Study on the hydrolysis/precipitation behavior of Keggin Al$_{13}$ and Al$_{30}$ polymers in polyaluminum solutions

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**Abstract**

The hydrolysis/precipitation behaviors of Al$^{3+}$, Al$_{13}$ and Al$_{30}$ under conditions typical for flocculation in water treatment were investigated by studying the particulates' size development, charge characteristics, chemical species and speciation transformation of coagulant hydrolysis precipitates. The optimal pH conditions for hydrolysis precipitates formation for AlCl$_3$, PAC$_{Al13}$ and PAC$_{Al30}$ were 6.5–7.5, 8.5–9.5, and 7.5–9.5, respectively. The precipitates' formation rate increased with the increase in dosage, and the relative rates were AlCl$_3$ $>$ PAC$_{Al30}$ $>$ PAC$_{Al13}$. The precipitates' size increased when the dosage increased from 50 $\mu$M to 200 $\mu$M, but it decreased when the dosage increased to 800 $\mu$M. The Zeta potential of coagulant hydrolysis precipitates decreased with the increase in pH for the three coagulants. The iso-electric points of the freshly formed precipitates for AlCl$_3$, PAC$_{Al13}$ and PAC$_{Al30}$ were 7.3, 9.6 and 9.2, respectively. The Zeta potentials of AlCl$_3$ hydrolysis precipitates were lower than those of PAC$_{Al13}$ and PAC$_{Al30}$ when pH $>$ 5.0. The Zeta potential of PAC$_{Al30}$ hydrolysis precipitates was higher than that of PAC$_{Al13}$ at the acidic side, but lower at the alkaline side. The dosage had no obvious effect on the Zeta potential of hydrolysis precipitates under fixed pH conditions. The increase in Zeta potential with the increase in dosage under uncontrolled pH conditions was due to the pH depression caused by coagulant addition. Al–Ferron research indicated that the hydrolysis precipitates of AlCl$_3$ were composed of amorphous Al(OH)$_3$ precipitates, but those of PAC$_{Al13}$ and PAC$_{Al30}$ were composed of aggregates of Al$_{13}$ and Al$_{30}$ respectively. Al$^{3+}$ was the most un-stable species in coagulants, and its hydrolysis was remarkably influenced by solution pH. Al$_{13}$ and Al$_{30}$ species were very stable, and solution pH and aging had little effect on the chemical species of their hydrolysis products. The research method involving coagulant hydrolysis precipitates based on Al–Ferron reaction kinetics was studied in detail. The Al species classification based on complex reaction kinetic of hydrolysis precipitates and Ferron reagent was different from that measured in a conventional coagulant assay using the Al–Ferron method. The chemical composition of Al$_{13}$, Al$_{30}$ and Al$_{1}$ depended on coagulant and solution pH. The Al$_{30}$ measured in the current case was different from Keggin Al$_{13}$, and the high Al$_{30}$ content in the AlCl$_3$ hydrolysis precipitates could not be used as testimony that most of the Al$^{3+}$ was converted to highly charged Al$_{13}$ species during AlCl$_3$ coagulation.

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1. Introduction

Coagulation/flocculation is commonly used as pretreatment process in water and wastewater treatment for destabilizing dissolved and colloid impurities, and producing large floc aggregates that can be removed from the water in subsequent sedimentation/floation and filtration processes. Coagulant is key to flocculation efficiency. Inorganic polymer flocculants, especially partially pre-hydrolyzed Al salts such as polyaluminum chloride, have been developed and used worldwide since the 1980s (Jiang, 2001). Aluminum hydrolysis reaction plays a very important role in destabilizing and aggregating the suspended particles and organic matter in coagulation processes. Coagulant is usually added to the water to be treated without dilution and pretreatment. After dosing into water, it is diluted, and it undergoes a serial of hydrolysis, polymerization, aggregation and precipitation processes, which result in various metastable and transient species existing in bulk solution. The hydrolysis of polymeric Al coagulants is quite different from that of monomeric Al coagulants. Generally, the conventional Al(III) salt coagulants have lower coagulation efficiency than...
polymeric Al coagulants because its hydrolysis is hard to be controlled. However, the hydrolysis degree of polymeric Al coagulants can be controlled during manufacture, and the formation rate of hydroxide precipitates upon dilution is slowed, which consequently allows the positively charged polymeric Al species to remain for a greater duration, and thereby enhances the charge neutralization capacity of polyaluminum coagulants (Tang and Luan, 1996; Matsui et al., 1998; Duan and Gregory, 2003). Maximizing the active species content and optimizing the species distribution were the guidelines for coagulant production. In polyaluminum coagulants, the highly charged Al13 species ([AlO4]2Al12(OH)24(H2O)12)7þ, due to its high charge neutralization capacity and high species stability against hydrolysis, was considered to be the optimal active species for coagulation. So it has received the most attention (Bi et al., 2004; Gao et al., 2005). Al30 species ([Al2O2]2Al28(OH)56(H2O)26)18þ was first discovered in 27Al nuclear magnetic resonance (NMR) spectra about twenty years ago (Akitt and Farthing, 1981; Fu and Nazar, 1991). But its structure and stoichiometry were not determined, until 2000 it was characterized by Allouche et al. (2000) and Rowsell and Nazar (2000) using X-ray diffraction and in situ 27Al NMR. Al30, with 2 nm in length (Phillips et al., 2003), was the largest Al polycation that was identified in polyaluminum solution. Al30 formed by further polymerizing two Al13 and four Al monomers under hydrothermal treatment (Allouche and Taulelle, 2003; Shafran and Perry, 2005a). Al30 species was more thermal resistant and more stable in low pH solution than Al13 species (Chen, 2006; Chen et al., 2007). It became a dominant polymeric Al species in highly concentrated polyaluminum solutions (Shafran et al., 2005b; Chen et al., 2005). Our recent research results indicated that Al30 species was more effective for turbidity removal than Al13 species. Compared with Al13 species, Al30 achieved effective turbidity removal within a broad dosage range and a wide pH range (Chen et al., 2006a). However, the detailed coagulation mechanism of Al30 species is unclear.

