Hydrolyzed Al(III)-clusters. II: Speciation transformation and stability of Al_{13} aggregates

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HIGHLIGHTS

- ▶ The speciation of Al_{13} aggregates exhibits quite stable nature.
- ▶ The Al_{13} aggregates might maintain the Keggin- Al_{13} structure for more than one month.
- ▶ Aggregates disappear quickly in ^{27}Al -NMR detection with increasing OH/Al ratio while maintain efficient Ferron reactivity.
- ▶ The Al_b in Ferron assay corresponds with Al_{13} only under certain conditions.

GRAPHICAL ABSTRACT

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ABSTRACT

Pure nano- Al_{13} and aggregates at various concentrations were prepared to examine their stability and potential role in coagulation processes and natural systems. Alkalinity titration experiments showed that the hydrolysis of Al_{13} solutions exhibits significant difference from that of the normal Al(III) solutions. The transition OH/Al ratio (pH points) shifts from normal 2.5 to higher values (~ 2.9). No significant structural rearrangement takes place during Al_{13} aggregation. The aggregates exhibit stability during short aging up to 1 month. The Al_b species obtained by Ferron assay in the initial aging period no longer corresponds to Al_{13} . The aggregates disappear quickly in ^{27}Al -NMR detection with increasing B value (OH/Al ratio) maintaining efficient Ferron reactivity. This shows that the Al_b in Ferron assay corresponds with Al_{13} only under certain conditions.

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1. Introduction

Inorganic polymer flocculants (IPFs) are widely applied as efficient coagulants 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, lower sludge volume and flexibility to various water quality conditions [1–3]. Among the IPFs, polyaluminum chloride (PACl) is the most efficient, widely applied coagulant and has a mature production technology. PACl

containing high content of Al_{13} -nanoflocculant (containing more than 70% Al_{13}) and methods to prepare pure Al_{13} have become recently the target in the research of nano-IPFs [4,5]. They are also of interest in several other fields such as catalysis, pharmaceuticals and paper industry [6,7]. However, due to the quite complicated nature of Al(III) hydrolysis, the full possibilities and properties of Al_{13} -nanoflocculant remain to be exploited.

In fact, PACl is an intermediate product during the hydrolysis-polymerization-precipitation process of Al(III) ions under specific conditions [8]. A large amount of investigation and practical application shows that the $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}^{7+}$ (simplified as Al_{13}) is the most efficient species in PACl coagulant [9,10]. The content of Al_{13} is therefore the main quality index in PACl products besides the basicity B , i.e. OH/Al mole ratio. In the current

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industrial PACl products, Al_{13} content shown as Al_b with Ferron assay is normally less than 40% [11]. In some cases, it remains a minor component in the products [2]. The preparation of PACl with high content Al_{13} -nanoflocculant (containing more than 70% Al_{13}) has become recently the target in the research of IPFs.

The objective of this study is to investigate the role of Al_{13} and its aggregates during coagulation with emphasis on the effect of particle size. A previous paper discussed in detail the stability of pure Al_{13} [3]. This paper aims to characterize Al_{13} aggregates at various concentrations by using ^{27}Al -NMR, PCS, and Ferron assay in combination. The coagulation behavior and role of coagulant particle size of Al_{13} aggregates will be investigated in another paper.

2. Materials and methods

2.1. Preparation of Al_{13} and aggregates

The separation and preparation of pure Al_{13} was carried out shown in a previous publication [3,10]. Batches of purified Al_{13} samples were mixed together and freeze-dried to a white solid powder. Preparation of Al_{13} aggregates was achieved by further base addition to pure Al_{13} solutions. Two set of Al_{13} solutions were used, viz. 0.056 and 0.011 mol Al/L . The Al_{13} solutions were titrated slowly with predetermined amount of NaOH solution to the desired final B (OH/Al) values, 2.6, 2.7, 2.8, 2.9 and 3.0.

