13}$  sample. (a)  $\text{Al}_{13}$  sulfate; (b)  $\text{Al}_{13}$ .

Table 2 Stability of pure  $\text{Al}_{13}$  solutions measured by Ferron assay

$\text{Al}_t$ (mol/L)	Aging (day)	pH	Observation	$\text{Al}_a$ (%)	$\text{Al}_b$ (%)	$\text{Al}_c$ (%)
0.11	0	5.50	Clear	2.31	97.33	0.36
	1	5.51	Clear	1.58	97.51	0.90
	7	5.42	Clear	1.43	97.44	1.13
	30	5.27	Clear	1.21	94.81	3.98
0.42	0	5.16	Clear	2.06	97.38	0.56
	1	5.15	Clear	0.96	97.20	1.84
	7	5.00	Clear	1.80	94.71	3.49
	30	4.83	Some precip.	2.42	86.16	11.42
1.06	0	4.96	Clear	2.02	96.80	1.18
	1	4.93	Clear	1.08	96.07	2.85
	7	4.88	Some precip.	1.01	94.49	4.50
	30	4.67	Some precip.	0.93	85.70	13.37
2.11	0	4.81	Clear	1.91	96.59	1.50
	1	4.80	Clear	0.47	90.27	9.26
	7	4.70	Turbid	0.86	86.79	12.35
	30	4.36	Turbid	1.04	77.31	21.65

$\text{Al}_t$ : total aluminum concentration;  $\text{Al}_a$ : the fraction reacted suddenly within 1 min;  $\text{Al}_b$ : the fraction reacted quickly between 1 min and 2 hr;  $\text{Al}_c$ : the un-reacted fraction.

Table 3 Speciation of pure  $\text{Al}_{13}$  solutions under aging by  $^{27}\text{Al}$ -NMR analysis

$\text{Al}_t$ (mol/L)	Time (day)	$^{27}\text{Al}$ -NMR	
		$\delta = 80$ (refer.)	$\delta = 63$ (peak area %)
0.11	0	1.000	0.55
	7	1.000	0.54
0.42	0	1.000	2.70
	7	1.000	2.66
1.06	0	1.000	4.23
	7	1.000	3.88
2.11	0	1.000	8.60
	7	1.000	6.50

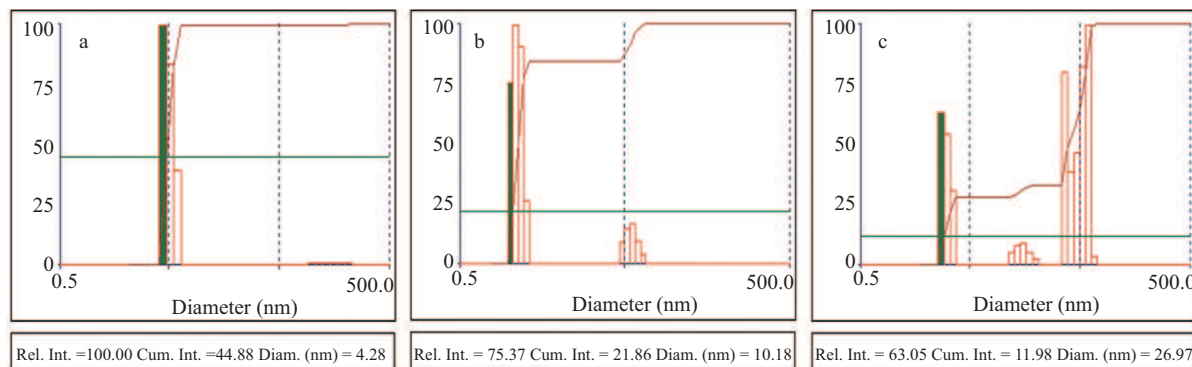
size distribution (PSD) of  $\text{Al}_{13}$  solutions exhibit different features on aging, depending on the concentration. At low concentrations,  $\text{Al}_{13}$  exhibits only weak light scattering because of its small particle size. The scattering intensity is not strong enough to give precise analysis. An increasing intensity can be observed from 4.8 to 13.7 kcps for the 1.06 and 2.11 mol/L solutions. The PSD exhibits a mono-modal distribution around 2 nm, close to the reported dimension of  $\text{Al}_{13}$ . During aging, aggregation of  $\text{Al}_{13}$  occurs, as shown by stronger scattering intensity. Double peak distribution and triple peak distribution appear gradually with aging especially at higher concentrations. After 7 days aging, particle size of 0.11 mol/L  $\text{Al}_{13}$  increases to 4–5 nm, while the 0.42 mol/L sample exhibits two-peak distribution feature with 84.79% the particles around 10 nm and 15.21% around 47.93–64.39 nm. The sample of 1.06 mol/L exhibits also two-peak distribution with 85.59% at 34–40 nm and the other around 69.88–83.27 nm. However, three-peak distribution exhibits with 27–34 nm (28%), 118–193 nm (5%) and 359–664 nm (67%) for the sample of 2.11 mol/L. It shows that most of the particles become as large as in the dimension of several hundred of nms.

