Historical perspective

Speciation, stability, and coagulation mechanisms of hydroxyl aluminum clusters formed by PACl and alum: A critical review

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ABSTRACT

The physicochemical property of coagulant species plays a significant role in the coagulation process. Recent progress on speciation, stability, and coagulation mechanisms of the hydroxyl aluminum clusters formed by PACl and alum has been critically reviewed. The complicated nature on species formation, stability, and transformation of various hydrolyzed aluminum clusters formed by PACl and Alum are discussed. Based on the aspects of spontaneous hydrolysis, forced hydrolysis, and dual-hydrolysis models, the special stability of aluminum clusters that results in various coagulation behaviors is compared with the traditional salts. The coagulation behavior of the hydroxyl aluminum clusters in terms of particle aggregation and restabilization, surface adsorption and coverage, microfloc formation and kinetics, modified DLVO simulation, and finally, the coagulation model is then analyzed in detail. It is indicative that the coagulation mechanism of inorganic coagulants can be understood better with the hydroxyl clusters being tailor-made.

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Contents

1. Introduction	78
2. Chemical speciation of hydroxyl aluminum clusters	79
2.1. Speciation characterization through ESI-MS	80
2.2. ²⁷ Al NMR combined with Ferron assay	80
3. Hydrolysis pathway of aluminum salts in aqueous solution	80
3.1. Spontaneous hydrolysis	80
3.2. Forced hydrolysis	81
3.3. Dual-hydrolysis model	81
4. Stability of Keggin-Al ₁₃ in PACl	81
5. Coagulation mechanism of hydroxy-aluminum clusters	82
5.1. Adsorption and surface coverage	82
5.2. Coagulation of silica microspheres suspension	82
5.3. Microfloc aggregation and simplified DLVO simulation	82
5.4. Morphological observation	82
5.5. Coagulation calculation model	82
6. Conclusions	83
Acknowledgement	84
References	85

1. Introduction

Aqueous chemistry of hydroxyl aluminum clusters, involving the comprehensive hydrolysis processes and the formulation of polymeric species, has been a permanent and controversial subject in many fields

of science and technology. It is widely concerned both in geochemical, medical, environmental sciences, and many industrial applications such as pharmaceutical, petroleum, ceramic, catalysis, and other areas [1–5]. It is also closely related with the coagulation and flocculation process in water and wastewater treatment especially with the recent development and application of novel inorganic polymer flocculants (IPFs). Basically, there are two major types of IPFs, i.e. cationic type including polyaluminum chloride (PACl), polyaluminum sulfate (PAS),

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polymeric ferric sulfate (PFS), and polymeric ferric chloride (PFC), and anionic type including polymeric silicates. In addition, complex coagulants such as polymeric ferroaluminum chloride (PAFC) and polyaluminum silicate chloride (PASiC) have also emerged as a new type of IPFs receiving much attention. The development of IPFs is now becoming a series of coagulant productions, where the Al-based varieties are dominating among them [1]. The details of IPFs are shown in Table 1.

However, many arguments remained obviously on the chemical species and structures of the hydrolyzed aluminum clusters or polymers, and even more arguments on the proposed model of their formation pathways [2,6–9]. The first step towards resolving these knotty problems would be a comprehensive understanding of chemical speciation information obtained by a battery of analytical techniques under various experimental conditions. In recent years, due to the great contribution of the advanced instrumentations such as ^{27}Al NMR and ^{17}O MAS NMR, SAXS, ESI Q-TOF-MS, and Ferron assay, the speciation, structure, and transformation of hydroxyl aluminum clusters have been more clearly defined [2,5–12]. The effect of the sulfate ion on coagulation indicated that sulfate had a significantly different effect on PACl coagulation as a result of performed hydrolysis products, where charge neutralization and precipitation play different parts in the coagulation process [7]. Based on the kinetic difference of the reactions between the aluminum and ferron agent, the ferron method enables one to partition soluble aluminum species into such categories as monomeric, fast-reacting polymeric, or slow-reacting colloidal species denoted simply as Al_a , Al_b , Al_c , respectively [9].