Two main flocculation mechanisms were usually used to explain the observed flocculation phenomena: (1) compression of electric double layers of colloidal particles, adsorption–charge neutralization and adsorptive-bridging by the positively charged Al species in treated water; (2) precipitation–charge neutralization, floc enmesh and sweep by coagulant hydrolysis precipitates (Duan and Gregory, 2003; Wang et al., 2002; Dentel, 1988). It was generally thought that the conventional Al salts performed mainly through the second flocculation mechanism due to their rapid hydrolysis and precipitation, and the first flocculation mechanism played a more important role than the second one when polyaluminum coagulants were used due to the high stability of polymeric Al species (Luan, 1997). For a practical flocculation process, the flocculation effects are the combination of the above various coagulation mechanisms. The dominant flocculation mechanism depends on the coagulant and dosage employed, the chemical compositions of the treated water, etc. So the coagulation performance of polyanionic coagulant is not only related to Al species distribution in coagulants, but also closely related to the hydrolysis, polymerization and precipitation behavior of coagulants after dosing into water. The hydrolysis and polymerization rates, as well as the structure, surface properties and charge characteristic of freshly formed hydrolysis precipitates, are very significant to the coagulation performance of polyaluminum coagulants.

Although there were some investigations on hydrolysis/precipitation behavior and precipitates properties of Al salts and polymeric Al species, little information was available regarding to the hydrolysis/precipitation of Al13 and Al30 species in water treatment flocculation process. Benschoten and Edzwald (1990) studied the chemical aspects of alum and polyaluminum chloride during coagulation. The results indicated that the precipitates derived from alum and polyaluminum chloride possessed different light scattering characteristics, electrophoretic mobility and solubility. The solid phase of alum was composed of amorphous Al(OH)3, and the precipitates of polyaluminum chloride retained the polymeric structure. Solomentseva et al. (1999, 2004) studied in detail the effect of working solution concentration, dosage, pH and ionic strength on the surface properties and aggregation of basic aluminum chloride/sulfate hydrolysis products. Wang et al. (2004) studied the species transformation of polyaluminum coagulants with different OH/Al ratios using Al–Ferron complex colorimetry. The results indicated that polyaluminum chloride coagulants with high OH/Al ratio remained higher speciation stability than coagulants with low OH/Al ratio under various conditions.

In this work, the hydrolysis/precipitation behaviors of Al13 and Al30 under conditions typical for flocculation in water treatment were compared and studied. AlCl3 was used as a reference. The purposes of the research are: (1) to compare the hydrolysis rate and species stability of Al13, Al30 and AlCl3; (2) to study the differences of morphology, structure and charge characteristics of hydrolysis precipitates of Al13 and Al30 species; (3) to provide a theoretical interpretation for the coagulation performance differences between Al13 and Al30.

2. Materials and methods
2.1. Materials

The reagents used in this work were all of analytical grade except those pointed out specifically. All solutions were prepared using deionised water. The coagulant containing high content of Al13 (abr. PACAl13) was prepared by slowly neutralizing 1.0 M AlCl3 aqueous solution with 0.6 M NaOH solution at 80 °C under vigorous stirring until the Al hydrolysis ratio \( B = [\text{OH}] / [\text{Al}] \) reached 2.4. The coagulant containing high content of Al30 (abr. PACAl30) was prepared by heating PACAl13 at 95 °C for 12 h under stirring and refluxing. Both PACAl13 and PACAl30 had a total Al concentration \( [\text{Al}] \) of 0.2 M.