2.2. ^{27}Al -NMR spectroscopy

Hydroxyl Al solutions were examined with a 400 MHz ^{27}Al -NMR spectrometer (Brookhaven Co., USA). The instrumental settings and experimental conditions were: NS = 128, P1 = 20 s, PL1 = -3 dB. Solvent: D_2O , and $T = 298\text{ K}$. The $\text{Al}(\text{OD})_4^-$ solution of 0.05 mol/L was used as inner standard with chemical shift of 80 ppm. The signals near 0 and 62.5 ppm represent mononuclear species (Al_m), six-coordinated species and the tetrahedral core of Al_{13} [$\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$], respectively.

2.3. Ferron speciation

The Ferron chemical were purchased from Sigma-Aldrich Chemical Co. Ferron colorimetric solution was obtained by mixing the Ferron solution (0.2%, w/v), NaAc solution (20%, w/v), and HCl solution (1:9, v/v) at a ratio of 2.5:2:1 [11]. 5.5 ml of the pre-mixed Ferron solution was pipetted into a 25 ml graduated glass tube and then diluted to the marked line with distilled water. The samples were added by using a micropipette and mixed rapidly (more than 300 rpm). 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 UV-Visible spectrophotometer (USA), were carried out after 30 s and recorded for further 2 h. The first 30 s absorbance was designed as Al_a , and the absorbance from 30 s to 2 h as Al_b . The Al_c was obtained as Al_{Total} minus Al_a and Al_b .

2.4. Photon correlation spectroscopy

Samples were filtered twice using a 0.45 μm Millipore membrane and then put into the clean sample bottle. The samples were measured at an angle of 90° using BIC 9000SM laser light scattering instrument (BIC Company, USA). The size distribution analysis was performed using CONTIN program (software attached) at the particle size range 0.1–2000 nm.

Fig. 1. The titration curve for alkalization of pure Al_{13} solution: slow titration vs. rapid mixing. (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)

3. Results

3.1. Alkaline titration of Al_{13}

The alkaline titration curves for Al_{13} solutions are shown in Fig. 1. It can be seen that the titration curves of Al_{13} solution are significantly different with those of the traditional salts [12]. Although a plateau exists still with increase of alkaline addition and OH/Al ratio (B value), the turning point of B value is delayed to a large OH/Al ratio. Under rapid mixing using the 0.028 mol/L solution, the precipitation occurs only until OH/Al reaches 2.8, which is obviously larger than the normal 2.4–2.5 for $\text{Al}(\text{III})$ salts. Under the slow titration conditions, precipitation is delayed to an even larger B value, viz. 2.9 as indicated by the red arrow. Therefore, it suggests that once formed, Al_{13} is quite stable and undergoes further aggregation only when the surface charge is greatly neutralized.

3.2. Speciation of Al_{13} aggregates by Ferron

The results of Ferron assay for the stability of Al_{13} aggregates prepared are shown in Table 1, Figs. 2 and 3. It can be seen that the samples prepared at 0.028 mol Al/L contain mainly Al_b species, viz. around 94–96% for 24 h aging. Only the B 3.0 sample shows a slightly decrease to 92.5%. No Al_c fraction exists significantly as the Ferron method has an analytical error normally around 1%. After further aging for about 1 month, the Al_b species decrease 10% with transformation mainly to Al_c . From Fig. 2, it can be seen clearly that with increase in the B value, the speciation of Al_{13} aggregates keep similar (the results of Al_a and Al_c are shown in Table 1). This indicates that the reactivity of Al_{13} aggregates with Ferron is maintained actively even in aggregated state. The Keggin structure might still be unchanged. From Fig. 3 it can also be seen that the Al_b species in the aggregates remains quite stable for nearly a month.

Fig. 2. The change of Al_b with B during the alkalization of Al_{13} .

Table 1Speciation stability of Al_{13} aggregates: $\text{Al}_t = 0.028 \text{ mol Al/L}$.