Meanwhile, the general mechanisms of coagulation have been summarized recently in Duan and Gregory's review in detail [13]. There are two distinct mechanisms in the coagulation process: charge neutralization of negatively charged colloids and incorporation of impurities in an amorphous hydroxide precipitate. The relative importance of these mechanisms depends on factors such as pH and coagulant dosage. Due to the low solubility of aluminum, with increase of alum dosage, excessive aluminum hydroxide precipitation can form, and particles in water can be enmeshed by the hydroxide precipitate. This process is the so-called “sweep flocculation.” Chowdhury and Amy [14] claimed that precipitation is the main mechanism in the coagulation of alumina colloids with alum. According to the “sweep flocculation” model, the incorporation of colloids into precipitate follows two pathways: one is the heterogeneous nucleation involving charge neutralization and subsequent growth of precipitate at low pH value, and the other is homogeneous nucleation involving precipitation and subsequent particle aggregation at high pH. With respect to the coagulation/flocculation mechanisms of PACls, most current studies focused on the mode of charge neutralization [15–18]. Dentel [11,17] had tried to explain the coagulation mechanisms of different kinds of coagulants by a combined model of precipitation charge neutralization (PCN). Recently, “electrostatic patch coagulation” was proposed by Wang et al. [18] to interpret the coagulation behaviors of PACls, but it has not been examined systematically using controlled experiments in detail. The experimental results showed that there exists a remarkable difference in coagulation with various PACl formulation in accordance with the different species

being performed. This indicates that the assumption of all the surface species consisting of the same aluminum hydroxide solids is not correct, and some modification of the PCNM is therefore needed [18].

In fact, the hydroxyl aluminum clusters in PACl products are intermediate product during the hydrolysis–polymerization–precipitation process of $\text{Al}(\text{III})$ ions under specific conditions. A large amount of investigation and practical application show that the $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}^{7+}$ (simplified as Al_{13}) is the most efficient species in PACl coagulant [1–11, 19–23]. The Al_{13} polycation also has a number of industrial applications, including use as a flocculant in waste water treatment, as a primary constituent of pharmaceutical and cosmetic products, and ceramics [8]. However, the significance of Al_{13} in the coagulation process might be undermined by the transformation reaction after dosing into real water. Therefore, the stability of Al_{13} under various water quality conditions should be clarified. Moreover, the coagulation behavior of the Al_{13} in terms of particle aggregation and restabilization, microfloc formation, kinetics, and modeling needs to be addressed. The Al_{13} polymer and polyaluminum chloride (PACl) were comparatively investigated for the coagulation of humic acid (HA). The results showed that the floc properties were essentially dependent on pH. Compared to PACl, Al_{13} polymer displayed better stability and functioned more rapidly after addition, and the flocs formed by Al_{13} were denser across the pH values investigated.

The structure of hydroxyl aluminum clusters in coagulants not only is important in understanding the basic chemical aspects of coagulation but also has a great impact on the practical operation level of coagulation. However, a comprehensive understanding of aluminum speciation in coagulation involves multidisciplinary methods and knowledge. This paper focuses on the following three aspects: (1) to summarize the methodology involved in aluminum speciation and the hydrolysis models of aluminum clusters under different situation, (2) to reveal the distinct coagulation mechanism of PACl by comparing its behavior with the alum's, (3) to provide coagulation calculation models for PACl, the future development tendency and the compatibility of tailor-made PACl coagulants with following process such as microfloc filtration, flotation, membrane separation.

2. Chemical speciation of hydroxyl aluminum clusters

The study on chemical speciation of aqueous aluminum hydroxyl clusters has achieved significant progress in recent years [1,2,6]. It was contributed by the concurrent utilization of the advanced instrumental techniques like NMR, SAXS, PCS, ESI Q-TOF MS, and Ferron assay.

The comprehensive formula for Al-hydroxyl species can be written as $\text{Al}_x(\text{OH})_y(\text{H}_2\text{O})_n^{(3x-y)+}$ or $\text{Al}_x\text{O}_z(\text{OH})_y(\text{H}_2\text{O})_n^{(3x-y-2z)+}$. Their classification may be exemplified in Table 2, in which the oligomers are limited and denoted only as Al_2 and Al_3 clusters to show their special importance. The Al_a , Al_b , and Al_c are the categories of species defined by Ferron assay.