Two coagulants were stored at room temperature for 5 days before analysis, characterization and experimentation. \( [\text{Al}] \) was measured by inductively coupled plasma-atomic emission spectroscope (Vista-MPX ICP-AES, Varian). B value was measured by chemical analysis according to the Chinese standard method (GB 15892-1995). The pH values were measured using a pH meter (Orion 710A). The Al species distribution in these two coagulants and 0.2 M AlCl3 aqueous solution (abr. AlCl3) was determined by the time-developed Al–Ferron complex colorimetry (abr. Al–Ferron method) on UV–vis spectrophotometer (DR/4000U, Hach) and by high-field 27Al NMR method on Fast Fourier Transformation spectrometer (JNM-ECA600, JEOL). Based on the difference of the dissociation and complex reaction kinetic rate between Ferron and Al species, Al species in coagulants were divided into three types: monomeric species (Alm) reaction with Ferron within 1 min, planar oligomeric and medium polymeric species (Alc) reaction with Ferron from 1 to 120 min, and three-dimensional species or sol–gels (Alg) reaction with Ferron after 120 min or non-reaction with Ferron. Alm was obtained by Al13 minus Al30 and Alg (Parker and Bertsch, 1992). In 27Al NMR analysis, the aluminum at 0 ppm was multiplied by 13 and 15, respectively. This is to obtain the concentration of Al13 and Al30, respectively. The concentration of Al species that cannot be clearly detected (Alu) was calculated by Alm minus Al13 and Al30. The detailed coagulants’ preparation and characterization methods can be found in our research.
previous reports (Chen et al., 2006b, 2007). The detailed specifications of the three coagulants used in this work are listed in Table 1. In order to avoid changing Al species arose from dilution, all coagulants were used directly.

Synthetic water containing 5.0 mM NaHCO₃ and 5.0 mM NaNO₃ was prepared by diluting a calculated amount of 0.5 M NaHCO₃ and 0.5 M NaNO₃ aqueous solution with deionised water. Then the turbidity of synthetic water was adjusted to about 2 NTU with a very small amount of kaolin stock suspension prepared according to Chen et al. (2006a). The kaolin particles in synthetic water were used as nucleating agent, and were helpful to eliminate the uncertainty and randomness during coagulants’ nucleation process, which thereby enhanced the reproducibility of experimental results. The pH of the synthetic water was adjusted to predetermined values with 0.1 M HCl solution or 0.1 M NaOH solution before used.

2.2. Measurement of size development of coagulant hydrolysis precipitates

The particle size development of hydrolysis precipitates after coagulants were added into the synthetic water was measured on a modified Laser Particle Size Analyzer (LPSA) (Mastersizer 2000, Malvern). The inlet and outlet of the LPSA were connected to a jar test flocculator with a single-paddle stirrer, and a peristaltic pump was connected in the outputs tubes. The suspension in the beaker of the flocculator was sucked into the LPSA by the peristaltic pump continuously for online measuring particle size during coagulants’ hydrolysis process. The measurement procedures were as follows: 1000 mL synthetic water was added into the beaker. The stirrer was adjusted to 200 rpm. The peristaltic pump was started up, and the rotational speed and clamp of the peristaltic pump should be adjusted carefully in case the hydrolysis precipitate was crushed by peristaltic pump. After the instrument background data were measured, a measured amount of coagulant was added into the synthetic water to reach the target Al concentration. The solution was stirred rapidly at 200 rpm for 2 min after coagulant dosed, followed by slow-stirring at 30 rpm for 15 min. The mean diameter of the precipitates was measured once every 20 s after coagulant addition. The pH value of the synthetic water was depressed by the acidity and hydrolysis of coagulants. In order to ensure the coagulant hydrolyzed under fixed pH condition, 0.1 M NaOH solution was added to compensate the pH decrease using an automatic titrator (716 DMS Titirno, Metrohm Co.). All experiments were repeated at least three times in this work.

2.3. Measurement of Zeta potential of coagulant hydrolysis precipitates

The experiments were carried out on a jar test flocculator with a single-paddle stirrer. 1000 mL synthetic water sample was added into the beaker, and a measured amount of coagulant was pipetted into the synthetic water to give a certain Al concentration under rapid stirring. The solution was stirred rapidly at 200 rpm for 2 min after coagulant dosed, followed by slow-stirring at 30 rpm for 1 min. A sample was taken using a syringe immediately after the 1 min slow-stirring for the measurement of Zeta potential (Zetasizer 2000, Malvern). The pH decrease caused by coagulants addition was compensated as the method described in Section 2.2.

2.4. Measurement of Zeta potential of re-suspension of coagulant hydrolysis precipitates

1000 mL synthetic water with pH = 7.5 was added into the beaker of a jar test flocculator with a single-paddle stirrer. A measured amount of coagulant was added into the water under rapid stirring to give an Al concentration of 800 µM (calculated by Al³⁺). The solution was stirred rapidly at 200 rpm for 2 min after coagulant dosed, followed by slow-stirring at 30 rpm for 15 min, and then settled for 30 min. The fixed condition of pH = 7.5 was controlled using the method described in Section 2.2. After 30 min settlement, the supernatant liquid was decanted, and 200 mL suspension of coagulant hydrolysis precipitates was collected and divided into seven parts. Every part of the precipitates was diluted with 200 mL deionised water. The pH of the dilution was adjusted to the desired values with 0.1 M HCl solution or 0.1 M NaOH solution. Zeta potential of the solution was measured immediately on Zetasizer 2000 after the pH adjustment.

2.5. Chemical speciation of coagulant hydrolysis precipitates

200 mL suspension of coagulant hydrolysis precipitates was obtained according to the jar testing procedure described in Section 2.4 except the dosage of Al was 200 µM. Three methods were taken to study the Al chemical speciation in the suspension using Al–Ferron method: (1) The Al–Ferron analysis was carried out without any pretreatment of the suspension; (2) The suspension was adjusted to a pH of 4.0 with 0.1 M HCl solution, and then immediately sampled for Al–Ferron analysis; (3) The suspension was filtered with 0.45 µm microporous membrane, and the filtrate was collected and sampled for Al–Ferron analysis.