It needs to be noted that there are limitations for the PCS analysis. The precise analysis of PSD remains a problem for PCS. The presence of large particles will affect the

**Table 4** Change of particle size distribution (PSD) of Al<sub>13</sub> solution with aging by PCS analysis

Al <sub>t</sub> (mol/L)	Aging (day)	Inten. (kcps)	PSD (nm)	Peak (%)	Al <sub>t</sub> (mol/L)	Aging (day)	Inten. (kcps)	PSD (nm)	Peak (%)
0.11	1	–	–	–	0.42	1	–	–	–
	7	5.4	4.28–5.85	99.84		7	24.3	10.18–12.70	84.79
	15	9.8	11.53–14.73	79.68		15	28.3	47.93–64.39	15.21
			44.30–72.27	20.02				31.78–39.52	92.00
			124.8–170.1	84.21				79.38–98.71	8.00
1.06	1	4.8	26.54–36.17	15.79	2.11	1	13.7	38.96–55.40	24.16
			148.5–211.1	75.84				2.26–5.58	99.91
	7	29.5	34.66–39.88	85.59		7	503.9	26.97–34.50	28.10
			69.88–83.27	14.41					118.3–193.6
	15	34.3	34.75–45.40	61.38		15	537.6	28.00–50.31	28.32
			101.2–132.2	38.62					140.3–252.0
	30	56	34.02–42.61	51.04		30	604.8	29.82–47.70	4.15
			105.2–131.9	48.96					228.3–427.1
								934.5–2044	56.03

–: only very weak light scattering observed.



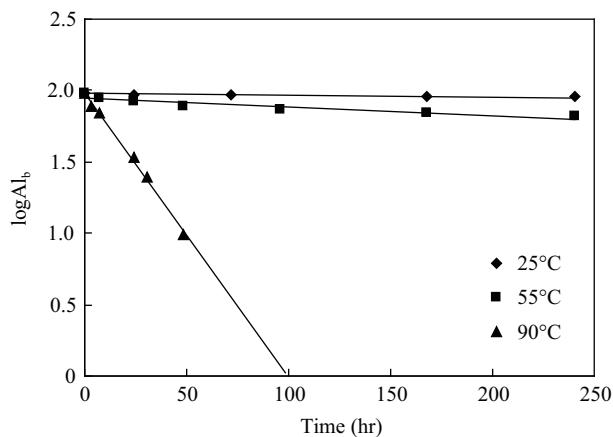
**Fig. 3** PCS analysis of the Al<sub>13</sub> solutions at various concentrations. (a) Al<sub>t</sub> = 0.11 mol Al/L for 2 days; (b) Al<sub>t</sub> = 0.42 mol Al/L for 7 days; (c) Al<sub>t</sub> = 2.11 mol Al/L for 7 days.

detection of small particles. However, the trend of particle size increasing with aging is clearly observed as shown by the increase of scattering intensity. Compared with the Ferron assay and <sup>27</sup>Al-NMR results, it seems that during aging the aggregates with a wide PSD contribute partially to the disappeared/decreased Al<sub>13</sub> in <sup>27</sup>Al-NMR spectrum while remaining in Al<sub>b</sub> fraction.

