Speciation stability of inorganic polymer flocculant–PACl

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Received 27 November 2003; accepted 27 April 2004

Abstract

The speciation distribution, physico-chemical properties of coagulants, and principles for their further species transformation under various water and wastewater treatment conditions are of paramount importance in coagulation processes. In this paper, the effect of various factors on the speciation transformation of typical inorganic polymer flocculants (IPFs)–polyaluminum chloride (PACl) was investigated by ferron assay. Dilution and co-existing electrolyte exhibit little effect on the speciation distribution of PACl after dosing. Solution pH has significant effect on the species transformation, depending mainly on OH/Al ratio (denoted as *B* value). The lower the *B* value, the more significant the effect pH exhibits. A large amount of Al_b, i.e. rapid reactive species by ferron assay, could form for alum and PACl₀ in the weak acidic pH range, which transforms quickly into Al_c after aging. PACl, at high *B* values, maintains high speciation stability under the various conditions investigated. The ferron method provides a measure to explain the reactivity of different species with ferron. The classification of three kinds of aluminum hydrolysis species based on kinetic differences needs further modification.

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Keywords: PACl; Speciation stability; Ferron method; Coagulation; Mechanism

1. Introduction

Coagulants are one of the key factors in the coagulation process. Alum is the most frequently applied traditional coagulant in the world. Recently, based on conventional iron and aluminum salts, inorganic polymer flocculants (IPFs) have been developed rapidly and become applied widely, especially in China, Japan, Russia, and west Europe [1–5]. Many kinds of IPFs have been developed including aluminum-based, iron-based, inorganic–inorganic composite flocculants, inorganic–organic composite flocculants, and multifunctional composite IPFs [1–8]. Among them, polyaluminum chloride (PACl) is one of the typical kinds and has become most widely applied. The property and general coagulation behavior of IPFs have been extensively investigated [2–5,8–11]. The differences between traditional coagulants and IPFs have been gradually examined. However, previous studies paid most attention to the preparation, characterization, and application of IPFs. Little study has been focused directly on the features of

chemical speciation during coagulation. There exist few established conclusions as to why their efficiency is superior to the traditional coagulants. It is generally thought that the pre-produced products contain species of superior quality and possess structure fairly stable to further hydrolysis and solution chemistry, resulting in higher coagulation efficiency. The action and mechanism of IPFs are not fully understood.

IPFs are actually clusters or aggregates of a combination of intermediate products with various anions, during hydrolysis of metal salts under suitable conditions. Hence, the study of their aqueous chemistry, especially the species distribution and transformation principles, would build the theoretical basis for IPFs and their further improvement [2]. There are many excellent reviews with large amounts of literature on the aqueous chemistry of Al(III) and Fe(III) [2,12–15]. However, there exist a few firmly established principles due to the complex nature of hydrolysis. The hydrolysis of Al(III) follows multiple pathways. A series of hydrolysis species can be formed depending on various factors such as aluminum concentration, sorts of bases adopted, methods of alkalization, speed for base addition, co-existing anions and particles. Therefore, the species formed are

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largely system specific and methodology dependent. Characterization of the different structures and further transformation under various conditions becomes the focus of this field. A number of experimental methods and approaches have been applied. Apart from normal chemical analysis, the analytical methods applied were potential titration, small angle X-ray diffraction, infrared spectroscopy, nuclear magnetic resonance spectroscopy, laser light scattering, small angle X-ray scattering, various electron microscopy, and atomic force microscopy. The timed spectrophotometric method involving reaction of 8-hydroxyquinoline or ferron (8-hydroxy-7-iodo-5-quinoline-sulfonic acid) has also been widely applied to quantify the different species present.

The ferron method was introduced in 1971 as a means of operationally distinguishing between the forms of soluble aluminum in an aqueous system, and it has found wide application in fundamental studies as well as in studies of environmental samples [16–20]. Based on the kinetic difference of the reactions between the aluminum and ferron reagent, 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 , and Al_c , respectively. As currently practiced, most previous investigation has focused on the effect of co-existing factors on the kinetic differentiation of aluminum species and possible relationship between Al_b and Al_{13} [21]. Studies have also been restricted to soluble species, although mention has been made of the possible reaction between ferron reagent and solid aluminum compounds. Little attention has focused on the kinetic intermediate species formed during preparation, or after dosing in water and wastewater treatment process. Though of paramount importance to the understanding of the mechanism of coagulation, species distribution and transformation after dosing has not been studied sufficiently.

