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Minimizing residual aluminum concentration in treated water by tailoring properties of polyaluminum coagulants

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ABSTRACT

Aluminum coagulants are widely used in water treatment plants to remove turbidity and dissolved substances. However, because high aluminum concentrations in treated water are associated with increased turbidity and because aluminum exerts undeniable human health effects, its concentration should be controlled in water treatment plants, especially in plants that use aluminum coagulants. In this study, the effect of polyaluminum chloride (PACl) coagulant characteristics on dissolved residual aluminum concentrations after coagulation and filtration was investigated. The dissolved residual aluminum concentrations at a given coagulation pH differed among the PACls tested. Very-high-basicity PACl yielded low dissolved residual aluminum concentrations and higher natural organic matter (NOM) removal. The low residual aluminum concentrations were related to the low content of monomeric aluminum (Ala) in the PACl. Polymeric (Alb)/colloidal (Alc) ratio in PACl did not greatly influence residual aluminum concentration. The presence of sulfate in PACl contributed to lower residual aluminum concentration only when coagulation was performed at around pH 6.5 or lower. At a wide pH range (6.5–8.5), residual aluminum concentrations <0.02 mg/L were attained by tailoring PACl properties (Ala percentage ≤0.5%, basicity ≥85%). The dissolved residual aluminum concentrations did not increase with increasing the dosage of high-basicity PACl, but did increase with increasing the dosage of normal-basicity PACl. We inferred that increasing the basicity of PACl afforded lower dissolved residual aluminum concentrations partly because the high-basicity PACls could have a small percentage of Ala, which tends to form soluble aluminum–NOM complexes with molecular weights of 100 kDa–0.45 μm.

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1. Introduction

Alum and polyaluminum chloride (PACl) coagulants are widely used at water treatment plants to remove turbidity and dissolved substances from water. However, concerns have been raised that the use of such coagulants may increase aluminum concentrations in treated water (Miller et al., 1984;

Ohno et al., 2009). High aluminum concentrations in treated water are associated with several problems, including increased turbidity due to the formation of aluminum precipitates. Also of concern are human health hazards (Flaten, 2001; World Health Organization, 2004; Gupta et al., 2005).

The concentration of residual aluminum remaining in water treated with aluminum coagulants is influenced by

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many factors. Among these, control of solution pH is key to minimizing the aluminum concentration (Licisko and Szakal, 1988; Van Benschoten and Edzwald, 1990; Van Benschoten et al., 1994; Driscoll and Letterman, 1995). The use of aluminum coagulants at around pH 6.5 is one approach for minimizing residual aluminum concentrations. Although residual aluminum concentrations can be controlled by adjusting pH to slightly acidic values, this strategy is not widely practiced, because it requires a pH increase post-treatment to control corrosion in water distribution networks. In addition, small water treatment facilities still experience difficulties in attaining this pH optimization, because the small size of the plant provides little buffering for fluctuation in operation. Moreover, such small facilities often have limited resources and limited access to the expertise needed to control acid/base addition and to optimize pH conditions. In Japan, the drinking water quality guideline for aluminum is 0.1 mg/L, but water treatment plants usually set stricter values for finished water, e.g., <0.05 mg/L. However, meeting such values is often difficult, particularly when the pH of raw water is high due to algae growth. Under such alkaline conditions, high concentrations of residual aluminum often remain following water treatment. Therefore, the development of coagulants that can easily decrease residual aluminum concentrations to <0.05 mg/L, even for treated water in which coagulation pH is not optimized, is highly desired.

Residual aluminum concentrations after water treatment can also vary with coagulants (alum and PACls). For example, Jekel (1991) conducted jar tests with alum and four commercial prehydrolyzed aluminum salts and reported that, at pH values of >7.5, the use of two of the four prehydrolyzed products resulted in lower residual aluminum concentrations than did the use of alum. Simpson et al. (1988) suggested the use of PACl instead of alum as an approach for reducing residual aluminum concentrations. Yan et al. (2008a) reported that the dissolved residual aluminum concentrations for high-basidity (basidity = $\text{OH}/\text{Al} = 2.0$ or $\text{OH}/(\text{Al} \times 3) \times 100 = 67\%$) PACl at acidic and basic pH (<5.5 and >7.5) were lower than that for medium-basidity PACl and AlCl_3 . However, at neutral pH (7.0), dissolved residual aluminum concentrations were the same for AlCl_3 and the PACls. These investigators attributed the lower aluminum concentrations to the low content of monomeric aluminum species in the high-basidity PACl (Yan et al., 2007). However, a low residual aluminum concentration (<0.1 mg/L) was not attained at any pH for any coagulants with basicities 0–2.5. In practice, controlling residual aluminum concentration to <0.1 mg/L is difficult, in particular when PACls are used at pH > 7.5 (Matsukawa et al., 2006). Very recently, Yang et al. (2011) reported that residual aluminum concentrations varied in the following order: PACl of basidity $1.5 > 2.3 \geq 2.0$. However, the comparison, which was made on different coagulation pH values because pH after dosing coagulants depressed differently depending on coagulant basidity, might be imprecise. Overall the previous results suggest that the residual aluminum concentration could be controllable by adjusting PACl properties, but the specific PACl properties for lowering residual aluminum concentrations <0.05 mg/L have yet to be investigated. It should also be noted that most of the previous studies used non-sulfated PACls, although sulfated PACls are widely applied in practice because

sulfate enhances the flocculation performance of PACls. However, inclusion of sulfate ions in high-basidity PACls with high aluminum content limits the PACls' long-term chemical stability, so the basicity of practically applied PACls with Al content >5% (w/w) is typically limited to 2.0 to allow storage of the compounds for >6 months.

In this study, we evaluated the efficacy of PACls, including those with an extremely high basicity of 2.7, in terms of residual aluminum concentration at neutral and alkaline pH.