### 2.3 Effect of temperature on the stability of Al<sub>13</sub>

The 0.11 mol/L Al<sub>13</sub> was further aged under different temperatures and results are indicated in Fig. 4. The decrease of Al<sub>b</sub> follows a pseudo-first order kinetic reaction. The kinetic constants are 0.0001, 0.0006, and 0.0197 hr<sup>-1</sup> at room temperature (22–25)°C, 55°C and 90°C, respectively. Figure 5 shows the NMR characterization of the samples aged at 90°C. It shows that Al<sub>13</sub> decreases markedly with aging time. The phenomenon is similar to those observed by ferron method. It should be noted that the peak of monomer Al appears after 24 hr aging, which indicates the dissolution of Al<sub>13</sub> during aging with heat.

The PCS results clearly show the particle aggregation feature of the samples heated under different conditions. It is observed that the initial solution scatters little light and shows little change for several days heating at 55°C. Results show that particles distribution are in the size range of 29–52 nm only after 10 days aging. However, heating at



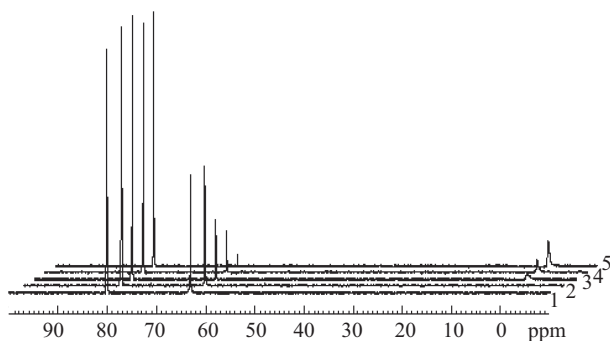
**Fig. 4** Effect of temperature on the stability of Al<sub>13</sub>.

90°C the scattering intensity increases quickly. Two-peak distribution is observed for 24 hr heating, with 60% of 200–260 nm and 40% of 600–700 nm. With further aging, the particle grows markedly and becomes 60% at 700 nm for 48 hr.

## 3 Discussion

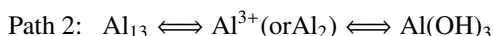
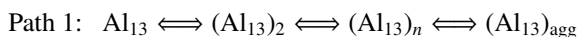
The experimental results show that temperature has a significant effect on the transformation of Al<sub>13</sub>. At room

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**Fig. 5** <sup>27</sup>Al NMR analysis for Al<sub>13</sub> aged under 90°C at different periods. (1) 0; (2) 3 hr; (3), 24 hr; (4) 31 hr; (5): 48 hr.

temperature, Al<sub>13</sub> remains stable for a long time. With the increase of temperature, the stability of Al<sub>13</sub> decreases markedly and transformation to other species occurs quickly. There are two possible pathways of aggregation: one goes to soluble high polymers, the other one is to form solid Al(OH)<sub>3</sub> species as follows.



The exact pathway will depend on the presence of nuclei and their quantity. With the presence of nuclei, Al<sub>13</sub> will be depolymerized/dissolved into dimer or monomer, and then deposited onto the nuclei to form Al(OH)<sub>3</sub> precipitate. In the absence of nuclei, Al<sub>13</sub> will aggregate to form large particles, which would depend on the solution conditions. The follow-up step will be structure re-building and further transformation to Al(OH)<sub>3</sub> will be slower.