The purpose of this paper is to examine the effect of the various factors involved during coagulation with the typical IPF–PACl, paying special attention to the speciation stability. The effect of dilution, electrolyte concentration, pH, and aging is discussed in detail by using ferron method. The implications for the coagulation mechanism are then discussed.

2. Materials and methods

2.1. Preparation of PACl

The various PACl samples were prepared using laboratory alkalinity titration method at room temperature [3]. The reagents used in this study were all of analytical grade except those specifically highlighted. The concentrated stock solution of 2.5 mol Al/L was first prepared by dissolving $AlCl_3 \cdot 6H_2O$ in distilled water. Prior to the preparation of PACl, a working solution of 0.5 mol Al/L was prepared by diluting the above stock solution in distilled water. A calculated amount of 0.5 mol/L $Al(III)$ solution was then

Table 1

The speciation distribution and pH value of PACl samples

No.	<i>B</i>	$Al_a(\%)$	$Al_b(\%)$	$Al_c(\%)$	pH
PACl ₀	0.0	91.9	8.1	0.0	3.03
PACl ₁₀	1.0	60.7	21.2	18.1	3.66
PACl ₂₀	2.0	23.6	34.5	41.9	3.94
PACl ₂₅	2.5	7.3	40.1	52.6	5.32
AS	0.0	87.6	12.4	0.0	3.00

transferred into a 300 mL jar. Under rapid stirring and bubbling with nitrogen gas, the above solution was titrated slowly with 0.5 mol/L NaOH using a titrometer (665 Dosimat, Metrohm, Switzerland). The amount of NaOH added varied with the target OH/Al ratio (simplified as *B* values), i.e. 0, 1.0, 2.0, and 2.5, denoted, respectively as PACl₀, PACl₁₀, PACl₂₀, and PACl₂₅. The final concentration of aluminum is 0.1 mol/L. Meanwhile, 0.1 mol Al/L $Al_2(SO_4)_3$ solution, denoted as AS, was prepared by dissolving alum in distilled water. The samples, after being left to age one week, were analyzed using the ferron method as described below. The results of speciation and pH measurement are shown in Table 1.

2.2. Ferron methods

A slightly modified ferron method was used here. The ferron reagent used by some previous researchers exhibited some unstable features [19,22]. A continuous change in the absorption spectrum of the ferron reagent with aging was observed. Therefore, it has been suggested that different aging times of the mixed ferron solution may be used. The change in the spectrum is thought to be due to reduction of the sulfonate group of ferron to a protonated sulfide group. It can be removed by avoiding the use of hydroxyl ammonium chloride reagent [19]. The main procedure was used as follows.

Reagent A (0.2% ferron): under rapid stirring, 2 g ferron (Sigma Chemical Co., MO63178, USA) was dissolved in 1020 mL distilled water (boiled to remove dissolved CO_2). Then, filtered and preserved in a 1 L volumetric bottle.

Reagent B (20% w/v NaAc): 200 g NaAc was dissolved in 1 L of distilled water.

Reagent C (1:9 v/v HCl): 100 mL HCl (37%) was mixed with 900 mL of distilled water.

Prior to the speciation experiments, the mixed ferron solution was obtained by mixing above reagents A, B, and C according to a ratio of 2.5:2:1. Then, 5.50 mL of the mixed reagent was transferred into 25-mL graduated glass tube and diluted to certain volume with distilled water. A certain amount of the sample was then added into the glass tube and quickly diluted to 25 mL. After homogeneous mixing, the reacting sample was quickly added to a 1-cm glass cuvette. The timed absorbance measurements (at 366 nm), using a DU650 Beckman UV–Visible spectrophotometer, were carried out after 1 min and recorded for further 2 h. It was operationally divided that the first 1 min absorbance as Al_a , and

1 min to 2 h as Al_b , then Al_c was obtained by Al_t minus Al_a and Al_b .