2. Materials and methods

2.1. Coagulants

Five aluminum-based coagulants were evaluated in the first set of experiments (Table 1S, Supplementary Information). Commercially available PACls with standard basicities of 1.8 and 1.5 (designated PACl-61s and PACl-51s, respectively. The numbers, "51" and "61", in the names indicate percent basicity values. "s" indicates "sulfated".) were provided by Taki Chemical Co. (Kakogawa, Japan). PACl-71s is a trial coagulant product (presently commercially available) provided by the same company. These PACls were produced by dissolving $\text{Al}(\text{OH})_3$ solids in hydrochloric and sulfuric acid (as described by, e.g., Itoh and Sato, 1995; Sato and Matsuda, 2009). Alum was provided as a solution (Taki Chemical Co.). The PACls and alum were used in jar tests immediately after dilution with Milli-Q water. AlCl_3 solution was prepared by dissolving reagent-grade $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Osaka, Japan) in Milli-Q water (Milli-Q Advantage, Nihon Millipore, Tokyo, Japan); this solution was considered as a reference PACl with a basicity of zero (Yan et al., 2008a).

After the experiments using the five coagulants described above were completed, we conducted the second set of experiments by using 12 additional coagulants. Four PACls out of 12 were prepared by a base titration method in the authors' laboratory (Shen and Dempsey, 1998; Yan et al., 2008b). PACl-72b and PACl-90by ("b" in the name indicates high Alb percentage relative to other PACls of the same basicity. "x", "y", and "z", some of which appear later, have no special meaning.) was prepared with the following procedure. NaOH (0.3 M) was titrated to a 500-mL Erlenmeyer flask containing an 80 mL of AlCl_3 solution (0.5 M) by a peristaltic pump at rate of 4 mL/min to bring the target basicity. During the titration the solution in the flask was agitated and the temperature was kept at 85–90 °C by a combined hot-plate magnetic-stirrer device. PACl-90bx was prepared from 0.6 M NaOH and 1.0 M AlCl_3 solutions by the same method. For PACl-72c ("c" in the name indicates high Alc percentage), after titrating 0.9 M NaOH into 1.5 M AlCl_3 solution, the solution was kept at 85–90 °C for 12 h. PACl-50, PACl-61, and PACl-70 were trial coagulant products (Taki Chemical Co.) produced from NaOH and AlCl_3 . PACl-85x, y, and z and PACl-90x and y were also trial coagulant products that produced from commercial aluminum chlorohydrate solution (Al_2O_3 23%, sulfate ion 0%, relative density of 1.3, Taki Chemical Co.) and soda ash.

The distributions of aluminum species in the coagulants were analyzed by the ferron method. On the basis of their

reaction rates with ferron reagent (8-hydroxy-7-iodo-5-quinoline sulfonic acid, Wako Pure Chemical Industries), the aluminum species were divided into three categories: Ala, Alb, and Alc. Ala denotes aluminum species that reacted with ferron instantaneously (within 30 s). Alb denotes species that reacted within 120 min. Alc denotes species that did not react. These species were assumed to be monomeric, polymeric, and colloidal aluminum species, respectively (Wang et al., 2004). Ferron analyses of the coagulants were conducted immediately (1–2 min) after diluting coagulants with Milli-Q water to 2.7 g-Al/L (Wang et al., 2004; Jia et al., 2004). Dilution reportedly has little effect on the ferron speciation distribution of PACl (Wang et al., 2004), and we also observed a negligible effect of dilution on ferron speciation distribution in the present study (data not shown). After adding the ferron reagent into diluted coagulant, the mixture was immediately shaken, and then the absorbance at 366 nm in an 1-cm or 5-cm cell was measured by using at the predetermined times.

Using membranes with various molecular weight cutoffs (MWCs), we also investigated the MW distributions of aluminum species in the coagulants. Coagulants containing 2.7 g-Al/L (the same concentration as that used for the ferron method) were filtered through ultrafiltration (UF) membranes with nominal MWCs of 500 Da (cellulose acetate membrane, Amicon YC, Nihon Millipore) and 3 kDa (regenerated cellulose membrane, Ultracell PL, Nihon Millipore) in a 50-mL stirred cell (Amicon 8050 series, Nihon Millipore) under 0.5 MPa pressure immediately after preparation of the solution. Filtration was performed until 2 mL was collected from a 50-mL sample. Aluminum concentrations were analyzed with an inductively coupled plasma mass spectrometer (ICPMS, HP-4500 and HP-7700, Agilent Technologies, Inc.).

2.2. Jar tests

Jar tests were performed with a jar test apparatus at room temperature (~ 20 °C) unless otherwise noted. Raw water (Table 1) was transferred to a 1-L square plastic beaker. After a predetermined volume of HCl (0.1 N) or NaOH (0.1 N) was added to bring the final coagulation pH to a target value, a coagulant was injected into the raw water sample. The mixture was stirred rapidly for 1 min ($G = 200 \text{ s}^{-1}$, 136 rpm) and then slowly for 10 min ($G = 20 \text{ s}^{-1}$, 30 rpm). The mixture was then left to rest for 1 h so that the aluminum floc particles generated would settle. Then samples were taken from the beaker and filtered through a 0.45- μm polytetrafluoroethylene (PTFE) membrane filter (DISMIC-25HP; Toyo Roshi Kaisha, Ltd.,

Tokyo) unless otherwise noted for quantification of the dissolved organic carbon (DOC; Sievers 900 TOC Analyzer, GE Analytical Instruments, Boulder, Colorado, USA) and aluminum. The coagulation pH and turbidity were measured after settling. Decreases in turbidity were high in most of the experiments because the coagulant dosages were sufficient for formation of floc particles. Therefore, coagulant performance was evaluated mainly in terms of DOC removal. For the first set of experiments, we investigated the size distribution of the residual aluminum particles by using membranes with nominal MWCs of 100 k, 3 k, and 500 Da, as well as 0.45- μm pore size. Jar tests were performed at a constant dosage with varying pH. The data at a fixed pH value were obtained by interpolation because final coagulation pH hardly coincided with the target value, e.g., the interpolation of the results for two pH ranges (pH 7.2–7.4 and 7.6–7.8) surrounding the target pH value of 7.5.