The ^{27}Al NMR spectroscopy is the most useful technique to identify the hydroxyl $\text{Al}(\text{III})$ species according to the response peak at specific chemical shift (δ , ppm) on the spectrum. The four-fold coordinated tetrahedral $\text{Al}(\text{III})$ can be observed at the range above $\delta = 60$ ppm and the six-fold coordinated octahedral $\text{Al}(\text{III})$ is below $\delta = 20$ ppm. Generally,

Table 1
Category and series of inorganic polymer flocculants.

Cationic		Inorganic composite	
Poly Al chloride	PACl, ACH	$\text{Al} + \text{Fe} + \text{OH} + \text{SO}_4$	PAFS
		$\text{Al} + \text{Fe} + \text{OH} + \text{Cl}$	PAFC
Poly Al sulfate	PAS	$\text{Al} + \text{Si} + \text{OH} + \text{Cl}$	PASi
Poly Fe sulfate	PFS	$\text{Fe} + \text{Si} + \text{OH} + \text{Cl}$	PFSi
Poly Fe chloride	PFC	$\text{Fe} + \text{OH} + \text{PO}_4$	PFP
Poly Al phosphate	PAP	Inorg + Org Composite	
Anionic		PACl + Anionic Polymer	
Poly-silicate	PSi	PACl + Nonionic Polymer	
Activated silica	ASi	PACl + Cationic Polymer	
		PACl + Chitosan	

Table 2
Aqueous hydroxyl $\text{Al}(\text{III})$ species.

Degree of polymerization	Possible chemical formula	Ferron assay
Monomer	Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$	Al_a
Oligomer	$\text{Al}_2(\text{OH})_6^{4+}$, $\text{Al}_2(\text{OH})_5^+$, $\text{Al}_3(\text{OH})_4^{5+}$	
Low-mer	$\text{Al}_6(\text{OH})_{12}^{6+}$, $\text{Al}_6(\text{OH})_{11}^{5+}$, $\text{Al}_8(\text{OH})_{20}^{8+}$	Al_{b1}
Mid-mer	$\text{Al}_{13}(\text{OH})_{32}^{7+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ (Al_{13})	Al_{b2}
High-mer	$\text{Al}_{15}(\text{OH})_{36}^{9+}$, $\text{Al}_{30}\text{O}_8(\text{OH})_{56}^{15+}$ (Al_{30})	
Sol, gel	$(\text{Al}_{13})_n$, $\text{Al}(\text{OH})_3^a$	Al_c
Precipitates	$[\text{Al}(\text{OH})_3]_n^a$	

^a $\text{Al}(\text{OH})_3(\text{s})$ is very special depending on preparation mode and coagulation experiments.

sharp peaks refer to the responses of monomer Al_1 ($\delta = 0$ ppm), tridecamer Al_{13} ($\delta = 62.5$ ppm). The responses of oligomers Al_2 , Al_3 are difficult to distinguish from that of monomer [1,2]. In recent years, the polycation Al_{30} has been observed and assigned in high-temperature conditions [19,20]. Both Al_{13} and Al_{30} can be identified due to their tetrahedral $\text{Al}(\text{O})_4$ core in Keggin structure that yields diagnostic peaks in ^{27}Al NMR spectra. So far, the responses on the ^{27}Al NMR spectrum to be identified are listed in Table 3.

In Table 3, the clusters of $\text{Al}(\text{O})_6$ series beyond Al_3 with the structure of pure octahedral cannot be assigned accurately by ^{27}Al NMR due to their broad peak responded. Originally, the pure octahedral species with the six-member ring structure were suggested as their basic configuration. This structure was proposed on the core-link theory and the building block of aluminum hydroxide gel. It has been accepted by mainly geochemists for many years. However, their existence was suspected and arguable for decades due to lacking of definitive instrumental identity other than potentiometry. In recent years, the hexamer $\text{Al}(\text{O})_6$ clusters were more clearly identified by using the SAXS [10], ab initio molecular dynamics [6], and other methods [24]. These studies demonstrated the existence of the hexamer clusters in solution according to the molecular size determination and structural computation.