The Alferon reagent was prepared referring to the methods described by Parker and Bertsch (1992). The operation procedures were as follows: 5 mL Al containing sample and 15 mL Ferron reagent were added into a 50 mL colorimetric tube, and it was diluted to the scale with deionised water. The solutions were mixed vigorously and were pipetted into a 10 mm path-length quartz cuvette. Then it was placed into a UV–vis spectrophotometer (DR/4000U, HACH) to test its absorbance at a wavelength of 370 nm at a frequency of one reading per minute. All these operations finished within 1 min. The pseudo first-order rate constant (k) of Al–Ferron complex reaction within 1–30 min was calculated according to the method described by Luan (1997).

2.6. Dilution experiment and measurement of chemical speciation of hydrolysis precipitates

Generally, the dosage of polyaluminum coagulants is about 10⁻⁴ mol/L order of magnitude during flocculation process. In order to investigate the Al species distribution after the coagulants were dosed into water, the coagulants were diluted to Al concentration of 2 × 10⁻⁴ mol/L using model water under fixed pH condition, and the Al species distribution in the diluent was measured by Al–Ferron method at different dilution time. The pH decrease of the model water caused by coagulants addition was compensated as the method described in Section 2.2. The model water was prepared by adjusting the alkalinity, electrolyte and pH of deionised water to target values using 0.5 M NaHCO₃, 0.5 M NaNO₃, and 0.1 M HCl or 0.1 M NaOH solution, respectively.
3. Results and discussion

3.1. Effect of dosage on size development of coagulant hydrolysis precipitates

Different dosages of AlCl₃, PAC₆₃ and PAC₃₀ were added into the synthetic water at fixed pH = 7.5. The precipitates’ size developments of hydrolysis precipitates measured by online LPSA are displayed in Fig. 1. As can be seen from Fig. 1, the particle diameter (d₅₀) increased rapidly after a certain induction period (period from the coagulant dosing to the beginning of rapid growth of precipitates), and then leveled off or decreased slightly for all three coagulants. The induction periods and the ultimate particle size depended on the coagulant and dosage. The precipitates’ sizes were very small during the induction period, and the tiny increase of particle size was due to the coagulation of the small amount of kaolin existed in synthetic water by charge neutralization.

For all three coagulants, the formation rate of hydrolysis precipitates increased with the increase in dosage, and the induction periods reduced. When the dosage increased from 50 µM to 200 µM, the precipitates’ size increased, but when the dosage increased to 800 µM, the precipitates’ size decreased instead for all three coagulants, especially for AlCl₃. The reason that the precipitates’ size decreased at a dosage of 800 µM need further investigated. This maybe resulted from the transitory low pH shock caused by high dosage of coagulants addition suddenly. The pH compensation by automatic titration was hysteretic to the solution pH decrease. The higher the coagulant added, the greater the hysteresis effect was. A large number of small precipitates formed initially at low pH conditions possessed high charges and were difficult to aggregate as dense particles when the solution pH restored 7.5.

Comparing the size development trajectory of hydrolysis precipitates of the three coagulants, the precipitates’ size of AlCl₃ was obviously larger than that of PAC₆₃ and PAC₃₀. There was no obvious difference on hydrolysis, aggregation and growth rate between PAC₆₃ and PAC₃₀ under high dosage conditions (100–800 µM). Al³⁺ in AlCl₃ underwent rapid hydrolysis, aggregation and precipitation, and ultimately converted to amorphous Al(OH)₃ sediment, so the induction period was short, and the repulsion among these precipitates was small due to its low charge. Although the low charge and small repulsion favored the rapid aggregation and growth of precipitates, the hydrolysis precipitates of AlCl₃ were fragile because the combination between these particles was physical aggregation. The broad and non-uniform particle size distribution could be seen clearly during AlCl₃ hydrolysis and precipitation experiments. However, Al₁₃ and Al₃₀ species in PAC₆₃ and PAC₃₀, respectively, were more stable and more tolerant to alkaline hydrolysis and aggregation than Al³⁺ after dosing into water. Al₁₃ and Al₃₀ species aggregated and grew up slowly via by deprotonation of external water molecules of these species. Because the hydrolysis precipitates derived from PAC₆₃ and PAC₃₀ were mainly composed of repeated Keggin Al₁₃ and Al₃₀ structural units (Bradley et al., 1993), their hydrolysis was not complete. The hydrolysis products possessed high positive charge, and the repulsive force among these precipitates was very large. And correspondingly, the hydrolysis and aggregation of PAC₆₃ and PAC₃₀ became slow, so the size of hydrolysis precipitates of PAC₆₃ and PAC₃₀ was relatively small as compared to that of AlCl₃.