3. Results and discussion

3.1. Coagulant properties

The percentages of aluminum species in the coagulants, as determined by means of the ferron method, are shown in Fig. 1A and C. Aluminum species distributions were very different depending on basicity and production methods. Among the PACls, Alc percentage generally increased with increasing basicity. The inclusion of sulfate in the PACls did not largely influence aluminum species distribution (compare PACl-50 and -51s, PACl-61 and -61s and PACl-70 and -72s in Fig. 1C). The aluminum speciations of PACl-51s (basicity 1.5) was similar to the speciation observed for another Japanese commercial PACl (basicity 1.4) analyzed by Lin et al. (2008). Most of the PACls, except some laboratory-prepared PACls (PACl-72b, -90bx, and -90by), contained small amounts of Alb, which is typically observed for commercial PACl products (Wang and Hsu, 1994; Chen et al., 2006).

MW distributions of aluminum species were determined for PACl-71s, -61s, and -51s, and for AlCl_3 and alum. PACl-71s had the highest percentage of aluminum in the high-MW fraction (>3 kDa), followed by -61s, -51s, alum, and AlCl_3 , in that order (Fig. 1B). The results from the ferron method and the MW distribution analysis strongly agree in indicating that, of the tested coagulants, PACl-71s contained the smallest amount of monomeric aluminum (low MW) and the largest amount of colloidal aluminum (high MW).

Table 1 – Characteristics of raw water samples used in this study.

Designation	pH	Turbidity (NTU)	Alkalinity (mg/L as CaCO_3)	DOC (mg/L)	UV ₂₆₀ (cm^{-1})	Source	Sampling date
Toyohira River A	7.7	1.4	40	1.0	0.033	Toyohira River, Hokkaido, Japan	26 September 2008
Toyohira River B	7.5	0.96	21	1.0	0.031	Toyohira River, Hokkaido, Japan	8 July 2009
Toyohira River C	7.4	9.0	17	1.0	0.031	Toyohira River, Hokkaido, Japan	24 June 2011
Chibaberi River A	7.7	4.9	105	4.0	0.25	Chibaberi River, Hokkaido, Japan	13 August 2008
Chibaberi River B	7.4	2.4	31	2.1	0.10	Chibaberi River, Hokkaido, Japan	13 November 2009
Wani River	7.6	5.4	80	3.2	0.065	Wani River, Ibaraki, Japan	26 December 2011

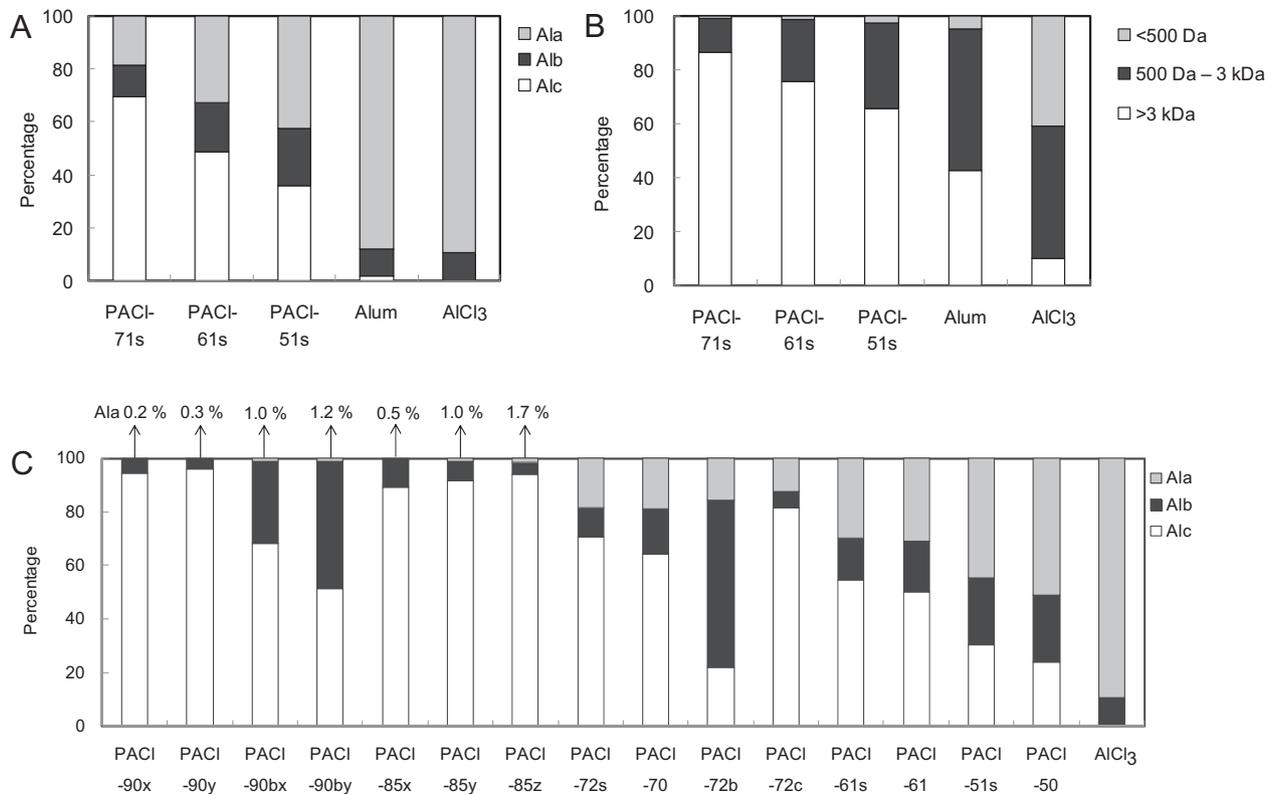


Fig. 1 – Coagulant properties determined by the ferron method (A and C) and membrane filtration fractionation (B). Coagulants in Panels A and B were used for the first set of experiments while those in Panel C were used in the second set of experiments. The standard deviations for the determination of Ala contents (%) were <math>< 0.1\%</math>.

