Effect of in-situ formed Al hydrates through long-term aging on enhanced particle destabilization by PACl coagulation

Jr Lin Lin*, Aldeno Rachmad Ika, Chun Chen Tseng
Department of Environmental Engineering, Chung Yuan Christian University, Chinese Taipei

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Abstract
Aging of polyaluminum chloride (PACl) coagulants could significantly influence hydrolyzed Al speciation ruling coagulation performance. The goal of this study was to investigate Al species transformation through long-term aging and its impact on coagulation performance. Two kinds of commercial coagulants (PACl-1 and PACl-2) were stored for in-situ aging tests in six months to evaluate Al species variation with time and the performance of coagulation with natural turbid waters. The results showed that CaSO₄ precipitation easily occurs in a commercial PACl coagulant with time as it contains SO₄²⁻ and Ca²⁺. It also activates the precipitation of gibbsite Al(OH)₃ in PACl with aging. Through 180 days aging, both monomeric Al (Alₐ) and polymeric Al (Alₐ) substantially transform into colloidal Al (Alₙ) and precipitated for both PACl coagulants. At low turbidity (10 NTU), PACl-1 has a superior turbidity reduction rate than PACl-2, while PACl-2 performs a little better turbidity reduction at high turbidity (1000 NTU) regardless of aging time. With aging time, an obvious decrease in turbidity reduction for PACl-1 coagulation is observed at low turbidity of 10 NTU, while the improvement in turbidity reduction for PACl-2 coagulation by enhanced sweep flocculation can be achieved as Alₐ mostly transform into Alₙ after 150 days aging. It is concluded that dominant in-situ formed Alₙ after a long time hydrolysis can improve PACl coagulation efficiency in turbidity reduction by enhanced sweep flocculation, especially for low turbidity water, but the increase in preformed Alₐ in PACl would worsen particle destabilization after aging.

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Introduction
Coagulation is an essential treatment process used to aggregate particles and form settleable flocs for efficient subsequent solid-liquid separation in drinking water treatment. Polyaluminum chloride (PACl) has been commonly used as coagulant for effective particles destabilization and aggregation in drinking water treatment plants (DWTPs) (Duan and Gregory, 2003). The performance of coagulation is subjected to hydrolyzed Al species in water (Lin et al., 2008a; Liu et al., 2009). However, the composition of hydrolyzed Al species is essential for the understanding of coagulation behaviors with PACl coagulants (Zhao et al., 2008). Species distribution of commercial PACl coagulants are generally described as monomer, oligomer, Al₁₃ (AlO₄Al₁₂(OH)₂₆(H₂O)₁₂⁺) and uncharacterized oligomer or colloidal Al (Al(OH)₃). Frequently, PACl coagulants are stored for longer than 2 or 3 months before they were

* Corresponding author.
E-mail address: jrlin@cycu.edu.tw (J.L. Lin).

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dosed into coagulation unit in DWTPs in Taiwan, especially in winter or drought seasons with fewer rainfalls that cause the low level of suspended solids in raw water. For this reason, the majority of white precipitates irregularly formed at the bottom of PACl storage tanks and cause clogging of dosing pipes as Al nucleation and precipitation occurs, which leads to an unstable dosing efficiency and costs in operating DWTPs. Thus, the stability and in-situ hydrolysis of PACl coagulants in stock with aging significantly rule Al nucleation and precipitation that affects coagulation performance in drinking water purification.