3.2. Effect of pH on size development of hydrolysis precipitates

The pH of raw water has an important effect on the coagulation performance of coagulants. Fig. 2 displays the particles’ size development of hydrolysis precipitates when the three coagulants were added into synthetic water with different pH values. As can be seen from Fig. 2, the optimal pH value for AlCl₃ hydrolysis was about 6.5–7.5, the particle size reached 350 µm at this pH range. But the particles’ size decreased below 250 µm when the pH raised to
aggregates under this pH condition. PACAl30 produced large size particles when it was added into synthetic water with pH = 7.5–9.5. It precipitated faster than PACAl13 under pH = 7.5. After dosing into synthetic water with pH = 6.5, PACAl30 could build a certain size of precipitates though the induction period was long. The above results indicated that PACAl30 is easier to hydrolyze and precipitate than PACAl13 in weak acidic and alkaline water.

3.3. Charge characteristics of coagulant hydrolysis precipitates

The charge characteristics of coagulant hydrolysis precipitates are important to the coagulation performance of coagulants, especially for the coagulation mechanisms of precipitation–charge neutralization or absorption–charge neutralization. The effect of the pH of synthetic water on the particles’ Zeta potential of coagulant hydrolysis precipitates is shown in Fig. 3. Two experimental methods had been adopted to investigate the variation of particles’ Zeta potential with the pH. In the first method, the hydrolysis precipitates were prepared in synthetic water under fixed pH = 7.5, then it was separated, diluted and the pH was adjusted to different values for Zeta potential measurement (Fig. 3a). In the second method, the Zeta potentials of hydrolysis precipitates were

8.5, and when the pH raised further and reached 9.5, the soluble Al(OH)4− existed in solution, and there was no precipitates formation. The optimal pH for PACAl13 hydrolysis and precipitation was 8.5–9.5. PACAl13 did not produce precipitates in synthetic water with pH = 6.5, which indicated that Al13 species in PACAl13 remained relative stable, and it hydrolyzed to form dissoluble Al13 aggregates under this pH condition. PACAl30 produced large size particles when it was added into synthetic water with pH = 7.5–9.5. It precipitated faster than PACAl13 under pH = 7.5. After dosing into synthetic water with pH = 6.5, PACAl30 could build a certain size of precipitates though the induction period was long. The above results indicated that PACAl30 is easier to hydrolyze and precipitate than PACAl13 in weak acidic and alkaline water.

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measured after the precipitates were prepared directly in synthetic water with different pH values under fixed pH condition (Fig. 3b).

The Zeta potential of coagulant hydrolysis precipitates decreased with the increase in pH for all three coagulants in these two methods. At low pH side, the Zeta potential of the hydrolysis precipitates had positive values, while at high pH side, it was negative. The Zeta potentials of AlCl₃ hydrolysis precipitates were lower than that of PACAl₁₃ and PACAl₃₀ when pH ≥ 5.0, but the reverse is true when pH ≤ 5.0. The Zeta potentials decreased slightly for PACAl₁₃ and PACAl₃₀ when pH ≤ 5.0. This maybe caused by the variation of solubility, structure and morphology of coagulant hydrolysis precipitates. Dense and visible precipitates could be seen during AlCl₃ hydrolyzing in synthetic water of pH ≤ 5.0. However, for PACAl₁₃ and PACAl₃₀, the hydrolysis precipitates are difficult to be observed due to the high stability of Al₁₃ and Al₃₀ at this pH condition. The dissoluble aggregates of Al₁₃ and Al₃₀ in PACAl₁₃ and PACAl₃₀ adding solution should be looser and have smaller fractal dimension than the precipitates formed from AlCl₃. The Zeta potentials of PACAl₁₃ were higher than that of PACAl₃₀ at high pH (pH ≥ 7.0), but lower at low pH. This is probably because Al₃₀ is more labile to deprotonation and aggregation than Al₁₃ under alkaline conditions.

According to Fig. 3a, the iso-electric points of hydrolysis precipitates of AlCl₃, PACAl₁₃ and PACAl₃₀ were 8.7, 10.2 and 9.8, respectively. However, these values in Fig. 3b were 7.3, 9.6 and 9.2, respectively. The discrepancy maybe caused by the following reasons: (1) The precipitates became more compact and dense during the settlement and separation processes, and the particle size increased, and at the same time, the chemical species of the particle interior and surface were different after re-suspension. (2) The deionised water addition may cause the decrease in ionic strength during the re-suspension of coagulant hydrolysis precipitates.

The dosages of coagulants have important effect on the charge characteristic of hydrolysis precipitates because the consumption of alkalinity by coagulants increased with the increase in dosage. The effects of dosage on the particles’ Zeta potential of hydrolysis precipitates under fixed pH condition and under uncontrolled pH condition are displayed in Fig. 4a and b, respectively. The Zeta potential of hydrolysis precipitates changed very little with the change of dosage when the coagulants hydrolyzed under fixed pH conditions, and it depended only on the pH and the type of coagulants (Fig. 4a). However, the Zeta potential of hydrolysis precipitates increased with the increase in dosage when the coagulants hydrolyzed under uncontrolled pH conditions (Fig. 4b). Because Al₁₃ and Al₃₀ in PACAl₁₃ and PACAl₃₀ caused much less pH depression than Al¹⁻ in AlCl₃, the Zeta potential of PACAl₁₃ and PACAl₃₀ hydrolysis precipitates increased slowly with the increase in dosage, while the Zeta potential of AlCl₃ hydrolysis precipitates increased rapidly (Fig. 4b). The results indicated that the coagulant dosage itself had no obvious influence on the Zeta potential of hydrolysis precipitates. The increase in Zeta potential with the increase in coagulant dosage under uncontrolled pH condition was due to the pH drop caused by coagulants addition.