<i>B</i>	Al_a (%)				Al_b (%)				Al_c (%)			
	0 h	24 h	4 d	1 m	0 h	24 h	4 d	1 m	0 h	24 h	4 d	1 m
2.60	1.63	2.21	1.71	1.21	95.65	95.70	92.20	88.10	2.72	2.09	6.09	10.69
2.70	2.44	2.32	1.63	1.59	94.40	93.90	89.70	84.17	3.16	3.78	8.67	14.24
2.80	1.89	1.89	3.54	1.67	97.94	97.94	93.50	86.52	0.17	0.17	2.96	11.81
2.90	1.98	2.47	3.08	3.72	94.63	97.13	95.70	90.85	3.39	0.40	1.22	5.43
3.00	3.20	3.81	3.72	3.20	95.00	92.51	91.00	82.70	1.80	3.68	5.28	14.10

Fig. 3. The stability of Al_{13} aggregates: change of Al_b with aging, $\text{Al}_t = 0.028 \text{ mol Al/L}$.

3.3. Particle size distribution and ^{27}Al -NMR analysis

The ^{27}Al -NMR responses are shown in Figs. 4 and 5 and the particle size distribution analyzed by PCS are shown in Table 2. It can be seen that although the aggregates exhibit efficient Ferron reactivity, their particle size distributions are different. As shown in the Table 2, the LLS intensity increases linearly with increase of *B* value and further aging. The average particle size increases from 2 mm to 10 mm for *B* values from 2.46 to 2.9, and the particles change gradually from mono-distribution to multiple-distribution [3]. With aging, the particles undergo slow growth. Thus the aggregation of Al_{13} does not occur significantly until a certain *B* value reached, which depends largely on the preparation mode, viz. titration rate and concentration. As shown in the titration curve Fig. 1, the turning point occurs at *B* 2.9 for slow titration, while it appears early at 2.8 for rapid mixing with NaOH.

The chemical speciation distribution by Ferron assay remains largely the same after preparation except at larger *B* value. Al_b decreases 5% with yield of 5% Al_c for *B* of 3.0. It is interesting that for the *B* = 3.0 sample already shows bulk precipitation. After filtration

Fig. 4. NMR analysis of Al_{13} aggregates at various *B*: $\text{Al}_t = 0.028 \text{ mol Al/L}$, *t* = 24 h. The decrease of Al_{13} is obvious with increase of *B* (1, *B* = 2.46; 2, *B* = 2.6; 3, *B* = 2.7; 4, *B* = 2.8; 5, *B* = 2.9; 6, *B* = 3.0). **Fig. 5.** The ^{27}Al -NMR characterization for samples with aging: $\text{Al}_t = 0.028 \text{ mol Al/L}$, *B* = 2.6 (1, aging for 24 h; 2, aging for 10 days; 3, aging for 2 months).

with a $0.45 \mu\text{m}$ membrane (the results shown in Fig. 6, no obvious Al(III) species can be found in solution, while the bulk precipitates react actively with Ferron similar to Al_{13} . With further aging as long as one month, the speciation undergoes only a slight change with slow decrease of Al_b and increased yield of Al_c . Even the precipitated Al_{13} exhibits some stable Ferron reaction, and only 23% Al_c is formed after 1 month aging.

4. Discussion

The Al_{13} cluster series is critical to studying the hydrolysis behavior of aluminum based coagulant. Although the hydrolysis behavior of Al_{13} has been very well investigated below the OH/Al

Table 2The particle size distribution (PSD) of the Al_{13} aggregates under aging.