To examine the effect of dilution, synthetic water containing 10^{-3} mol/L $NaNO_3$ was made up by adding 1 mol/L $NaNO_3$ to distilled water. Then, PACI was added under rapid stirring at 250 rpm for 2 min, followed by slow stirring at 40 rpm for 8 min. The solution was aged for 1 h. The final concentration of the solutions was 5×10^{-4} , 2×10^{-4} , and 5×10^{-5} mol Al/L, respectively. After 2 min and 1 h aging, the solution was analyzed subsequently by ferron assay.

During the examination of the effect of pH, the same procedure was applied except that the synthetic water contained respectively 5×10^{-4} mol/L $NaHCO_3$ and $NaNO_3$ in distilled water. A pre-determined amount of 0.2 or 0.05 mol/L NaOH or HCl solution was used and added first into the synthetic water to control the final pH. Under rapid stirring at 250 rpm, a certain amount of coagulants were then dosed. The final concentration of the solutions was 2×10^{-4} , 1×10^{-4} , 8×10^{-5} , and 5×10^{-5} mol Al/L, respectively (to examine the effect of dosage also). After 2 min and 1 h aging, the solution was subsequently analyzed by ferron assay.

3. Results and discussion

3.1. Effect of dilution and ionic strength

To examine the effect of dilution, the coagulants were dosed directly into distilled water containing 10^{-3} mol/L $NaNO_3$. The final concentration of solutions was 5×10^{-4} , 2×10^{-4} , and 5×10^{-5} mol Al/L, respectively. After aging for 2 min and 1 h respectively, the solution was subsequently analyzed by ferron assay. The results at dosage of 2×10^{-4} mol Al/L are summarized in Table 2. The original concentration of species distribution for the coagulants is also shown for comparison. It can be seen that dilution has little effect on the speciation distribution of PACIs after dosing. Similar results are observed for the other dosages investigated in the range of dilution factors of 200–2000 times. Speciation distribution

shows little alteration, especially for the high B value PACIs.

The pH recorded for the original $PACl_0$, $PACl_{10}$, $PACl_{20}$, and $PACl_{25}$ solution is 3.03, 3.66, 3.94, and 5.32, respectively. Considering the effect of spontaneous hydrolysis with the enhanced hydrolysis by alkalinity addition, the hydrolyticity for Al(III), i.e. B^* ($B^* = B_H + B - A$, see text of Tang and Stumm [1], in detail), could be calculated by using the method proposed previously. The B value equates to OH_{add}/Al_T . B_H is obtained from the spontaneous hydrolysis (SH) of Al(III), i.e. OH_{SH}/Al_T , while the A value equals the acid added, i.e. H_{add}/Al_T . Here, no acid has been added during the preparation of PACIs, therefore, $A = 0$. The B^* values calculated, considering the spontaneous effect of hydrolysis, are 0.009, 1.003, 2.001, and 2.500, respectively, for the original $PACl_0$, $PACl_{10}$, $PACl_{20}$, and $PACl_{25}$ solutions. Obviously, there is no significant difference between B and B^* in the original solutions.

However, a weak alkalization can be expected during dilution as the pH of solution is raised. Considering the case of final concentration of 2×10^{-4} mol Al/L, the solution pH of $PACl_0$, $PACl_{10}$, $PACl_{20}$, and $PACl_{25}$ becomes 4.34, 4.64, 4.89, and 5.32, respectively, after dosing. The calculated B^* values then are 0.239, 1.115, 2.065, and 2.524, respectively. Although a significant increase of B^* value occurs for the low OH/Al ratio PACIs, no evident alteration of the species distribution is observed, as shown in Table 2. It is indicative that the change of B^* corresponds mainly with the change of charge of the species, e.g. from $Al(OH)^{2+}$ to $Al(OH)_2^+$ and Al_{13}^{7+} to Al_{13}^{5+} . Therefore, no species transformations along categories of Al_a , Al_b , and Al_c take place, while the charge of the species decreases as B^* increases. Additional sets of experiments were also carried out to examine the effect of concentration of electrolyte on the speciation of PACIs after dosing. The range of concentration of $NaNO_3$ examined was 10^{-4} to 0.1 mol/L. Results show that the concentration of $NaNO_3$ examined has little effect on the speciation distribution of the primary coagulants.