3.2. First set of experiments

3.2.1. Dissolved residual aluminum and DOC removal in jar tests

We determined dissolved residual aluminum concentration as a function of coagulation pH for PACI-71s, PACI-51s, AlCl₃, and alum (Fig. 2). PACI-71s showed the lowest dissolved residual aluminum concentration at both neutral and weakly alkaline pH, followed by PACI-51s. Yan et al. (2008a) shows that at neutral pH the dissolved residual aluminum concentrations are the same for PACIs with different basicities (0–67%), as are the minimum dissolved residual aluminum concentrations attained by adjusting the pH. In contrast, in

our study we found that the dissolved residual aluminum concentration decreased with increasing basicity to 71% at both neutral and alkaline pH. In their other data (Yan et al., 2007), 83%- and 73%-basicity PACIs shows lower residual aluminum concentration than 53%-basicity PACI even though the coagulation pH values were slightly higher alkaline pH. Therefore, basicity >70% was suggested as a key for reducing residual aluminum concentration.

PACI-71s removed DOC slightly more efficiently than did the other coagulants in both of the tested raw water samples (Fig. 2). Large floc particles were formed with PACI-71s, whereas the floc particles formed with AlCl₃ and alum were small at the same dosage (as determined by visual inspection).

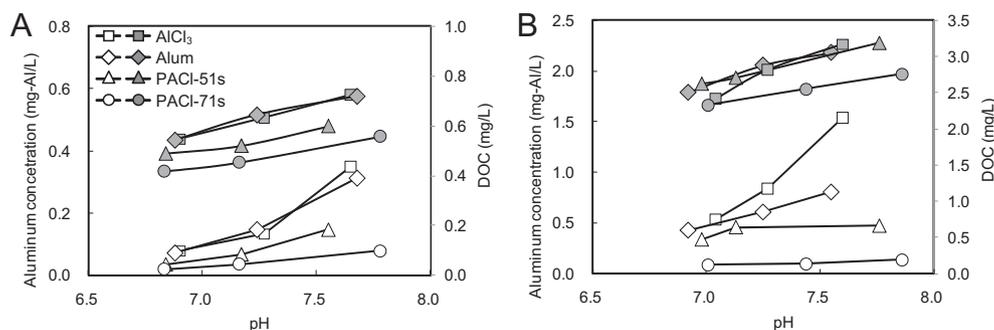


Fig. 2 – Plots of dissolved residual aluminum concentration (open symbols) and DOC (solid symbols) vs. pH for Toyohira River water A with a coagulant dosage of 1.06 mg-Al/L (A) and Chibaberi River water A with a coagulant dosage of 2.12 mg-Al/L (B).

Some investigators have assumed that Al_{13} species (Alb is an index of Al_{13}) are the most effective species for coagulation because they efficiently destabilize particles by means of charge neutralization (Parthasarathya and Buffle, 1985; Gao et al., 2005). On the basis of these previous results, we expected PACI-71s to be the least effective PACI coagulant because it contained the smallest amount of Alb. However, PACI-71s showed the best natural organic matter (NOM) removal. ^{27}Al NMR spectroscopy indicates that commercial PACI products contain less Al_{13} than laboratory-prepared PACIs (Lin et al., 2008). However, the coagulation efficiency of commercial PACIs is no worse than that of laboratory-prepared PACIs (Lin et al., 2008). Recently, Al_{30} polymer, which has been detected among the Alc species and which is formed in processes carried out at high concentrations and temperatures, has attracted attention as an effective coagulant (Chen et al., 2006, 2007, 2009). Because the conditions required for formation of Al_{30} polymer are met by the conditions under which commercial PACI coagulants are prepared, it is possible that some of the species in PACI-71s were structurally similar to Al_{30} polymer. Further study will be required for elucidating the high NOM removals.

3.2.2. MW distribution of dissolved residual aluminum, as determined by micro and ultrafiltration fractionation

The data in Fig. 3A–B, for Toyohira River water, indicate that the fraction with a MW range of 0–0.5 kDa was small for all coagulants, which means that most of the dissolved residual aluminum was not in monomeric form. At pH 7.0 for all the coagulants, some of the dissolved residual aluminum was

contained in the fraction with a MW range of 0.5–3 kDa. For alum and $AlCl_3$, dissolved residual aluminum was also present in the fraction at 100 kDa–0.45 μm , but aluminum of that MW range was observed at much smaller concentrations for the PACIs. Therefore, the lack of colloidal aluminum at 100 kDa–0.45 μm contributed to the overall low concentrations of dissolved residual aluminum observed for the samples after the PACI coagulation. PACI-71s showed a lower dissolved residual aluminum concentration in the fraction at 0.5–3 kDa than did PACI-51s; this further reduced the overall dissolved residual aluminum concentration for PACI-71s relative to that for PACI-51s. These same trends were also observed at pH 7.5.

For Chibaberi River water, which contained a higher NOM concentration than Toyohira water, most of the dissolved residual aluminum was observed in the fraction at 100 kDa–0.45 μm (Fig. 3C–D). The dissolved residual aluminum in this fraction may have been in the form of a soluble aluminum–NOM complex, which exists when the coagulant dosage is insufficient to precipitate all the NOM (Jekel and Henzmann, 1989). The aluminum concentration in this fraction was very low when PACI-71s was used, suggesting that PACI-71s has a smaller tendency to form the soluble aluminum–NOM complex but benefits to form insoluble precipitate Al–NOM. The observed highly efficient removal of NOM by PACI-71s (see Fig. 2) also supports this suggestion. Yan et al. (2007, 2008a) suggested that Ala might form a soluble complex with some types of NOM. If such a soluble complex had a size in the range 100 kDa–0.45 μm , the fact that the aluminum concentration was lowest for PACI-71s could be explained by the fact that PACI-71s had the lowest Ala percentage.