The stability of PACl coagulants is significantly influenced by physical and chemical parameters such as pH, Al concentration and aging time (Duan and Gregory, 2003; Zhao et al., 2008; Lin et al., 2008a; Liu et al., 2009). Al hydrate species are metastable and could transform into more stable species through aging (Zhang et al., 2017). In general, preformed polymeric Al (Al$_{13}$/Al$_{b}$) in PACl coagulants is quite stable in solution at low concentration regardless of pH variation (Zhao et al., 2008; Lin et al., 2008a). However, with storage time, the aging effect on PACl coagulants could make the chemical structure unstable and then easily hydrolyzed into stable precipitates (e.g. Al(OH)$_{3}$) (Tang et al., 2015). In the past, other study has also showed that PACl coagulants contain different hydrolyzed Al species in coagulation, where medium polymer (i.e., Al$_{b}$) would self-assemble and transform into larger polymer (Al$_{l}$) after more than 1 month aging (Bi et al., 2013). Al nucleation process through hydrolysis is strongly affected by Al concentration and pH changes (Zhang et al., 1989). Previous studies have proven that high concentration sulfate would react with Al$_{13}$ polycations to form an insoluble Al$_{13}$-sulfate salt, which inhibits the initial formation of Al$_{13}$ in the hydrolysis process (Furrer et al., 1992; Kerven et al., 1995). Al$_{13}$ forms clusters or aggregates of various sizes at increasing pH (Lin et al., 2008a), which presumably induce the undetectable of Al$_{13}$ by the Ferron method (Zhang et al., 2017). The stability of Al species with different ligands varies in the hydrolysis process and the overall reaction pathways is involved in the transformation of polymeric Al species to crystalline trihydroxide phases.

Hydrolyzed Al species is dominant in particle and organic matter destabilization for coagulation (Lin et al., 2008a; Lin et al., 2014; Tang et al., 2017). Occasionally, it is necessary to adjust the dosage of PACl coagulant for DWTPs to achieve the goal of residual turbidity in the effluent from sedimentation units as the quality and quantity of PACl coagulants changes with long-term aging. Thus, the effect of aging on hydrolyzed Al species before dosing PACl coagulants is crucial to coagulation performance for particle removal in drinking water treatment. Although most of the previous studies have well been concerned with the stability of Al species in solution with concentrations below 1 mol/L (Hu et al., 2006; Shi et al., 2007). To date, the stability and hydrolysis of Al species in PACl coagulants with high Al concentration has not been fully studied (Kloprogge et al., 1993; Zhao et al., 2009; Bi et al., 2013). Limited study investigated the long-term aging effect on in-situ formed Al nucleation and precipitation at ambient temperature in DWTPs. Besides, there has not been a convincing mechanism proposed that impart kinetic stability to a series of polymers prefiguring the highly thermodynamically favored Al hydroxide phases. The in-situ long-term aging effect on the Al nucleation and precipitation process for the use of PACl coagulants with high Al concentration (i.e., 10% W/W Al$_{2}$O$_{3}$) in DWTPs and its impact on the coagulation performance needs further investigation in natural turbid water treatment for stable drinking water supply.

This study aims to investigate more rational approaches to enhance coagulation for residual turbidity using commercial PACl coagulants in natural turbid water treatment. The coagulation behaviors with in-situ hydrolyzed coagulant species were compared to identify the aging time affecting the turbidity reduction (i.e., particle removal) by sedimentation. Two commercial PACl coagulants were used to evaluate their stability and hydrolyzed Al species distribution with 6 months aging. Meanwhile, the PACl coagulation performance for particle destabilization was determined at different aging times for low and high natural turbid water.