3.2. Effect of pH on the speciation transformation of PACI after dosing

During the examination of the effect of pH, synthetic water containing respectively 5×10^{-4} mol/L $NaHCO_3$ and $NaNO_3$ in deionized water was used. A pre-determined amount of 0.2 or 0.05 mol/L NaOH or HCl solution was used and added first into the synthetic water to control the final target pH. The speciation analysis was then carried out after coagulants were dosed. The results of speciation characterization at a PACI dose of 2×10^{-4} mol Al/L are summarized in Fig. 1. It can be seen that pH has a significant effect on further speciation transformation of PACI, corresponding with OH/Al values. For $PACl_0$ and AS, i.e. OH/Al = 0, in the acidic region, Al_a decreases rapidly as pH is raised, and reaches a minimum in the near neutral pH region. Upon increase of pH to the alkaline portion of

Table 2
The speciation distribution and pH value of PACI samples

No.	B	Time	Al_a (%)	Al_b (%)	Al_c (%)	pH
$PACl_0$	0.0	0	91.9	8.1	0.0	3.03
		2 min	93.6	6.4	0.0	4.34
		1 h	94.8	5.2	0.0	4.32
$PACl_{10}$	1.0	0	60.7	21.2	18.1	3.66
		2 min	61.5	20.0	18.5	4.64
		1 h	61.3	21.1	17.6	4.61
$PACl_{20}$	2.0	0	23.6	34.5	41.9	3.94
		2 min	23.8	34.9	41.3	4.89
		1 h	24.2	34.2	41.6	4.88
$PACl_{25}$	2.5	0	7.3	40.1	52.6	5.32
		2 min	6.9	44.6	49.5	5.32
		1 h	7.5	42.1	50.4	5.34

Fig. 1. The speciation characterization after dosing of PACl under various pH conditions at constant dosage of 2×10^{-4} mol Al/L: (A) Al_a ; (B) Al_b ; (C) Al_c . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

the figure, the Al_a species increases sharply again. In contrast, a rapid increase of the Al_b species can be observed in the acidic pH region. The maximum of Al_b occurs in the near neutral pH conditions. In the alkaline portion, a rapid decrease occurs as pH is raised. The distribution of Al_c is similar to that of Al_b , but the scale of change is smaller.

Similar trends of the change in Al_a , Al_b , and Al_c species are also observable for the other PACls at higher OH/Al ratio. However, the scale of change largely decreases with increasing OH/Al. For $PACl_{10}$, the decrease of Al_a with large yield of Al_b occurs obviously in the weak acidic conditions. Increasing OH/Al ratio to 2.0, i.e. $PACl_{20}$, the trend becomes less observable. Note that the decrease of Al_a is not so significant, as the original fraction of Al_a in $PACl_{10}$ is only 61% prior to dosing. While for $PACl_{25}$, there is not much difference of the speciation distribution throughout the pH range investigated.