2.1. Speciation characterization through ESI-MS

The ESI-MS showed some other promise. Feng et al. had improved the method for identification of Al species in ESI-MS spectrum [25, 26]. The general formula for identification of Al species form was $[\text{Al}_x\text{O}_y(\text{OH})_z(\text{H}_2\text{O})_m]^{(2y+z-3x)+}$. In the mass spectrum, the intensity of peaks often form many independent Gaussian-shaped clusters, shown by the curve. Al species identified from these peaks in one Gaussian-shaped cluster often have the same polymerization degree. The peaks in each cluster splitting at 18, 9, and 5 show that the positive charges of +1, +2, and +3 were identified from Al species. No chloride ligands were present in the formula as a result of the volatile of chlorine in neutralization and desolvation process.

Oligomeric species such as Al_1 , Al_2 , Al_3 , Al_4 , and Al_5 were observed in ESI-MS of AlCl_3 , while high polymeric species of Al_{13} , Al_{16} , Al_{19} , and Al_{20} were presented in their purified Keggin- Al_{13} spectrum. They also proposed that Al_{13} with three type of charges (+1, +2, and +3) was directly transformed from Keggin- Al_{13}^{7+} in the original solution. The decrease of the charges from +7 to +1, +2, and +3 should be mainly ascribed to the fragmentation of hydrogen ligands in the structure of Keggin- Al_{13}^{7+} during the nebulization and desolvation process in mass analyzer. Most of these species have also been identified in many former studies.

Besides, another series of aqueous aluminum clusters of pure $\text{Al}(\text{OH})_6$ octahedras were synthesized and isolated. "Flat" molecular species are favored when the synthesis conditions result in slow hydrolysis, such as oxidation of a metal in an acidic solution or in the presence of trapping or chelating ligands. These $\text{Al}(\text{O})_6$ clusters with 6, 8, 13, 15, and 32 Al atoms have been previously synthesized and structurally characterized, respectively [24,27–29]. They are most commonly synthesized with an aminocarboxylate ligand but also found in purely inorganic solutions as well. The new identified $\text{Al}(\text{O})_6$ clusters are different in structure from six-member-ring configuration. They are so-called flat-series and constructed upon a repeated set of cubane-like moieties arrayed in a lattice of edge-shared but with an octahedra core. The flat- Al_{13} [$\text{Al}_{13}(\text{OH})_{24}^{15+}$]

with the structure of pure $\text{Al}(\text{O})_6$ is also an Al tridecamer but different from either Keggin- Al_{13} [$\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}^{7+}$] or six-member ring Al_{13} [$\text{Al}_{13}(\text{OH})_{32}^{7+}$]. A schematic illustration of the proposed structure of hydroxyl polymeric aluminum species is shown in the Table 4 [1].

2.2. ^{27}Al NMR combined with Ferron assay

The structure of isolated flat clusters is a little different from the hypothetical six-member ring series with the central octahedral core. Nevertheless, both of them are pure $\text{Al}(\text{O})_6$ structure and unassignable by ^{27}Al NMR due to the quadrupole broadening nature of aluminum atoms. To distinguish the species of pure $\text{Al}(\text{O})_6$ structure, the method other than ^{27}Al NMR should be applied.

A new idea has been carried out to distinguish these species. The reactive Al_b was further divided into Al_{b1} as $\text{Al}(\text{O})_6$ species and Al_{b2} as Keggin- Al_{13} according to their different reaction rate with Ferron [8,9, 30–32]. The key difference between Al_{b1} and Al_{b2} was that the reaction kinetic constant of Al_{b1} was an order of magnitude higher than that of Al_{b2} . Less discrepancy was observed by using Al_{b2} instead of Al_{b1} to compare with the Keggin- Al_{13} , which confirmed this speculation. It was demonstrated by this combined procedure that the Al_{b1} series of $\text{Al}(\text{O})_6$ clusters actively existed at the area of $B(=\text{OH}/\text{Al ratio})$ around 0.5–1.5 and the Keggin- Al_{13} clusters dominated at B above 1.0–2.5. Then the position of $\text{Al}(\text{O})_6$ clusters in the system of hydroxy-aluminum can be determined along the ^{27}Al NMR spectrogram or even B [$\text{OH}/\text{Al ratio}$] sequence.