1. Materials and method

1.1. Characteristics of coagulants

Two kinds of commercial PACl coagulants were used to evaluate the aging effect on coagulation performance, designated as PACl-1 (Chung Hwa Chemical Industrial Works, Taiwan) and PACl-2 (Everest Chemical, Taiwan). Al speciation of PACl-1 and PACl-2 was characterized by Ferron method (Lin et al., 2008a). After the addition of the Ferron agent, the PACl sample was immediately shaken to ensure a complete reaction between the Ferron agent and Al. The aluminum species were quantified by timed absorbance at 366 nm with a UV–Visible Spectrometer (U3010, Hitachi, Japan). Based on the kinetics of the reactions between the aluminum species and Ferron agent, the hydrolyzed Al species can be categorized into three groups: Al$_{a}$, monomeric; Al$_{b}$, the polycations; and Al$_{l}$, the colloidal aluminum hydroxide. PACl-1 and PACl-2 coagulants were produced following different synthesis process where PACl-1 was preliminarily synthesized through the mixing of Al(OH)$_{3}$ with 98% H$_{2}$SO$_{4}$ and 32% HCl, with addition of CaCO$_{3}$ to extract the SO$_{4}^{2−}$ and adjust the basicity of solution. Meanwhile, PACl-2 was synthesized through the mixing of Al(OH)$_{3}$ with 32% HCl at 130°C and 73.5 PSI. PACl-1 contains about 50% monomeric Al (Al$_{a}$), 11% polymeric Al (Al$_{b}$) and 39% colloidal Al (Al$_{l}$), while the PACl-2 has 56% monomeric Al (Al$_{a}$), 32% polymeric Al (Al$_{b}$) and 12% colloidal Al (Al$_{l}$). Aluminum concentration was analyzed by an inductively coupled plasma atomic emission spectrometry (ICP-OES 7000 series, Agilent, USA). PACl-1 and PACl-2 characteristics and species distribution are as shown in Table 1. The working solutions containing 2000 mg/L Al were freshly prepared before each test.

1.2. Aging test

Before the coagulation test, the two commercial PACl coagulants were stored in independent PE tanks with a capacity of 1000 kg (Appendix A Fig. S1) outside for in-situ aging tests. Temperature was uncontrolled ranging from 14 to 27°C during the six months aging. The Al concentration and speciation...
of PACl coagulants with aging time were determined by ICP-OES (ICP-OES 7000 series, Agilent, USA) and Ferron method. The total aluminum concentration of each PACl sample was diluted to 0.37 mmol/L Al for the duration of the Ferron test. A field emission scanning electron microscope, FE-SEM, (SEM-6330F, JEOL, Japan) coupled with an X-ray energy-dispersive spectrometer (EDS) detector was used for imaging and characterization of the aged Al and Ca precipitates within the air-dried samples at acceleration voltages of 15 kV. Additionally, the X-ray diffractometer (XRD) (D1, Bede, UK) with Cu-Kα radiation was employed to diagnose the crystalline structure of the Al precipitates powder after PACl aging. XRD patterns were recorded between 5° and 100° (Lin et al., 2008a) at a scanning speed of 1 min⁻¹. All experimental samples for XRD survey were freeze-dried before each test.

### 1.3. Coagulation protocol

Standard jar trials (Phipps and Bird, USA) were conducted to evaluate the performance of coagulation. Raw water samples were collected from Banshin water treatment plants located in the north of Taiwan. At different aging times, the turbidity of the tested raw water varies at 10 NTU and 1000 NTU with pH ranging from 6.7±1.7 to ±1 and alkalinity ranging from 46–60 mg/L as CaCO₃. Two previously mentioned coagulants, PACl-1 and PACl-2, were used for this study to determine the optimal dosage in coagulation process. The optimal PACl dosage was chosen at 1 mg/L as Al and 4 mg/L as Al for coagulation with low and high turbidity water. Initial rapid mixing was conducted at 100 r/min for one min followed by a slow mixing at 50 r/min for 20 min. The suspension was left undisturbed for 10 min. After settling, the turbidity of supernatant was measured by a turbidity meter (2100 P, Hach, USA) and the residual dissolved Al was quantified by ICP-OES (ICP-OES 7000 series, Agilent, USA). The zeta potentials of the suspension were measured using a laser zeta analyzer (Zetasizer Nano ZS, Malvern Inc., UK) immediately after the rapid mixing without dilution. All tests were conducted in duplicate.