Obviously, further transformation of PACls species after dosing under the various conditions depends largely on the original composition. The PACls at low OH/Al ratio show a significant change of species under the various conditions. The high OH/Al ratio PACls exhibit efficient speciation stability and tend to maintain the original speciation distribution. As shown in Table 1, the $PACl_0$ and AS contain mainly Al_a monomers. After dosing in water, this species undergoes dramatic change as shown in Fig. 1. In the pH range 5.5–6.5, the Al_a species transforms largely to Al_b with fractions reaching 80–90%, plus 10–20% of Al_c . Above pH 7.0, a significant amount of Al_b changes further into Al_c . As OH/Al ratio increases, the quantity of Al_a in the primary coagulants decreases quickly, with large increase of Al_b and finally Al_c . For $PACl_{10}$, the Al_a species remains the main component, 60%, with 22% of Al_b and 18% of Al_c . As shown in Fig. 1, that maximum Al_b fractions is 60% with 40% Al_c . In comparison with the primary composition in $PACl_{10}$, it can be estimated that the original 60% of Al_a equates roughly to 40% of Al_b and 20% of Al_c . It is indicative that the Al_a constituent in $PACl_{10}$ exhibits a similar change to that in $PACl_0$. Similar results are seen for $PACl_{20}$, while for $PACl_{25}$, there is a minor quantity of Al_a (8%). The distribution of Al_a , Al_b , and Al_c remains almost the same throughout the pH range investigated. The results shown above indicate that the Al_a fraction in the primary coagulants contains the most labile species. After dosing, these species would quickly transform into Al_b , and finally Al_c depending 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 a quite different nature to the preformed species, as will be addressed in further detail later.

A comparison of the above results with the solubility diagram of Al(III) provides further insight to the principle of speciation transformation after dosing. Normally, the solubility diagram or a more comprehensive stability-coagulation diagram can be used to illustrate the behavior of the traditional coagulants, as suggested first by Amirtharajah and co-workers [23,24]. It is constructed

using the equilibrium constant from comprehensive compilation and collation of data from coagulation experiments. Such a diagram can be used to predict the relationship between concentration of aluminum (pC) and pH, addressing to some extent the coagulation mechanism. However, the choice of reaction schemes of possible species can often be arbitrary. The amorphous $Al(OH)_3(s)$ has normally been chosen as the controlling solid phase, while other investigations favored the more crystalline phase. Considering the probable existence of polymer species, either formed in solution or possibly adsorbed onto surfaces, much more complicated cases may be expected. In practice, some reactions are system specific. Furthermore, the kinetic aspect of aggregation is not included in the diagram. When coagulants are added, the solution is not highly supersaturated to the solubility limit and therefore is often metastable. The precipitation formation is kinetically slow and the solid phase may not form. In addition, the diagram is largely restricted to the traditional metal salts. Thus, the application to preformed PACl is limited. The solubility scheme based on the equilibrium with amorphous aluminum hydroxide can no longer be valid for the species being tailor-made. Although the coagulation diagram can be used to roughly differentiate between the state of coagulation-flocculation by full application of the available research results, this remains to be tested by experimental results. A quantitative calculation could not be reached.

Fig. 1A also includes the theoretically calculated solubility (the thin solid line and dotted line) and the experimental results of Van Benschoten and Edzwald (the thick solid line) [11]. The alum dose used by Van Benschoten and Edzwald was 1×10^{-4} mol/L, which equates to 50% of the dose adopted in this investigation (2×10^{-4} mol/L). The soluble species used in constructing the curve in Fig. 1A were Al^{3+} , $Al(OH)^{2+}$, and $Al(OH)_4^-$ (for the thin solid line). The dotted line is the theoretical solubility of Al including the fourth monomer, $Al(OH)_2^+$. Amorphous $Al(OH)_3$ is assumed to be the solid phase controlling solubility. Al hydrolysis constants are shown in Table 3. A temperature of 25 °C was used in the calculations. It can be seen that the experimental results of AS (alum) fit well to those of Van Benschoten and Edzwald. Note that the results obtained by Van Benschoten and Edzwald were carried out on the filtered samples, while the data in this study were determined directly as the Al_a

Table 3
Aluminum hydrolysis constants

Reaction	pK	Reference
$Al^{3+} + SO_4^{2-} = AlSO_4^+$	$pK_{sulf} = 3.50$	[12]
$Al^{3+} + H_2O = Al(OH)^{2+} + H^+$	$pK_{11} = 4.99$	[12]
$Al^{3+} + H_2O = Al(OH)_2^+ + 2H^+$	$pK_{12} = 10.1$	[12]
$Al^{3+} + H_2O = Al(OH)_4^- + 4H^+$	$pK_{14} = 23.0$	[12]
$Al^{3+} + 3OH^- = Al(OH)_3(s)$	$pK_{so} = 31.6$	[12]
$Al^{3+} + H_2O + SO_4^{2-}$ $= Al(OH)_{3-2x}(SO_4)_x(s)$	$pK_{so/sulf} = 35.2$	–

fraction. This indicates that the Al_b/Al_c fractions might be involved in the particle form, although no attempt has been made to characterize particle size evolution features after dosing.