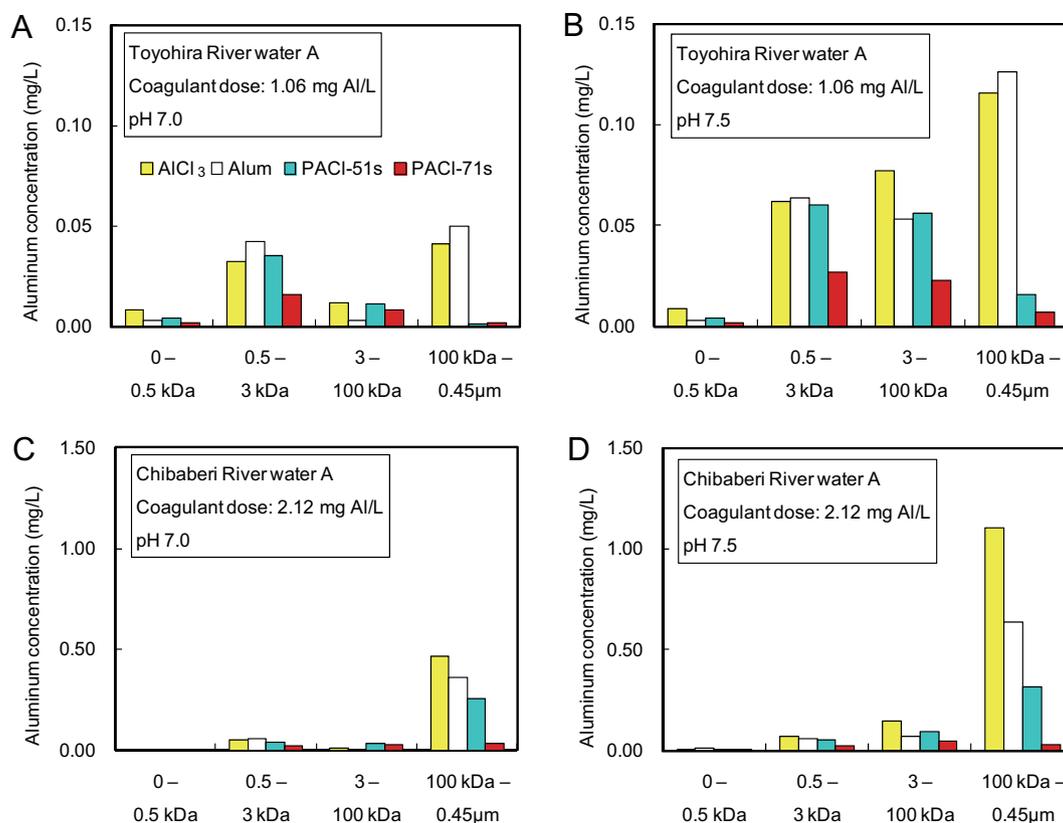


Fig. 3 – MW distribution of dissolved residual aluminum after jar tests, as determined by micro and ultrafiltration fractionation.

3.2.3. Effect of coagulant dosage on dissolved residual aluminum concentration

For PACl-51s, the dissolved residual aluminum concentration at pH 7.5 increased with increasing dosage and exceeded 0.2 mg/L at a dosage of 2.12 mg-Al/L (Fig. 1S-B, Supplementary Information). For PACl-71s, no such trend was observed. In all the experiments, PACl-71s removed more DOC than PACl-51s, in agreement with the results described earlier. For PACl-51s treating the other water at pH 7.5, the dissolved residual aluminum concentration approached 0.3 mg/L at the dosage 2.12 mg-Al/L (Fig. 1S-D, Supplementary Information), and almost no turbidity removal was observed (the turbidity of the treated water was 2.0 NTU, whereas that of the raw water was 2.4 NTU; Fig. 2S-D, Supplementary Information). At the same dosage and pH, PACl-71s lowered the dissolved residual aluminum concentration to <0.1 mg/L and lowered the turbidity to 0.4 NTU.

3.2.4. Effect of water temperature on dissolved residual aluminum concentration

The influence of water temperature on dissolved residual aluminum concentration was studied with PACl-51s, -61s, and -71s: PACl-61s was selected for these experiments because it has been widely used in commercial water treatment under low-temperature conditions. At high (28 °C) and low (4 °C) temperatures, as well as the standard temperature of 20 °C, PACl-71s reduced the residual aluminum concentration to its

lowest levels compared to those obtained for PACl-51s and PACl-61s (Fig. 3S, Supplementary Information). As predicted from the aluminum solubility diagram (Pernitsky and Edzwald, 2003; Geochemist's Workbench, ver. 6, RockWare, Inc., Golden, CO, USA), the higher the water temperature, the higher the residual aluminum concentrations. At pH 7.0, residual aluminum concentrations were almost unchanged between 4 and 20 °C but increased a little at 28 °C. At pH 7.5, the residual aluminum concentrations increased with increasing temperature.

3.3. Second set of experiments

To further investigate the low residual aluminum concentrations observed after PACl-71s coagulation, we conducted jar tests with a variety of PACls, including a very-high-basicity PACl (90%), sulfated and non-sulfated PACls, and PACls composed mainly of Alb or Alc (Fig. 1C).