3.4. Chemical speciation of coagulant hydrolysis precipitates

The above research indicated that the particle size development and charge characteristic of coagulant hydrolysis precipitates, as well as the pH depression of synthetic water caused by coagulants addition depended on the coagulants employed. The chemical composition and structure of hydrolysis precipitates should be different for different coagulants. The Al–Ferron analysis results of coagulant hydrolysis precipitates that were acidified to pH 4.0 before Al–Ferron analysis and that were analyzed without any pretreatment are displayed in Figs. 5 and 6, respectively.

As can be seen from Fig. 5, the chemical species of the acidified hydrolysis precipitates greatly depended on the original coagulant composition. The precipitates of AlCl₃ were amorphous Al(OH)₃, and this kind of precipitates was easy to dissociate into Al¹⁻ during acidification, so its Al₃ content reached 70%. The hydrolysis precipitates of PACAl₁₃ and PACAl₃₀ were the aggregates of Al₁₃ and Al₃₀. They were composed of repeated Al₁₃ and Al₃₀ structural units and possessed pseudo-boehmite structure. The bridging units (hydrogen bond and hydroxyl bridging bond between the external H₂O of Keggin units) between these repeated Keggin structural units were labile to dissociate and decompose into Al₁₃ and Al₃₀ units under pH 4.0. So the Al–Ferron time-developed complex colorimetry curves of the precipitates after acidification exhibited the same characteristics as the original coagulants. Al₅⁺ content of hydrolysis precipitates derived from PACAl₁₃ and PACAl₃₀ was 82%
and 25%, respectively. For AlCl₃, PACAl₁₃ and PACAl₃₀, the reaction rate constants between Ferron reagent and the acidified hydrolysis precipitates within 1–30 min were 0.309, 0.067 and 0.042, respectively. The reaction rate constants of PACAl₁₃ and PACAl₃₀ hydrolysis precipitates were consistent with that of the original coagulants (Chen et al., 2007). The high reaction rate constant for AlCl₃ hydrolysis precipitates indicated that the reactants that reacted with Ferron reagent within 1–30 min were Al monomers (Alₘ) and Al oligomers (Alₖ) such as Al dimers and Al trimers. The polymerization degrees of these Alₖ were lower than that of Al₁₃ and Al₃₀.

The Al–Ferron time-developed complex colorimetry curves shown in Figs. 5a and 6a were completely different. The absorbance increased slowly in Fig. 6, and the reaction rate constants for AlCl₃, PACAl₁₃ and PACAl₃₀ within 1–30 min were 0.016, 0.027 and 0.024, respectively. These reaction rate constants were lower than that in Fig. 5, especially for AlCl₃. However, Alₖ contents for these three coagulants were 67%, 73% and 22%, respectively. In order to further investigate whether the Alₖ species in these hydrolysis products were the same as our usually called Keggin Al₁₃ species, the suspension of coagulants’ hydrolysis precipitates obtained from these three coagulants was filtered with 0.45 μm microporous membrane, and the filtrate was collected and analyzed with Al–Ferron method. Because the diameter of Al₁₃ species was only 1.08 nm (Casey and Swaddle, 2003), these Alₖ species should be able to go through the 0.45 μm microporous membrane if the Alₖ species measured in this work was Keggin Al₁₃ species. The experimental results indicated that Al contents in the filtrates were very low for all the three coagulants. This verified that the dissolved Al species in these hydrolysis products were very low, and the Al species in these hydrolysis products existed in colloidal form. So the Alₖ species measured in these coagulants’ hydrolysis precipitates (Fig. 6) was not our usually called Keggin Al₁₃ species. The high Alₖ content measured by the above Al–Ferron method could not be used as a testimony that most of Al species were transformed to high charged Al₁₃ species during AlCl₃ coagulation.

In Al–Ferron method, the sulfonic functional group in Ferron reagent can only react with Al monomer, and the Al–sulfonic complex ion produces absorbance at 370 nm. The absorbance at 370 nm is directly proportion to the number of Al–sulfonic complex ion. The complex reaction between Ferron reagent and the hydrolysis products without acidification is shown in Scheme 1. The total reactions are composed of three-step reaction sequence. The first step was the hydrolysis products dissociated into dissoluble species by H⁺, carboxyl and sulfonic groups under weak acid conditions. The dissoluble species include Alₘ, Alₖ, [Al₁₃]ₙ, [Al₃₀]ₙ (the soluble aggregates of Al₁₃ or Al₃₀), etc. The second step was these dissoluble Al species were decomposed into Alₘ, Alₖ, Al₁₃ and Al₃₀ by H⁺ and ligands. The third step was Alₘ and Alₖ were complexed by Ferron.
The results are shown in Fig. 7. Al speciation of AlCl₃ hydrolysis dosed into model water with different pH values for 10 min, and the condition. The Al species distributions of hydrolysis products were consisted mainly of dissolved Alₘ and Al₀lig. A lb and Alc species Al₁₃ species in solution of pH 7.5 was very small; the second source as can be seen from the above experimental results, the dissolved Alb for AlCl₃, but the fourth source was the dominant source of Alb alkaline solutions, the second source was the dominant source of Alb for AlCl₃ or PACAl₁₃.