The K-value assay was based on the assumption that the reactions between Ferron and aluminum species conform to pseudo-first-order, and thus an equation could be applied to simulate the reaction:

$$\text{Al}_t = \text{Al}_0 + \text{Al}_{b1}(1 - \exp(-k_1t)) + \text{Al}_{b2}(1 - \exp(-k_2t)) + \text{Al}_c$$

Generally, the mononuclear aluminum and Ferron was regarded to react instantaneously, and Al_c was inert to Ferron in this reaction. Ye et al. calculated the k value of PACI with various basicities and proposed that the k_1 value of $\text{Al}(\text{O})_6$ fractions falls into a range of $(0.82 - 18.89) \times 10^{-3} \text{ s}^{-1}$ and k_2 value of Keggin- Al_{13} falls into a range of $(0.09 - 0.87) \times 10^{-3} \text{ s}^{-1}$ shown in Table 5 [30]. This could be used as a quantitative criteria to distinguish the species of different structures.

3. Hydrolysis pathway of aluminum salts in aqueous solution

3.1. Spontaneous hydrolysis

When the $\text{Al}(\text{III})$ salts are added and dissolved in aqueous solution, the hydrolysis reaction occurs spontaneously. This type of hydrolysis carries out automatically as a result of the typical aqueous chemical equilibrium. There will be firstly the transformation between the mononuclear complexes according to the corresponding pH and Al concentration.

The reaction inclines to precipitate at a rather low level of Al concentration. However, the polynuclear clusters with double hydroxyl bridges need to be formed before the precipitation takes place. The primary

Table 3
Possible responses of Al clusters on ^{27}Al NMR spectrum.

Al_x	Al_1	Al_2	Al_3	Al_6	$\text{Al}_6\text{-Al}_{13}$	$\text{Al}_6\text{-Al}_{30}$	Al_{13}	Al_{30}	$\text{Al}(\text{OH})_4^-$
δ ppm	0	2–3	5	10–12	10–12	12–15	62.5	70	80
n	$\text{Al}(\text{O})_6$	$\text{Al}(\text{O})_6$	$\text{Al}(\text{O})_6$	$\text{Al}(\text{O})_6$	$\text{Al}(\text{O})_6$	$\text{Al}(\text{O})_6$	$\text{Al}(\text{O})_4$	$\text{Al}(\text{O})_4$	$\text{Al}(\text{O})_4$

Table 4
The structure of hydroxyl polymeric aluminum determined by single crystal.

Al(O) ₆		Al(O) ₄	
Poly-degree	Polyhedron	Poly-degree	Polyhedron
Al ₂		ε-K-Al ₁₃
Al ₈		δ-K-Al ₁₃
M-Al ₁₃		Al ₃₀

dimers and trimers may be transformed further to the oligomers and polymers,

Owing to the change of solution pH, Al concentration, or aging, the transformation course will proceed further. The hydrolysis and polymerization reactions will go along alternately. When it reaches to a certain degree, the hydrolysis will be preferable to enter the polymerization stage because the increasing charges become strong enough to obstruct further access of the clusters. The net charge of the polymers will decrease due to further hydroxylation and then the precipitation will finally happen. The turning point is likely at the range of OH/Al = 2.2~2.5 and the maximum for the net charge could not be too high.

3.2. Forced hydrolysis

The Keggin-Al₁₃ species are considered as the most active coagulating components in PACl products. They are yielded in the special operational conditions either in laboratory by base titration or in the industrial production stage by dissolution of aluminum minerals. These processes generally adopted an intensive way of neutralization involving strong acid or base. In the mild spontaneous hydrolysis condition, it is difficult to produce the clusters like Keggin-Al₁₃ with a tetrahedral core. This is because the transform of double hydroxyl link (olation) between Al atoms to oxygen link (oxylation) or from the octahedral coordination to tetrahedral is promoted to occur at the higher pH and

in-homogenous neutralizing conditions. Usually, in the base titration situation, the Keggin-Al₁₃ generally begins to appear at pH higher than 3.5.