<i>B</i>	Aging time (day)	Intensity (kcps)	PSD (nm)	Volume (%)
2.6	0	8.5	1.80–2.65	–
	1	12.3	2.18–3.94	–
	4	18.5	5.79–6.95	–
	10	21.8	9.7–12.63	–
2.7	0	11.0	4.75–7.65	–
	1	13.4	8.09–15.73	–
	4	16.7	7.66–11.92	–
	10	23.1	9.45–16.20	–
2.8	0	15.8	4.31–6.95	–
	1	17.6	5.07–8.12	–
	4	21.7	11.30–13.37	–
	10	27.1	11.94–20.48	95.80
			46.03–78.99	1.62
2.9	0	18.6	7.30–13.25	–
	1	20.2	8.07–14.80	–
	4	26.6	7.79–13.31	95.96
	10	39.0	22.73–38.83	4.04
			12.37–22.00	94.86
3.0			52.17–92.78	1.58
			220.02–451.83	3.56

Fig. 6. Ferron reaction curves for sample before and after 0.45 μm filtration: 0.028 mol Al/L.

ratio of 2.5, very little is known about its hydrolysis behavior at higher OH/Al ratio. This is because it was believed that Al(III) would be quickly transformed into amorphous $\text{Al}(\text{OH})_3$ precipitate at such high OH/Al ratios. The results from this study show that the Al_{13} might firstly transform into aggregates while maintaining the Keggin- Al_{13} structure with increasing OH/Al ratio and this aggregates exhibit active Ferron reaction up to 1 month. These findings could be useful to study the hydrolysis and aging behavior of Al(III) salts.

Additionally, the results show again the stable nature of Al_{13} . Aggregation of Al_{13} occurs only under neutralization of surface charge reaches certain degree, viz. 2.9, as calculated from B value. A positive charge “7+” is then neutralized to 80%. Therefore, the surface charge of Al_{13} might play a significant role in its stability. This is also the reason for instability of another flat- Al_{13} species due to the lower surface charge [13]. Structural reorganization might occur to form more stable solution Keggin Al_{13} [14]. It is interesting that the aggregation of Al_{13} occurs at pH 6.0–6.5. This corresponds well with the optimum coagulation pH for Al-based coagulants as observed in much other research [15]. Further experiments should be carried on to clarify the role played by aggregated Al_{13} in coagulation process.

Moreover, it is of interesting to observe that the correspondence of Al_{13} and Al_b is conditionally dependent. As shown in a previous paper, there is a good relationship between the pure Al_{13} solution and Al_b in the initial aging period [3]. However, this dependent relationship might not be a general rule. Especially, when the Al_{13} species was present at OH/Al ratio higher than 2.5, this relationship was changed with the further aggregation process. The aggregates with a wide particle size distribution contribute partially to the decrease Al_{13} spectrum in ^{27}Al -NMR while remaining reactive with Ferron as shown in Al_b fraction. This decreased Al_{13} spectrum in ^{27}Al -NMR contributes partially to the remaining Al_b fraction during aging. At high temperature, the aggregates become relatively inert to react with Ferron. However, a part of the aggregates appears still as Al_b fraction while disappearing quickly from the ^{27}Al -NMR spectrum.

5. Conclusions

The conclusions can be summarized as follows.

The hydrolysis of Al_{13} solutions exhibits significant difference from that of the normal Al(III) solutions. A pH transition plateau is still observed, however, it extends to larger OH/Al ratio (B) from normal 2.5 to a higher 2.9 region. Bulk precipitation occurs only until B value reaches 3.0. Even in the rapid mixing case, the transition B value is delayed to 2.8 or so. No significant structural rearrangement occurs during Al_{13} aggregation. The aggregates exhibit some stability during one month aging period. The structure re-building and interchange of structural aluminum with bulk-aluminum is rather slow, so that the structure remains relatively stable. The Al_b species obtained from Ferron assay in initial aging period no longer corresponding to Al_{13} . Aggregates disappear quickly in ^{27}Al -NMR detection with increasing B value (OH/Al ratio) while maintaining efficient Ferron reactivity. This shows that the Al_b in Ferron assay corresponds with Al_{13} only under certain conditions.

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