Comparing Fig. 5 with Fig. 6, it could be concluded that the first step was the rate-determining step when Ferron reagent reacted with the hydrolysis products of AlCl₃ without acidification, however, the second step was the rate-determining step for PACAl₁₃ or PACAl₃₀. both the first and the second step had a certain effect on Ferron reagent reacting with the hydrolysis precipitates. As can be seen from Scheme 1, the Alₙ species measured under this condition consisted mainly of dissolved Alₘ and Al₀lig. Alb and Alₙ species existed in insoluble precipitates under pH 7.5. The value of Alₙ measured under this condition came from four sources: the first source was the dissolved Al₁₃ species in hydrolysis suspension, but as can be seen from the above experimental results, the dissolved Al₁₃ species in solution of pH 7.5 was very small; the second source was the dissolution of hydrolysis precipitates of AlCl₃ and Al₁₃₀ (SedAl₁₃ and SedAl₃₀), as well as [Al₁₃]₁₃ and [Al₃₀]ₙ, dissolved into Alₘ and Al₀lig directly, but the chance of the dissolution reaction taking place was small; the fourth source was the decomposition of SedAl₁₃ into [Al₁₃]₁₃, and then into soluble Al₁₃ species, which was the main reaction pathway that SedAl₁₃ reacted with Ferron reagent within 120 min. In the neutral and weak alkaline solutions, the second source was the dominant source of Alₙ for PACAl₁₃, but the fourth source was the dominant source of Alₙ for PACAl₁₃ or PACAl₃₀.

### 3.5. Al speciation transformation after coagulants dosing into water

A calculated amount of AlCl₃, PACAl₁₃ or PACAl₃₀ was added into model water to reach an Al concentration of 200 μM under fixed pH condition. The Al species distributions of hydrolys products were studied using Al–Ferron methods after the three coagulants were dosed into model water with different pH values for 10 min, and the results are shown in Fig. 7. Al speciation of AlCl₃ hydrolysis precipitates was significantly affected by the pH of model water. At the acidic region (pH < 6.0), Alₙ decreased rapidly with the increase in pH, and Alₐ increased rapidly. At pH 6.5–7.5, Alₐ reached the minimum, and Alₙ reached the maximum, Alₘ increased slowly. As the pH increased further, Alₐ increased again, Alₙ decreased continuously, and Alₒ reached the maximum at pH 8.0 and then decreased.

Because Al³⁺ in AlCl₃ had very high hydrolysis potential, Al³⁺ hydrolyzed rapidly when it was added into model water of pH > 4.0, and formed insoluble Alₘ, Al₀lig, Al₁₃ and other Al sol–gels (Alₙ-sol–gels) in solution of pH < 5.6 (Chen, 2006). So Alₙ species measured at this pH region denoted the content of Alₘ and Al₀lig, and Alₙ species denoted the dissociation of Al₁₃ and Alₙ-sol–gels. At this pH region, Alₘ and Al₀lig decreased, and high polymeric Al₁₃ and Alₙ-sol–gels increased with the increase in pH. When AlCl₃ was added into model water of pH > 5.6, amorphous Al(OH)₃ precipitates formed, and the dissolved Alₘ, Al₀lig and Alₙ-sol–gels decreased. The increase of Alₙ with the increase of pH was caused by the dissolution of the freshly formed amorphous Al hydroxides in Ferron reagent. These amorphous Al hydroxides possessed large surface area and structural flaw and were easy to be dissolved. When the pH of the model water increases to 6.5–7.5, Al³⁺ hydrolyzed very rapidly, and beyond 95% of Al converted to amorphous Al hydroxide directly. And at the same time, the structural adjustment and rearrangement of hydrolysis precipitates accelerated with the increase in pH. The solubility of Al hydroxide declined, so Alₘ increased with the increase in pH. As pH increased further, part of Al³⁺ in AlCl₃ converted to insoluble Al(OH)₃ due to the amphoteric characteristics of Al(OH)₃ increased with the increase in pH, so Alₙ increased again, and Alₑ and Alₙ decreased.

Compared to AlCl₃, the pH had much less effect on the Al species distribution of hydrolysis precipitates of PACAl₁₃ and PACAl₃₀ (Fig. 7b and c). For PACAl₁₃ and PACAl₃₀, Alₙ decreased slightly at low pH region, and it reached the minimum at pH 7.0–8.0, then it increased slowly again when pH increased above 8.0 due to alkaline dissolution of polymeric Al species. The change of Alₙ was contrary to that of Alₙ, Alₑ changed very little. Coagulant dosing process was equivalent to dilution and alkali dosing simultaneously. At acid
Al species distribution of AlCl₃ hydrolysis precipitates depended on the composition of coagulant and the solution chemical conditions. To a certain extent, Al₃ was controlled by the solubility of hydrolysis precipitates, and the pH range in which Al₃ reached the minimum was agreed with the reported pH range of the minimum solubility of coagulants in water (Peremitsky and Edzwald, 2003). Al₃ content reflected the change tendency of residual Al content in treated water after flocculation. PACₐ₃ and PACₐ₁₃ could achieve low residual Al content at a wider pH range than AlCl₃. It should be pointed out that Al₃ was not equal to the residual Al content because the soluble polymeric Al species at low pH side also contributed to the residual Al content, especially for AlCl₃. At the same time, the residual Al content in practical flocculation process was also reduced by the adsorption and sweeping of flocs. Al₃ and Al₆ were controlled by solution pH and the composition and structure of hydrolysis precipitates. The structures of Al₁₃ and Al₃₀ hydrolysis precipitates were completely different from that of Al₁₃⁺. The hydrolysis precipitates of Al₁₃⁺ were the amorphous Al(OH)₃, but the hydrolysis precipitates of Al₁₃ and Al₃₀ were the aggregates of Al₁₃ and Al₃₀, and the Keggin units remained in the precipitates.