Many experimental results demonstrated that the formation of Keggin-Al₁₃ needs precursors of either dimer or trimer and especially tetrahedral aluminum species, which must be first produced in solution or added as external reagent. In the common condition of base titration, the strong base injection creates micro-interfaces of pH junction in acid aluminum solution. It thereby promotes the self-assembling of precursors from both sides. This reaction in nanometer scale is a forced hydrolysis derived by the abrupt shock of pH. The resultants through forced hydrolysis would be an artificial outcome of Keggin-Al₁₃ different from flat-Al₁₃ produced by spontaneous hydrolysis.

3.3. Dual-hydrolysis model

A dual-hydrolysis model (Fig. 1) is proposed by comprehensive consideration of both the spontaneous and forced hydrolysis [1,33]. When forced hydrolysis takes place, the pH of the solution will be buffered to some extent and the presence of dimer or trimer which is required for Keggin-Al₁₃ to be formed. The spontaneous hydrolysis must then be promoted to transfer based on the hydrolytic equilibrium. Consequently, during the base addition step, both of the two hydrolysis reactions would be pushed forward in solution parallel and exchanging their species. The artificial forced hydrolysis may interrupt the spontaneous equilibrium to compel the system to become a steady state.

Accordingly, the Keggin-Al₁₃ clusters are the synthesized products from dual-hydrolysis processes. The dual-hydrolysis model can precisely describe the constitution and transfer pathways of the multiple reactions for Al(III) clusters in solution.

4. Stability of Keggin-Al₁₃ in PACl

Owing to the steady Al(O)₄ core, the Keggin-Al₁₃ species in artificial PACl solution and after dosing to water exhibit high stability to maintain their structure and resist to further hydrolysis. That is different from the hydroxyl Al(O)₆ species formed by alum or AlCl₃ in spontaneous hydrolysis after dosing.

The results of speciation characterization at PACl dose of 2×10^{-4} mol Al/L are summarized in previous publication [9]. It is indicative that pH has significant effect on further speciation transformation of PACl corresponding with the OH/Al values. Further transformation of PACl species after dosing under various conditions depends largely on the original composition. The PACls at low OH/Al ratio exhibit a significant change of species under various conditions. While the high OH/Al ratio PACls exhibits efficient speciation stability and tends to maintain the original speciation distribution. It shows also that the Al_a fractions in the primary coagulants are the most labile species. After dosing, it would quickly transform into Al_b and finally Al_c depending

Table 5
The K-value criteria of PACl with different basicities.

Sample	K value (10^{-3}S^{-1})	
	K ₁	K ₂
B = 0	13.91	0.11
B = 0.5	13.86	0.75
B = 0.8	18.89	0.82
B = 1	17	0.61
B = 1.2	15.78	0.74
B = 1.5	1.01	0.11
B = 1.8	1.04	0.09
B = 2	0.94	0.11
B = 2.2	0.99	0.12
B = 2.5	0.82	0.14
Al ₁₃	0.87	0.87

Fig. 1. The dual-hydrolysis model of Al(III).

on the reaction conditions. The polymeric and colloidal species, once preformed, are quite stable. In addition, the Al_b and Al_c species formed after dosing exhibit quite different nature with the preformed species as shown under further aging period [6,9].

A significant difference between the alum and PACIs can also be observed. The traditional coagulant-alum, after dosing into water of middle pH range, is hydrolyzed to species containing mainly Al_c . They consist of sol and precipitates with low surface charge density. Their coagulation effects and mechanism are distinct from the PACI because the Keggin- Al_{13} clusters with stronger charge density can retain their conformation to affect the particulates directly.

New technologies to tailor-make Al_{13} -PACI have been proposed and provide other direct verifications on the stability of Al_{13} [5,34–37]. The pure Al_{13} solutions can be prepared at high concentration, 2 mol Al/L, which is similar concentration to the liquid industrial PACI products.

5. Coagulation mechanism of hydroxy-aluminum clusters

5.1. Adsorption and surface coverage

PACI and alum as coagulants adsorbed on particles via different species and mode. PACI with the Keggin- Al_{13} clusters adsorbed directly to particle surface by complexation and underwent further hydrolysis in situ on the surface hydroxyl sites. Their adsorption isotherm appeared to be the Langmuir type with monolayer formation due to the inter-repulsion of the residual charges. Alum adsorbed mainly with the precipitated $Al(OH)_3(am)$ by attraction and adhesion and neutralized the particles by their low charges. Their adsorption isotherm presents the Freundlich type of multi-layer formation with enormous amorphous precipitates [38].