### 2. Results and discussion

#### 2.1. Aging effect on Al concentration and speciation of PACl coagulants

As illustrated in Fig. 1, the aging process can be divided into two stages based on the monomeric Al (Alₐ), polymeric Al (Alₖ) and colloidal Al (Alₖ) transformation rate by Ferron assay. As shown in Fig. 1a, the low content of Alₐ at around 10% in PACl-1 remains quite stable in the initial three months but halved after 4 months. However, Alₐ and Alₖ contents vary with time in the range between 40% and 55% where Alₐ decreases with increases in Alₖ, vice versa. At 4 months aging, it contributes to the maximum content of Alₖ, owing to the decrease in the content of Alₐ. In contrast, the content of Alₖ at 32% in PACl-2 starts to decrease after 1 month aging and further decreases significantly after 4 months aging before reaching to minimum (below 10%) at 6 months aging, while the content of Alₖ linearly increases between 10% and 40% over time within 5 months aging but suddenly rise to around 60% at 6 months aging, accompanying the substantial decrease in the content of Alₐ as shown in Fig. 1b.

On the other hand, the corresponding Al concentration of PACl-1 and PACl-2 slightly decrease from around 74,000 mg/L as Al to 70,000 mg/L as Al after 150 days aging, and the pH of both coagulants decrease from 2.5 to 2.3 and from 2.4 to 2.0 due to Al hydrolysis for PACl-1 and PACl-2, respectively. The decreases in Al concentration along with pH could be attributed to Al nucleation process (Zhang et al., 1989; Bi et al., 2013). At such a condition, two layers, namely interface layer and bulk solution layer, could be divided during the aging process. The total Al concentration of bulk solution would decrease with the increase in the Al concentration of the interface layer. Meanwhile, the pH of bulk solution would become lower with aging because Al hydrates change their soluble form into solid form over time, as evidenced in Fig. 1. Faster Alₖ transformation to Alₖ hydrates occurs at aging within 4 months for PACl-2 since it contains a higher amount of Alₖ, along with higher pH decrease compared to PACl-1. This indicates the aggregation of Alₖ is faster than the hydrolysis of Alₖ. The Alₖ trends to aggregate into Alₖ directly in short aging time, however, Alₖ-transforms under the hydrolysis process to form Alₖ through metastable Alₖ formation phase (Hu et al., 2006). Theoretically, it takes a longer path for Alₖ-to complete the hydrolysis and form stable colloidal Al or precipitates. The results of Al hydrolysis have shown that PACl with different Al speciation would present different Al hydrolysis pathway through aging. Xu et al. (2003) has reported that different species in various PACl undergo different reaction pathways with various Al/SO₄ ratio from 0.2 to 5 at a given Al concentration of 0.02 mol/L. The colloidal Alₖ would form nucleation and precipitation quickly with sulfate, while Alₖ undergo slow crystallization. Instead, monomeric Alₖ-reacts with sulfate to form soluble complexes.

In the case of aging effect on PACl-1, Alₖ-does not significantly hydrolyze to Alₖ with aging owing to the occurrence of soluble Al-SO₄ complexes as high concentration (2%) of sulfate presents in PACl-1 coagulant. In other words, concentrated sulfate can slow down the hydrolysis of Alₖ into Alₖ or Alₖ, which causes a slight decrease in Alₖ and less fluctuation in Alₖ compared to PACl-2 coagulant. However, Alₖ could form soluble Al species as pH decreases during aging with pH decrease from 2.5 to 2.3 for PACl-1 in this study. On the other hand, only a few amount of Alₖ would undergo aggregation to form Alₖ during aging, especially after 4 months aging. A hydrolysis reaction pathway corresponded to three kinds of Al species with aging can be expressed as follows:

\[
\text{Al}_\text{a} = \text{Al}_\text{k} = \text{Al}_\text{c}
\]
As illustrated by our findings in Al hydrolysis behaviors for PACl-1 in Fig. 1a, it indicates that three kinds of Al species (i.e., Ala, Alb and Alc) could vary in turn during long-term aging. Unlike PACl-1, based on our findings in Fig. 1b, it can be hypothesized that Ala-and Alb could transform into Alc in turn with aging for PACl-2 even though Alb composes of stable Al\textsubscript{13} with either Al(O)\textsubscript{6} or Al(O)\textsubscript{4} structure (Tang, et al., 2015). This suggests that a spontaneous Al hydrolysis process occurs for PACl-2. The reaction pathway and hydrolysis formula corresponded to three kinds of Al species with aging can be expressed as follows:

\[
\text{Al}_a \rightarrow \text{Al}_c \text{ or } \text{Al}_b \rightarrow \text{Al}_c
\]

\[
\Delta \text{Al}_a + \Delta \text{Al}_b \equiv \Delta \text{Al}_c
\]

In other words, the amounts of hydrolyzed Al\textsubscript{a} (\(\Delta \text{Al}_a\)) and Al\textsubscript{b} (\(\Delta \text{Al}_b\)) would be compensated by the amounts of Al\textsubscript{c} content (\(\Delta \text{Al}_c\)) during aging. However, the Al\textsubscript{b} would extensively aggregate into Al\textsubscript{c} as aging time extends to longer around 6 months, as illustrated in Fig. 1b. At such a condition, the in-situ formed Al\textsubscript{c} content increases about two times while Al\textsubscript{a}-and Al\textsubscript{b} fraction decrease substantially potentially due to the formation of Al nucleation and precipitation. Al nucleation likely occurs as colloidal Al concentration continuously increases to critical precipitation concentration after long-term aging. As a result, the majority of colloidal Al or Al precipitates form through Al nucleation and precipitation in the period of in-situ aging at changeable ambient temperature. The results indicate that PACl-2 coagulant shows a worse stability of Al hydrolysis with in-situ formed Al\textsubscript{c} than PACl-1.

2.2. Aging effect on the composition of precipitates in PACl coagulants

Aging effect can bring slow nucleation to PACl solution, thus the morphology of Al precipitates formed in the in-situ aging process were further studied. With aging time up to 120
days, PACl-1 solution starts to form hexagonal plate-like or flat shape precipitates with crystalline forms, while PACl-2 forms the majority of nano-size amorphous precipitates as aging time exceeds 150 days, as seen in Fig. 2. By EDS assay for metal element analysis on precipitates, it indicates that Al element level on the surface of precipitates in PACl-1 is a little higher than Ca element level, with a ratio of Al/Ca at 1.3; however, only Al metal element is observed on the surface of the precipitates in PACl-2. Fig. 3 shows the crystal form of precipitates in the aging of PACl-1 and PACl-2 coagulants through XRD analysis. Two peaks associated with CaSO\(_4\) precipitates are found, accompanying a few peaks of gibbsite Al(OH)\(_3\) crystal form for PACl-1, while a broadening peak corresponding to gibbsite Al(OH)\(_{3(\text{am})}\) is obtained for PACl-2, following the identification correspond to the JCPDS file. Previous studies have reported that crystal gibbsite Al(OH)\(_3\) precipitates present a hexagonal plate-like shape under preparation at room temperature (Souza et al., 2015) and CaSO\(_4\) precipitates possess flat crystal morphology (Fu et al., 2017). Generally, alum salts would transform into amorphous gibbsite Al(OH)\(_{3(\text{am})}\) precipitates in the absence of calcium ion (Dempsey et al., 1984). In the presence of calcium ion, sulfate ion in the solution can react with Ca\(^{2+}\) to form gypsum (CaSO\(_4\)), which generally occurs at higher (>1000 mg/L) sulfate concentration (Cohen and Mather, 1991).