As shown in Table 2, the 2.11 mol/L Al<sub>13</sub> sample becomes turbid after 7 days aging. However, the Al<sub>b</sub> from ferron assay remains as high as 86.79% and strong Al<sub>13</sub> signal is also observed as shown in <sup>27</sup>Al NMR. In contrast, the Al<sub>b</sub> in the sample heated at 90° for 48 hr decreases rapidly to 9.7% and the solution becomes turbid also. There is a difference between the two processes. At high concentration, the aggregation between Al<sub>13</sub> units takes place and precipitates form finally after reaching certain size. The aggregates or precipitates formed can undergo rapid reaction with ferron and yield high Al<sub>b</sub> also. However, when heated at high temperature, the Al<sub>13</sub> dissolves to form monomer or dimer as observed from <sup>27</sup>Al NMR and finally yield Al(OH)<sub>3</sub>, which is formed irreversibly and does not react with ferron. Two pathways have been proposed for the aggregation of Al<sub>13</sub>. Klopogge et al. (1992) considered that the decrease of Al<sub>13</sub> with little change of pH showed that the transformation of Al<sub>13</sub> was a kind of structure re-building, with no further hydrolysis involved. Many researchers agreed with this viewpoint and considered the final structure close to that of gibbsite (Tsai and Hsu, 1985; Bottero et al., 1987; Bradley et al., 1990), moreover, the crystal Al(OH)<sub>3</sub> was formed by free combination of Al<sub>13</sub> without re-hydrolysis. However, other researchers considered that the aggregation of Al<sub>13</sub> to form large particles resulted from the de-protonation in the edge or surface (Letterman and Asolekar, 1990). In the present study, it is also observed that the solution pH keeps

relatively stable during aggregation at high concentration, but not in the aggregation process at high temperature. This suggests that these two kinds of aggregation processes correspond well with the pathways shown above. The aggregation of Al<sub>13</sub> to form large particles increases mainly the degree of polymerization rather than changing the acid-base property. Therefore, the solution pH keeps relatively unchanged. The dissolution of Al<sub>13</sub> and further deposition onto nuclei will follow by the dissociation of H<sup>+</sup>. The solution pH then decreases. It should be noted that the two pathways will co-exist during aging of Al<sub>13</sub> under various conditions but one pathway will usually take the main role.

## 4 Conclusions

Pure Al<sub>13</sub> species exhibit certain stability. For the low concentration (Al<sub>t</sub> < 0.11 mol/L), it can keep stable for a long time. With increasing concentration, the stability of Al<sub>13</sub> decreases and has the tendency to transform to other species but at relatively slow rate. On the one hand, Al<sub>13</sub> exhibits Keggin structure with AlO<sub>4</sub> in the center surrounded by 12 octahedral Al(III). Therefore protons cannot easily access the AlO kernel. On the other hand, this kind of structure results in the slow interchange of the inner-Al atom with the outer-Al atoms. The structure re-building and interchange of structural aluminum with bulk-aluminum is rather slow, so that the structure remains relatively stable.

The correspondence of Al<sub>13</sub> and Al<sub>b</sub> is conditionally dependent. A good relationship exists for pure Al<sub>13</sub> solutions in the initial aging period. However, this relationship changes during further aggregation process. At room temperature, high solution concentration promotes aggregation of Al<sub>13</sub>. The aggregates with a wide particle size distribution contribute partially to the disappeared/decreased Al<sub>13</sub> spectrum in <sup>27</sup>Al-NMR while remaining reactive with ferron as shown in Al<sub>b</sub> fraction. The decreased Al<sub>13</sub> spectrum in <sup>27</sup>Al-NMR contributes partially to the remaining Al<sub>b</sub> fraction during aging. At high temperature, the aggregates become relatively inert to react with ferron. However, part of the aggregates appears still as Al<sub>b</sub> fraction while disappearing quickly from the <sup>27</sup>Al NMR spectrum.

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