4. Conclusions

The hydrolysis/precipitation behaviors of Al₁₃⁺, Al₁₃ and Al₃₀ under conditions typical for flocculation in water treatment were dependent on coagulants, solution pH and dosage employed, etc. The coagulants hydrolyzed and precipitated very rapidly in neutral and weak alkaline solutions. The optimal pH regions for hydrolysis precipitates formation for AlCl₃, PACₐ₃ and PACₐ₁₃ were 6.5–7.5, 8.5–9.5, and 7.5–9.5, respectively. With the increase in dosage, the formation rate of hydrolysis precipitates increased, and the induction period shortened. Among the three coagulants, the rate of hydrolysis and precipitation of AlCl₃ was the fastest, and PACₐ₁₃ took the second place, PACₐ₃ ranked the last. The differences among the three coagulants enlarged at low dosage range and low pH region. The ultimate size of the precipitates increased when the dosage increased from 50 μM to 200 μM, but when the dosage increased to 800 μM, it decreased instead due to the transitory low pH shock caused by high dosage of coagulants addition suddenly. The Zeta potential of the hydrolysis precipitates decreased with the increase in pH for all three coagulants. The iso-electric points of the fresh formed precipitates for AlCl₃, PACₐ₁₃ and PACₐ₃ were 7.3, 9.6 and 9.2, respectively. The Zeta potentials of AlCl₃ hydrolysis precipitates were lower than that of PACₐ₁₃ and PACₐ₃ when pH > 5.0. The Zeta potentials of PACₐ₁₃ hydrolysis precipitates were higher than that of AlCl₃ at the acidic side, but lower at the alkaline side due to Al₁₃ is more tolerable to alkaline hydrolysis than Al₃₀. The coagulant dosage had little effect on the Zeta potential of hydrolysis precipitates under fixed pH condition. The increase in Zeta potential with the increase in dosage under uncontrolled pH condition was due to the pH depression caused by the coagulants addition. Al₁₃ and Al₃₀ caused much less pH depression than Al₁₃⁺, so the Zeta potential of PACₐ₁₃ and PACₐ₃ hydrolysis precipitates increased slower than that of AlCl₃ when the dosage increased.

The Al–Ferron assay indicated that the hydrolysis precipitates of AlCl₃ were composed of amorphous Al(OH)₃, but the hydrolysis precipitates of PACₐ₁₃ and PACₐ₃ were composed of aggregates of Al₁₃ and Al₃₀, respectively. The Keggin Al₁₃ and Al₃₀ units were basically intact in their hydrolysis precipitates. Al₁₃⁺ was dissolution of the precipitates in Ferron reagent became slow due to inter-particle coalescence and internal structure adjustment and rearrangement. For PACₐ₁₃ and PACₐ₃, the Al speciation of hydrolysis precipitates changed slowly with aging, which further indicated that Al₁₃ and Al₃₀ units in hydrolysis precipitates could remain stable for a relatively long time.
the most un-stable species in coagulants. It hydrolyzed rapidly and formed amorphous sediments after dosing into water. And its hydrolysis process and products were remarkably influenced by pH. However, Al13 and Al30 species in PACAl13 and PACAl30 exhibited very high hydrolysis stability, and solution pH and aging had little effect on the chemical species of their hydrolysis products.

The three kinds of Al species (Alp, Alb, and Alc) measured in hydrolysis precipitates based on Al–Ferron reaction kinetics were different from that measured in coagulants. Alp, Alb, and Alc measured in coagulant hydrolysis precipitate depended on Al speciation in coagulant and the solution pH in that the hydrolysis precipitates formed. Alp included the dissoluble Alm and Alolig existed in solution, and it was controlled by the solubility of hydrolysis precipitates. Alb reflected the change tendency of residual Al content in treated water after flocculation. Alc contained the dissoluble Al13 existed in solution, the Al13 unit dissolved from SedAl13, and the Alm and Alolig dissolved from [Al13]m [Al30]olig SedAl13 and SedAl30 directly. Alp and Alb were controlled by the solution pH, the composition of coagulants, and the structure of the hydrolysis precipitate. Alc measured in current case was different from Kegggin Al13 species, and high Alb content in AlCl3 hydrolysis precipitates could not be used as a testimony that most of Al3+ converted to high charged Al13 species during AlCl3 coagulation.

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