With aging, the PACl-1 originally contains not only Al ions but 0.5% Ca\(^{2+}\) that can react with 2% SO\(_4^{2-}\) to form CaSO\(_4\) precipitates at 150 days aging. Enough SO\(_4^{2-}\) could also combine with Al species, such as Al\(_{13}\)\(^{3+}\), to form Al-based precipitates (Cohen and Mather, 1991; Wang et al., 2011; Zhang et al., 2017). As PACl-1 contains about 2% SO\(_4^{2-}\) along with few Ca and extensively concentrated Al, it is easier to form highly crystalline Al(OH)\(_3\) and CaSO\(_4\) composite precipitates, but PACl-2 containing Al in the absence of Ca\(^{2+}\) along with lower than 0.3% SO\(_4^{2-}\) precipitates large amounts of Al(OH)\(_{3(\text{am})}\) as illustrated in Fig. 2 and Fig. 3. The results have shown that PACl-1 coagulant is prone to precipitate into CaSO\(_4\) after long term aging but PACl-2 favors amorphous gibbsite Al(OH)\(_3\) precipitation at similar aging conditions. In addition, the existence of SO\(_4^{2-}\) along with Ca\(^{2+}\) in PACl coagulants would make the nucle-
ation and precipitation happen easier and earlier in long-term in-situ aging process. It indicates that PACI-1 with preformed Alc and concentrated sulfate would undergo crystallization to form crystalline Al(OH)₃ precipitates sooner, while PACI-2 with less preformed Alc and sulfate carries slower transformation from Alₜ to in-situ formed Alc followed by amorphous Al(OH)₃ precipitation.

### 2.3. Aging effect on PACI coagulation performance for particle destabilization

The changes in Al speciation of PACI coagulants through in-situ hydrolysis or aging time could govern the coagulation behaviors and performance for particle destabilization and turbidity removal by coagulation-sedimentation processes (Zhao et al., 2008; Zhang et al., 2017; Lin and Ika, 2019a). The turbidity removal rate by PACI-1 and PACI-2 coagulation at same optimal dosage (i.e., 1 mg/L at low turbidity and 2 mg/L at high turbidity) varies with aging time for low and high turbidity waters (i.e., 10 NTU and 1000 NTU), as shown in Fig. 4. A turbidity removal rate higher than 70% was achieved by PACI-1 coagulation at different dosages for low turbid water within 150 days aging regardless of aging time. Even though the turbidity of raw water increases, PACI-1 still shows a high turbidity removal rate of over 98%. However, the turbidity reduction rate becomes worsen for PACI-1 coagulation with the majority of preformed Alc after aging. In contrast, an increase in turbidity removal rate from around 20% to 60% is obtained for PACI-2 coagulation at turbidity as low as 10 NTU as aging time increases up to 150 days. However, a decreased turbidity removal rate occurs for PACI-2 coagulation at 90 days aging. This is owing to the decreased polymeric Al (Alₜ) along with an unsatisfied increase in colloidal Al (Alc), as illustrated in Fig. 1b. This indicates that preformed Alc would worsen particle destabilization and turbidity reduction for PACI-1 coagulation but the hydrolysis of Alₜ towards Alc could improve the turbidity removal rate for PACI-2 coagulation, depending on the quantity of in-situ formed Alc from Alₜ hydrolysis. Unlike poor turbidity removal rate at 10 NTU, PACI-2 performs relatively high turbidity removal rate at turbidity as high as 1000 NTU, as shown in Fig. 4b, owing to the reaction between colloidal Al with SO₄²⁻. A few amounts of SO₄²⁻ could assist in particle aggregation in PACI coagulation by inter-complexation between positively charged Al species and SO₄²⁻.
Al(OH)₃ (Liu et al., 2009). Furthermore, increases in particle and turbidity removal by enhanced sweep flocculation with after 150 days aging. This improves particle destabilization species of PACl-2 is significantly affected by aging, especially hydrates with insignificant hydrolysis of Al. However, the Al removal rate is insensitive to the aging effect at various turbidity and PACl coagulation (Rosenqvist et al., 2002). The turbidity reduction and turbidity removal for PACl coagulation at optimal dosage with coagulant aging time at various turbidity regardless of Al species variation with aging time.