3.3.1. Effect of sulfate in PACls on dissolved residual aluminum concentration

As shown Fig. 4A–C, the presence of sulfate ion in PACls did not affect the residual aluminum concentration for pH > 6.5. For pH < 6.5, however, sulfate ions contributed to reducing the residual aluminum concentration. Low residual aluminum concentration, as well as good turbidity removal (Fig. 4S, Supplementary Information), was observed for pH > 7.0 for the non-sulfated PACls, but the pH range for the minimum

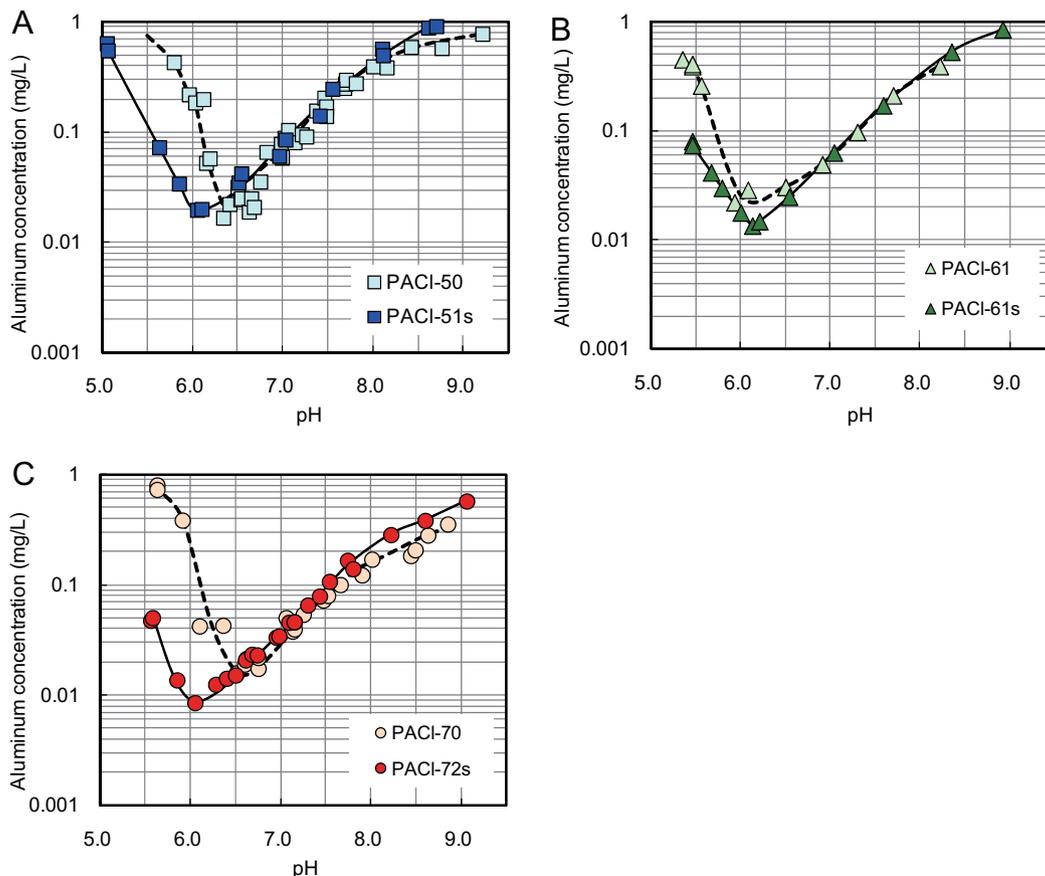


Fig. 4 – Comparison of residual aluminum concentrations between sulfated and non-sulfated PACls (Toyohira River water C, coagulant dosage: 1.89 mg-Al/L).

residual aluminum concentration was shifted to the slightly acidic pH range around 6–6.5 by the presence of sulfate in the PACls. Because sulfate suppresses charge reversal and accelerates the kinetics of aluminum hydroxide precipitation (Amirtharaja and O'Melia, 1990), sulfate is often added to PACls, in particular to effectively treat raw water of low turbidity and low NOM concentrations. In these experiments, we observed that larger floc particles were formed by sulfated PACls than by non-sulfated PACls. The observed lower residual aluminum concentration at acidic pH for sulfated PACls compared to non-sulfated PACls could be due to charge the neutralization effect: the suppression of positively charged polynuclear and microcrystalline hydrolysis products through adsorption and complexation of sulfate (Wang et al., 2002). It should be noted, however, that our results do not agree with those of Pernitsky and Edzwald (2003), who reported that the presence of sulfate did not affect aluminum solubility. They used pure water for comparing aluminum solubility, whereas we used natural waters. Therefore, ionic strength or the presence of other ions in our natural water samples may have affected the residual aluminum concentrations.

3.3.2. Effects of basicity and polymeric/colloidal species on dissolved residual aluminum concentration

The effect of the aluminum species (Alb/Alc) on residual aluminum concentration was investigated by comparing the results of PACl-72b and -72c, for which the basicity values are

the same but for which the dominant aluminum species are polymeric (Alb) and colloidal (Alc), respectively. Residual aluminum concentrations were almost the same between PACl-72b and -72c at the tested pH range of 5.5–8.5 (Fig. 5A): this data suggests that the residual aluminum concentration was determined by the Ala percentage.

The effect of aluminum species on residual aluminum concentration was further investigated by using a series of PACl coagulants, including the very-high-basicity PACls (PACl-90bx and -90y). As shown in Fig. 5B, aluminum concentrations at pH > 6.5 were the lowest with PACl-90y followed by PACl-90bx and PACl-70. Aluminum concentrations were not largely different between PACl-61 and PACl-50. At coagulation pH of 7.5–8.5, where problematic levels of residual aluminum are generally seen, a residual aluminum concentration <0.02 mg/L was attained with PACl-90y. Good turbidity removal after settling was observed at a coagulation pH of 7.0–8.5 (Fig. 5S, Supplementary Information). Among the PACls, aluminum concentrations decreased with increasing PACl basicity. For sulfated PACls, a similar trend was observed (Fig. 5C). The reason why AlCl₃ exhibited a lower aluminum concentration than PACl-50 was not clear, but the results suggest that a basicity ≥70% was required to reduce residual aluminum concentration. PACl-90bx and PACl-90y, in particular, exhibited extremely low residual aluminum: their minimum residual aluminum concentrations were <0.007 mg/L, which was far below the aluminum solubility