The fractional surface coverage on particles along the coagulation course can be estimated by the ratio of adsorbed coagulant amounts to total surface sites on silica microspheres in suspension. The maximum surface coverage of PACI was around 0.4, whereas surface coverage of alum accumulated enormously. Corresponding to the coagulation process, the optimum effects for PACI occurred at the coverage of only around 0.1 and the restabilization occurred long before the maximum coverage. As for the alum, the optimum coagulation appeared at coverage around 0.2–0.3.

5.2. Coagulation of silica microspheres suspension

Based on the coagulation diagram, the alum exerted its function mainly by the low-charged $Al(OH)_3(am)$ to cover the surface and adhere the particles with a combined actions of charge neutralization and sweeping sedimentation. The Keggin- Al_{13} clusters in PACI maintain their polycation structure to perform the surface complexation and deposition on particles and to aggregate them to form flocs. The distinct performances of coagulation between the two sorts of coagulants were investigated further by using several stoichiometric methods.

The suspensions of silica microspheres (2–3 μm) were coagulated with alum and PACI 2.2, respectively. The results are shown in the Fig. 2 [38]. The chemical speciation of the coagulants was identified both by Ferron assay and ^{27}Al NMR. The whole coagulation process was simulated by jar test with residual turbidity and zeta potential determination. The results showed that the optimum dosage for PACI was achieved at 1–2 $\mu mol/L$ before the IEP but the restabilization appeared after overdosing. The optimum dosage for alum was 4–5 times of that for PACI but appeared just around IEP and no restabilization occurred with overdose.

5.3. Microfloc aggregation and simplified DLVO simulation

The hydroxyl aluminum clusters exhibited significant difference on microfloc formation and the aggregation kinetic behaviors. The

increasing volumes of microfloc via aggregation were observed by the PDA system and their fractal dimensions were calculated based on static laser scattering absorption. The investigation was carried out under the conditions of three different dosages. Under the low dosage of 10^{-6} mol/L, the PACI microfloc aggregated rapidly to form compact flocs, but the alum microflocs remained unchanged. Under the higher dosage of 10^{-5} mol/L, the PACI particulates aggregated slowly but the alum floc enlarged very fast. Under the high overdosing condition of 10^{-4} mol/L, the PACI flocs started to be dispersed due to restabilization, and the alum flocs became voluminous.

The traditional DLVO theory is an ideal and multi-factorial model for the estimation of potential energy between homological particles. Its pertinent application to coagulation of aquatic particulates could be only at a simplified simulation level. The calculation scene would be the interaction potentials between the particulates charged with preliminary adsorbed coagulants in the step to form the microflocs. The resulted integrated potential curves showed that beyond the fade away of the potential peak, the second minimum appeared at about 20 nm of distance between particles. When the second minimum of potential achieved to the deep over 10 kT, the particulates can be effectively aggregated through the dominated attractive potential.

The simulated results from the various concentrations of aluminum were closely corresponding to the dosage in coagulation test for both coagulants, respectively.

5.4. Morphological observation

The microfloc of purified Keggin- Al_{13} under atomic force microscope is a branched chain as shown in Fig. 3. Their units are at the nanometer scale.

The electromicroscopy images showed that the microflocs made by PACI at low optimum dosage are patched bridging aggregates and that at overdose are dispersed away particles. On the other hand, the microflocs coagulated by alum at the same low dosage remained like single particulates but transformed to enormous sweeping flocs at overdose.

By using the colloid probe microscopy, it was observed more microscopically. The images looked like flocs that assumed patched and covered models, respectively.

5.5. Coagulation calculation model

According to above studies, it was demonstrated that the coagulation mechanism between alum and PACI are distinctly different mainly due to their chemical speciation and structural stability to pH and other factors in solution after dosing.

The PACI dominated by Keggin- Al_{13} clusters persisted to remain their artificially produced structure and adsorbed to particles via surface complexation. On the surface, they may be hydrolyzed further in the reaction with surface OH groups to build patches there. The high charged Al_{13} may neutralize simultaneously more particles with their residual charges and link them with electro-patches into aggregates and microflocs to be removed. Sometimes, these strong charged clusters tend to promote the restabilization of particles during overdosing.