PACl-1 and PACl-2 coagulation behaves differently in turbidity reduction along with similar zeta potential at optimal dosage for low and high turbid waters with aging time, as shown in Fig. 5. The zeta potential varies from -3 to -7 mV for low turbidity water samples of 10 NTU and -15 to -17 mV for high turbidity water samples of 1000 NTU, respectively. The lowest residual turbidity occurs for low and high turbid waters at optimal dosage where the zeta potential is between +2 and +7 mV for PACl-1 and PACl-2 coagulation regardless of aging time in response to sweep flocculation due to abundant Al₃⁺ formation. Another study has reported that short-term aging of PACl within 5 min would cause Al hydrates aggregation in size causing adverse effects on particle removal and turbidity reduction for PACl coagulation (Zhang et al., 2017), which is opposing to the findings in this study. A long-term aging time likely increases active colloidal Al formation that enhances the turbidity reduction for PACl coagulation (Bi et al., 2013). The occurrence of nanosized gibbsite Al(OH)₃ at neutral pH present positively charged surface due to its high isoelectric point at pH 10 (Rosenqvist et al., 2002). It also implies that heterogeneous reactions between particles and positively charged Al(OH)₃ predominates the coagulation via sweep flocculation for particle destabilization and floc formation (Lin et al., 2008c; Lin et al., 2009), resulting in turbidity reduction in the supernatant after sedimentation (Duan and Gregory, 2003; Liu et al., 2009). This result is in accordance with our previous study that has reported similar results for PACl coagulation with natural high turbid water (Lin et al., 2008b). Moreover, it is possible that some further hydrolyzed colloidal Al (Alc) species act as polymers (Zhang et al., 2017), which could destabilize particles and improve floc formation. Thus, the optimal particle destabilization can be achieved by sweep flocculation for PACl coagulation with natural turbid waters even though Al(OH)₃ precipitates form after long-term aging.

### 2.4. Effect of Al hydrolysis pathways on particle destabilization with Al hydrates

Al species are metastable intermediates and could transform into more stabilized species through aging (Fu et al., 1991). Based on the findings through a long-term in-situ aging test in field study, a hypothesis is proposed to illustrate the possible Al transformation pathways along with pH and Al concentration variations correspond to a series of Al species formed in hydrolysis process under ambient temperature, as shown in Fig. 6. With the aging time of PACl coagulants, the Al hydrolysis and transformation occur along with slightly decreased pH and Al concentration. In the case of PACl with low content of Al₃⁺, the Al₃⁺ could transform into Al₅⁺ and Alc, but Alc could be dissolved into Al₅⁺ in the presence of concentrated sulfate (i.e., approximately 2% SO₄²⁻). However, the high content of Al₅⁺ would transform into Alc tremendously in a faster reaction process for PACl with few SO₄²⁻. High concentrated sulfate through long-term aging also could significantly complex with Al₅⁺ or Alc to activate the dissolution of those Al species happen as a result from decreased pH. At such a condition, a reversible transformation pathway exists among Al₃⁺, Al₅⁺ and Alc, which could transform into more stabilized species through aging (Fu et al., 1991).
there is an irreversible reaction pathway among colloidal Al, Al nucleus and Al precipitates. Hence, both reversible and irreversible Al could behave different coagulation performance for particle destabilization because of their different affinities to particles. In that case, when the in-situ reversible colloidal Al precipitate into dominantly irreversible crystalline Al(OH)₃, it is not effectively adsorbed onto particles to cause improved particle destabilization and floc formation. In contrast, a significant improvement in particle destabilization is induced by dominant in-situ formed colloidal Al along with amorphous Al(OH)₃, which could effectively incorporate particles to settling flocs.