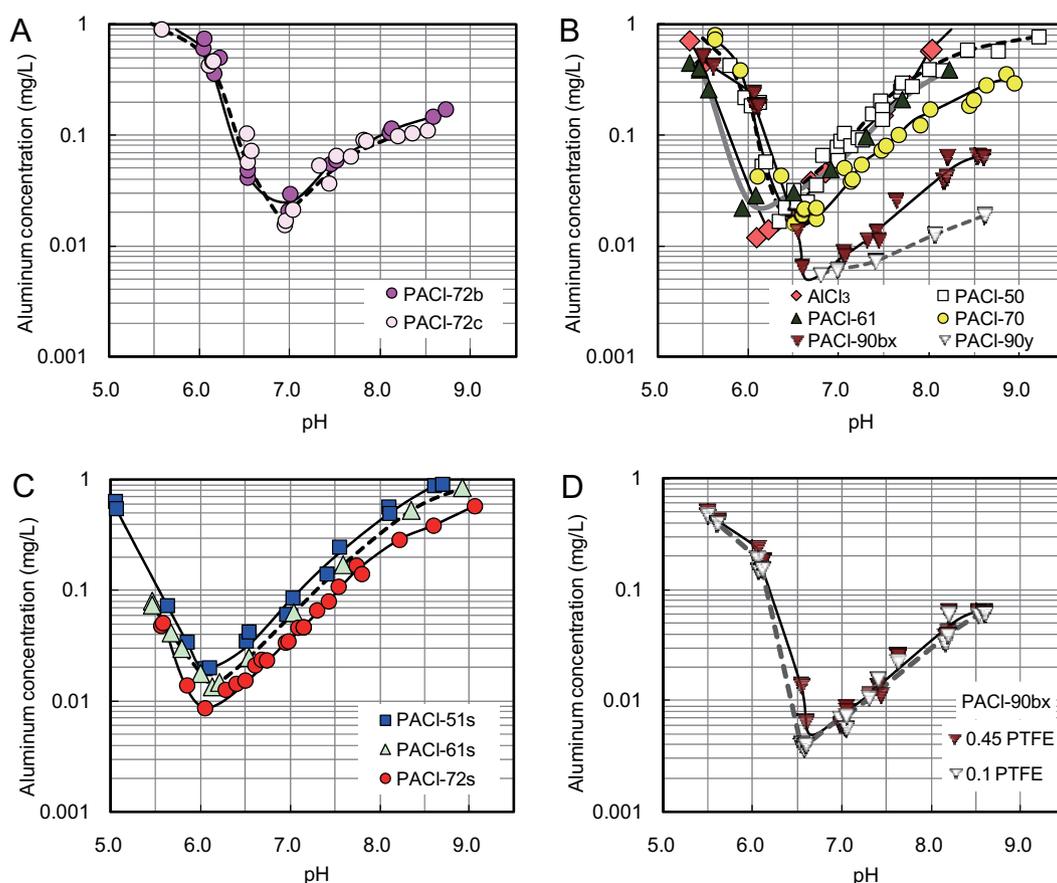


Fig. 5 – Effect of Alb/Alc (Panel A), basicity (Panels B and C), and membrane pore size on residual aluminum concentrations (Panel D) for Toyohira River water C (coagulant dosage: 1.89 mg-Al/L).

reported by Pernitsky and Edzwald (0.03 mg/L; 2003). While concentrations <0.007 mg/L were attained after 0.45- μm membrane filter filtration, residual aluminum concentrations decreased even further, to <0.004 mg/L, when sample water was filtered by a 0.1- μm membrane filter (Fig. 5D).

3.3.3. Effect of monomeric species on dissolved residual aluminum concentration

The concentration of residual aluminum observed after PACl-90y coagulation was clearly lower than that after the coagulation by PACl-90bx of the same basicity (Fig. 5B); this discrepancy would be due to the lower Ala percentage in PACl-90y compared with that in PACl-90bx because Alb/Alc ratio did not affect residual aluminum concentration. Therefore, we hypothesized that low Ala percentage, rather than high basicity, was a better indicator for minimizing residual aluminum concentration, although PACl basicity roughly determines the Ala percentage in PACl. The effect of Ala percentage on dissolved residual aluminum was verified by using water samples with high and low NOM concentrations and additional very-high-basicity PACls. Because of the necessity of discussing small differences of Ala percentages, the analytical accuracy of very low Ala percentage was evaluated in multiple measurements for the very-high-basicity PACls. Ala percentages of PACl-90x, 90by, 85x, and 85y were 0.22 ± 0.10 , 1.18 ± 0.02 , 0.43 ± 0.10 , and 1.00 ± 0.07 (avg. \pm sd.), respectively: the standard deviations were all <0.1 . Fig. 6 shows plots of dissolved residual aluminum concentration against Ala percentage. Among the three PACls with a basicity of 85% (circles in the

figure), dissolved residual aluminum concentrations increased with increasing Ala percentage in the order of PACl-85x (Ala: 0.5%) $<$ PACl-85y (1.0%) $<$ PACl-85z (1.7%) (Fig. 6A). A similar trend was also seen for the three PACls with a basicity of 90%. One with a lower Ala percentage showed lower residual aluminum concentrations. Comparison of Figures A–B and C–D demonstrates superiority of Ala percentage over basicity as an index determining residual aluminum concentration, in particular for concentrations <0.1 mg/L. Residual aluminum concentrations <0.015 mg/L were attained by the PACls (Ala $\leq 0.5\%$, basicity $\geq 85\%$) even at a weakly alkaline pH of 8.0. The PACls exhibited residual aluminum concentrations <0.02 mg/L at a pH range of 6.5–8.5 (some data are shown Fig. 7). At the optimum pH at which residual aluminum concentration was minimized, residual aluminum concentrations were <0.007 mg/L. Residual aluminum concentrations after the coagulation by high-basicity PACls was studied previously (Yan et al., 2007; Yang et al., 2011). However, such low residual aluminum concentrations were not attained. Our study suggests that their non-attainment would be due to the high Ala percentage ($>5\%$) even though the basicity was as high as 83%. In those studies, the observed residual aluminum concentration achieved with a PACl with 15.6% Ala was around 0.07–0.09 mg/L at pH 7.8 (Yang et al., 2011), and 0.1 mg/L with a PACl with 5.5% Ala at pH 8 (Yan et al., 2007). These data are roughly in line with our observation shown in Fig. 6. Notably, in our study the residual aluminum concentration drastically decreased to <0.015 mg/L at pH 8.0 when the Ala percentage of the PACl decreased to $<0.5\%$.