After dosing, the alum dissolved and spontaneously hydrolyzed to form $Al(O)_6$ octahedral series species. They may exist as oligomers or clusters with pure double OH linkage structures and easily transformed to sol and precipitates under the conditions of around the natural pH range and common Al dosage. The low charged amorphous precipitates may be adsorbed or adhered to particles, neutralize them and cover on their surface to form microflocs. They can further bundle more particles to make enormous flocs and sweep up other pollutants.

The PACI coagulants can coagulate and flocculate pollutants in water treatment process more economically (lower dosage) than alum. However, they require more accurate dosing in operation to avoid

Fig. 2. Mechanistic difference of coagulation of silica microspheres with alum and PACI 2.2.

restabilization. Therefore, a quantitative model of coagulation with inorganic polymer flocculants was developed by using PACI as an example. Application of a modified precipitation charge-neutralization model (M-PCNM) was examined and discussed, including variation of dose, pH, and B value on the resulting coagulation diagram. The model was improved by using measured Al fractions as model inputs. The experimental results showed that there exists a remarkable difference in coagulation with various PACI formulations in accordance with the different species being performed. This indicates that the assumption of all the surface species consisting of the same aluminum hydroxide solids is not correct, and some modification of the PCNM is therefore needed. By invoking different final hydroxide precipitates, the M-PCNM can be used quite well to predict the general behavior of coagulation with IPF-PACI (Fig. 4). In addition, they cannot exert their superiorities completely in traditional water treatment reactors that were designed mainly for alum to form bulky flocs to facilitate sedimentation. The water treatment technologies more compatible to tailor-made PACI coagulants would be the surface contact coagulation units like microfloc filtration, flotation, membrane and fiber separation, etc.

6. Conclusions

The relative importance of three different Al species (Al_a, Al_b, Al_c) defined by timed complexation reaction rate measured by using ferron reagent in polyaluminum chloride (PACI) was investigated in terms of DOC, UV₂₅₄, and turbidity removal efficiencies. The results show that DOC removal is correlated well to the content of Al_b. Removal of UV₂₅₄ is determined by the content of Al_b and Al_c, particularly Al_c. Al_a shows a strong ability to react with some unsatisfied coordinate bonds of organic matter to facilitate particle and DOC removal [17]. The fraction distributions of NOM and residual Al after coagulation in solution, colloid, and sediment were analyzed as changes of coagulant dosage and pH. Medium polymerized Al species (Al_b) can destabilize particle and NOM efficiently, while some flocs formed by Al_b are not large and not easy to precipitate as compared to those formed by colloidal of solid Al species (Al_c). Thus, Al_c could adsorb and remove NOM efficiently [39].

As shown by the many examples covered in this review, different hydroxyl aluminum had different coagulation mechanisms. The species

Fig. 3. The microphotological observation of the floc formation: 1) AFM; 2) TEM; 3) CPM.

formation, stability, and transformation of various hydrolyzed aluminum clusters were complicate. Many of technologies were used to analyze the chemical speciation of hydroxyl aluminum clusters, and different hydrolysis pathways of aluminum salts in aqueous solution were presented to better understand the Al speciation distribution. But the hydrolysis pathway of aluminum salts in aqueous solution was speculative that need more laboratory proofs. The stability of Keggin- Al_{13} was affected by solution pH, and the PACIs at low OH/Al ratio exhibit a significant change of species under various conditions, while the high OH/Al ratio PACIs exhibit efficient speciation stability and tend to maintain the original speciation distribution. The alum exerted its function mainly by the low-charged $\text{Al}(\text{OH})_3$ to cover the surface and adhere the particles with a combined actions of charge neutralization and sweeping sedimentation. Keggin- Al_{13} clusters in PACI maintain their

polycation structure to perform the surface complexation and deposition on particles and to aggregate them to form flocs. The microfloc of purified Keggin- Al_{13} under atomic force microscope is a branched chain, and their units are at the nanometer scale.

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Fig. 4. Micro-interface model and patch coagulation schematic chart.

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