A significant difference between the alum and PACls can also be observed. The experimental data for alum appear to show slightly more insolubility than the theoretical curve, and the curve for PACls. As shown in Fig. 1A, a systematic move of the curve to low pH region can be observed for alum versus the other PACls in the acidic region. The data near pH 4 are undersaturated with respect to the solid phase, but the remaining data between pH 4.5 and 6.5 indicate more insoluble solid phase than in theoretical predictions. These data exhibit the significant effect of the sulfate. The precipitate is easily formed in the presence of sulfate, therefore, the solubility diagram moves to the low pH range. This has been shown in the coagulation experiments carried out previously [3]. Meanwhile, although sulfate complexes moderately with Al(III) species [25], it is reasonable to consider the solubility controlling solid phase in the acidic pH range as amorphous $Al(OH)_{3-2x}(SO_4)_x$ ($0 < x < 2.5$). The corresponding value of the formation constants could be inferred by comprehensively combining reactions 1 and 4. A regression line in the pH 5–6 range gave a slope = -2.4 and a $\log K_{so/sulf} = -35.2$, as indicated also by Van Benschoten and Edzwald [11]. Considerable evidence suggests that Al solubility in the acidic pH range may be controlled by an Al– SO_4 precipitate [26,27], although other investigators [28] disfavor such findings.

Comparison of Al_a fractions of PACl to the Al solubility curve gives some interesting features. It was shown from Fig. 1A that the Al_a fractions of PACls correspond well to the dotted theoretical Al solubility curve. This is indicative that Al_a fractions follow well the control of solubility limit. The Al_b/Al_c species are the metastable species, which would transform finally into precipitates. The results indicate further that the involvement of $Al(OH)_2^+$ monomer is a reasonable hypothesis, although some investigators question the validity of the reaction constant of $Al(OH)_2^+$. No alteration of the amount of Al_a , Al_b , and Al_c occurs by simply changing $Al(OH)^{2+}$ to $Al(OH)_2^+$ as solution pH is raised. The difference of the analysis from Van Benschoten and Edzwald might be explained by the remarkable effect of the sulfate ion. It can also be seen from Fig. 1A that the solubility of $PACl_{20}$ and $PACl_{25}$ is slightly increased in the acidic region. The data points near pH 4 are undersaturated with respect to the solid phase. The smaller the Al_a fractions in the primary PACls, the more the effect of undersaturation is evident. However, in the pH 5.0–6.5 range, a slight increase of solubility for PACl with increasing OH/Al ratio indicates different solubility controlling solid phases. For $PACl_0$, amorphous Al hydroxide with large surface area may be formed as evidenced from the different reactivity with ferron. Precipitate formation is far away from the stable state. Upon further aging, part of the adsorbed species becomes dissolved and the structure re-arranges, resulting in

the increased solubility. For the PACls at high OH/Al ratio, the polymer species are quite stable. A metastable solution is formed.

If the species fraction diagram is arbitrarily divided at the point of onset of rapid decrease of Al_b and increase of Al_c , a value of pH 7.5 can be roughly established as shown in Fig. 1B and C. This value corresponds well to the set point of precipitation of polymer species as reported in the study of Van Benschoten and Edzwald. Additional experiments have been carried out on the effect of coagulant dosages—the results (abbreviated) exhibit a similar trend to that observed here.