2.5. The implication of aging PACl on coagulation in drinking water treatment

Aging of PACl coagulants are commonly attributed to be one of the reason why poor particle destabilization occurs in most
of drinking water treatment plants. Unsatisfactory coagulation performance for particle or organic matter removal due to the effect of Al hydrolysis in PACl coagulation has been extensively studied (Gao et al., 2017; Hu et al., 2006; Lin et al., 2014; Wang et al., 2002). In practice, commercial PACl containing low content of polymeric Al (Alb) or colloidal Al (Alc) would easily result in disqualified level of residuals in coagulation process for natural turbid water treatment (Lin and Ika, 2019a; Lin and Ika, 2019b).

Based on the major findings in this study, in-situ formed Alc (colloidal Al or Al(OH)₃ precipitates), after several months of aging, play different roles in particle destabilization at low turbidity because of metastable Ala and Alb. With aging, the pre-formed colloidal Al transform into Al precipitates (crystalline Al(OH)₃) in presence of concentrated sulfate in PACl containing 10% Alb remain dominantly over 5 months, which worsens particle removal at low and high turbidity (10 NTU and 1000 NTU) in coagulation-sedimentation process. However, dominant in-situ formed colloidal Al or amorphous Al(OH)₃ in PACl containing 30% Alb with aging would substantially improve particle removal at low turbidity and it performs similar particle removal regardless of aging at high turbidity. This indicates that in-situ formed Alc (colloidal Al or amorphous Al(OH)₃) carries more reactive affinity to suspended particles in coagulation process compared to aging Alc (crystalline Al(OH)₃). Thus, it is important to determine the storage time of PACl to improve turbidity removal rate for low turbidity water, depending on its Alb content. Therefore, it is suggested for drinking water treatment plants to use PACl with higher Alb content more than 30% after aging over 5 months to improve turbidity reduction in coagulation for low turbidity water. In addition, it is recommended to use PACl with high content of preformed Ala and Alc, at more than 50% and 40%, respectively, for enhanced turbidity reduction in coagulation of low turbidity water before severe aging.

3. Conclusion

The long-term aging effect influences the variations of hydrolyzed Al species for commercial PACl coagulants, especially after 150 days aging, causing the occurrence of Al precipitates. Inevitably, PACl forms numbers of crystalline Al hydroxides and CaSO₄ precipitates as it contains about 2% SO₄²⁻ and 0.5% Ca²⁺. Meanwhile, PACl forms the majority of amorphous Al hydroxides (Ala) from monomeric Al (Ala) and polymeric Al (Alb) transformation in spontaneous hydrolysis process. The existence of calcium and sulfate ions would activate Al nucleation and precipitation process. The impact of aging on Al speciation of commercial PACl coagulants strongly affects their coagulation performance for particle destabilization and further turbidity reduction after sedimentation in drinking
water treatment. The results have indicated that increasing aging time for PACl coagulants to enable the majority of Al\textsubscript{A} and Al\textsubscript{B} transform into Al\textsubscript{C} significantly improve turbidity reduction after coagulation-sedimentation for natural water with turbidity as low as 10 NTU. However, Al\textsubscript{A} and Al\textsubscript{B} species would slightly hydrolyze into each other in turn with aging time as PACl coagulant initially contains 50% Al\textsubscript{A} and Al\textsubscript{C} content higher than 40%, and the corresponding coagulation performance for particles reduction would slightly decrease with long-term aging time at low and high turbidity. In drinking water treatment, long-term aging effect brings slow nucleation and precipitation to PACl coagulants, thus significantly enhances the particle destabilization by sweep flocculation as in-situ formed Al\textsubscript{C} becomes dominant for low turbidity water but worsen particle destabilization since aging Al\textsubscript{A} forms mostly. It is concluded that PACl containing in-situ formed Al hydroxide after aging brings an improvement in particle destabilization for coagulation in natural turbid water treatment instead of aging Al hydroxide.

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Supplementary materials

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