3.3. Effect of aging

After dosing into water, the speciation of coagulants undergoes complex transformation depending on the original composition and solution conditions as shown above. It is believed that the species formed immediately undergo structure rearrangement with aging. Further experiments were thus carried out to examine the effect of aging. The results obtained upon 1 h aging are shown in Figs. 2–6 as separate diagrams for clarity—AS, $PACl_0$, $PACl_{10}$, $PACl_{20}$, and $PACl_{25}$ respectively. The results of 2 min aging are also included for comparison. From these figures, it can be seen that there is significant change in speciation distribution with aging, depending on the OH/Al ratio and the presence of sulfate ion. From Fig. 2, it can be seen that for alum the amount of Al_a stays almost constant with aging. However, a significant decrease in Al_b with a high yield of Al_c occurs in the meantime. In the pH range of 4–4.5, a large proportion of Al_b remains stable, while in the pH range of 4.5–5.5, a significance change of Al_b to Al_c takes place. The change becomes more rapid as pH is raised further above 6.5. The same effect of aging is observed for $PACl_0$ except that the rapid change of Al_b to Al_c occurs at higher pH. This again indicates the strong effect of the sulfate ion. The kinetics for polymer aggregation and precipitation are markedly accelerated in the presence of sulfate. For PACls at higher OH/Al ratio, the same trend can be observed, but it becomes gradually less observable with increasing OH/Al ratio. For $PACl_{25}$, the effect of aging is very small. The change of Al_b to Al_c occurs relatively slowly.

The results shown above indicate that the effect of aging on PACls is largely dependent on solution conditions. For alum and $PACl_0$, in the two pH limits examined, (i.e. pH 4 and 10), the species remains mainly as Al_a , which shows little change with aging. However, an increase in the Al_a fraction with aging can be observed for PACls at higher OH/Al ratio. This indicates that in the presence of free H^+ (low pH) or free OH^- (high pH), dissolution of the polymer species occurs during aging. In the pH range 4.0–4.5, the Al_b fraction formed is relatively stable with aging. A rough estimate of the relevant OH/Al ratio is the range of 0.5–2.5 for alum and $PACl_0$. This illustrates that a fraction of stable polymer species could also be formed under this solution

Fig. 2. The effect of aging on speciation distribution after dosing for alum (the same condition as in Fig. 1). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

condition. Increasing pH to the range of 5.5–6.5 means that the OH/Al ratio is raised to 2.5–3.0 for alum and PACl_0 , which results in a rapid aggregation of the polymer species. Upon further increase of the solution pH, flocculation occurs, promoting particle aggregation and formation of amorphous hydroxide precipitates. In the presence of the sulfate ion, precipitation is accelerated at lower pH.

Furthermore, there is a significant difference between the stability of the pre-formed Al_b species and that formed in-situ after dosing. As shown above, although the maximum of Al_b is formed in the near neutral pH range for alum and low OH/Al ratio PACls, upon short aging this species undergoes rapid transform into Al_c . The preformed Al_b remains relatively stable throughout the pH range. The difference in stability of preformed Al_b to that formed in situ after dosing is indicative of a structural difference between them. This

Fig. 3. The effect of aging on speciation distribution after dosing for PACl_0 (the same condition as in Fig. 1). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

may be due to the likely different reaction pathways for the formation of these Al_b species.

3.4. General discussion

A review of aluminum hydrolysis chemistry reveals that two main kinds of mechanism for hydrolysis–polymerization exist. The most popular is the “core-link” or hexameric ring scheme, in addition to the more recent model of polynuclear formation involving a typical species of tridecameric, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ (also reported to range from 3+ to 7+, normally simplified as Al_{13}). The basic unit of the first model for aluminum polynuclear formation is either the $[\text{Al}_6(\text{OH})_{12}(\text{H}_2\text{O})_{12}]^{6+}$ (single ring) or the $\text{Al}_{10}(\text{OH})_{22}(\text{H}_2\text{O})_{16}^{8+}$ (double ring) species [29]. The main feature of this mode is that the hydrolysis species may be

Fig. 4. The effect of aging on speciation distribution after dosing for PACI₁₀ (the same condition as in Fig. 1). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

continuously formed from monomer to polymer by bidimensional growth of the hexameric ring units. Therefore, many possible polynuclear species can be formed. The principal species will then depend mainly on the experimental conditions. In essence, the basic hexameric ring or “core-link” model was originally proposed as a logical extension of the solid state, crystalline aluminum trihydroxide structure. Although there is no direct verification of all of the possible structures, the model gains quite popular approval especially among the area of geochemistry and soil chemistry, since the resulting polymers prefigure the crystal structure of the aluminum trihydroxide polymorphs, gibbsite, bayerite, and nordstrandite. It is therefore possible to write the schematic reaction pathways from polymerization towards precipitation as Oct-Path 1:

Fig. 5. The effect of aging on speciation distribution after dosing for PACI₂₀ (the same condition as in Fig. 1). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

More recently, based on the direct measurement by ²⁷Al NMR and small angle X-ray diffraction, the polynuclear formation model was proposed. It is postulated that only several possible species in solution and direct transformation among them exist, such as monomers, dimers, tridecamer (Al₁₃), and aggregates. The existence of a tridecamer with a so-called Keggin structure has been verified by several investigators [30–32]. This species forms rapidly and irreversibly when Al(OH)₄[−] interacts with 12 octahedrally coordinated aluminum ions, and does not form on aging via polymer intermediates as suggested by Baes and Mesmer [30]. Akitt and Farthing proposed a mechanism of Al₁₃ polynuclear formation whereby six dimeric species nucleate around Al(OH)₄[−] [33]. However, several uncertainties

Fig. 6. The effect of aging on speciation distribution after dosing for PACl₂₅ (the same condition as in Fig. 1). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

remain in this model. It can not explain the entire process of species formation, distribution and transformation. There are some species beside the total aluminum concentration that can not be detected using the ²⁷Al NMR technique. And the mechanism for further transformation of Al₁₃ structure to aluminum trihydroxide is still to be confirmed, though some progress has been made in this regard [34,35]. Regardless, based on the direct instrument detection, the Al₁₃ model has gained more and more approval. The possible schematic reaction pathways from polymerization towards precipitation involving Al₁₃ might be written as Tetra-Path 2:

It is therefore reasonable to infer a third pathway (Path 3) by mixing/combining Paths 1 and 2, with changes depending on the experimental conditions. For alum and PACl₀ after dosing, Path 3 might occur resulting in Al_b species of different structure around the wide pH range. For tailor-made PACls, the reaction scheme might follow Path 2 after dosing. However, the Al_b fraction is formed in situ through Path 3, in the main contribution from the Al_a fraction in the original composition, as addressed previously. Upon aging, a structure rearrangement occurs rapidly through transformation of the hydroxy-bridge to an oxo-bridge:

While such an aging effect might occur spontaneously on the adjacent bridge points among aggregated polymers and polymer species, the shape and size of the structure undergo some consequent changes. The reactivity of species with ferron evidently slows with aging. Bottero et al. [35] observed more dense and less open clusters formed extremely rapidly at the onset of precipitation (OH/Al = 2.6), protecting the structure components from hydrolysis. Upon aging, the clusters were smaller but their density remained approximately the same. The authors considered that octahedral hydroxyls belonging to adjacent units may condense into oxo-bridges. Al tetrahedral with perturbed symmetry was compacted between growing octahedral layers, and remained protected against the hydrolysis induced by OH⁻.

The information provided by the ferron method is mainly based on the reactivity of species with ferron reagent, as indicated by the kinetic difference of absorbance over time scales of 2 h. It becomes difficult to distinguish the possible differences in structure among the species exhibiting a similar reactivity with ferron. As shown previously, the PACl₂₅ after dosing shows relatively constant reactivity with ferron throughout the pH range investigated. It is known that the polymer species become aggregated and precipitate out above pH 7.5 [11]. Therefore, a detailed examination of the kinetic aspects of ferron assay in combination with particle size information would give much insight into species formed in situ after dosing.

In conclusion, the speciation transformation of coagulants after dosing depends to a large extent on primary composition, and the solution chemical conditions such as coexisting anions, OH/Al ratio, and pH. PACls with high OH/Al ratio exhibit quite stable speciation and tend to maintain original composition under the various conditions.

Acknowledgements

The kind comments by the anonymous reviewers are greatly appreciated. This work is supported by the NSF of China 50078051 and 20277042.

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