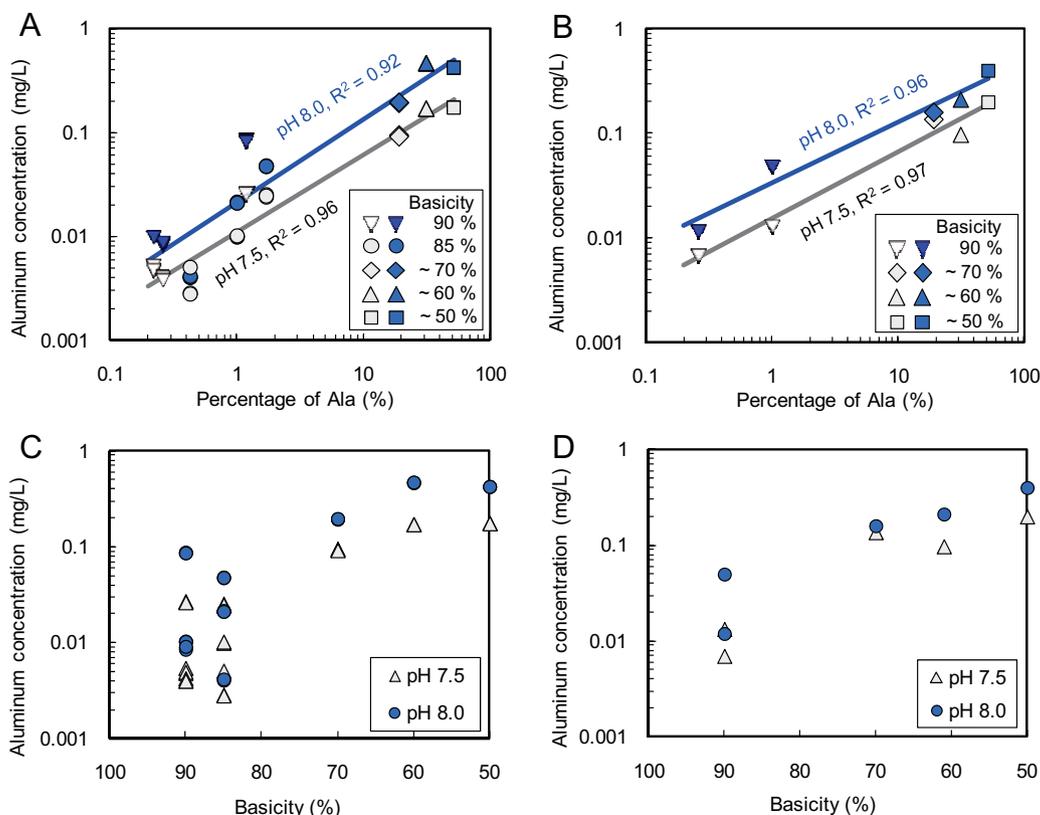


Fig. 6 – Effect of Ala percentage in PACls and their basicity on residual aluminum concentrations: (Panels A and C) Wani River water, coagulant dosage: 2.86 mg-Al/L; (Panels B and D) Toyohira River water, coagulant dosage: 1.89 mg-Al/L.

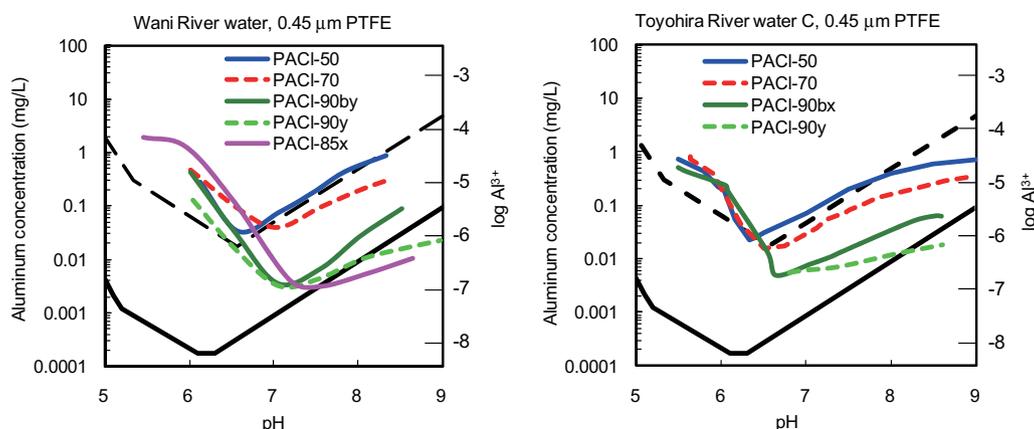


Fig. 7 – (solid black lines) Solubility diagram for aluminum at 20 °C calculated by Geochemist's Workbench, ver. 6 (RockWare, Inc., Golden, CO, USA), (dashed black lines) theoretical solubility for Al species in equilibrium with Al(OH)₃(am) at 20 °C calculated by Pernitsky and Edzwald (2003), and experimentally observed residual aluminum concentrations of PACI-50, PACI-70, PACI-85x, PACI-90bx/90by, and PACI-90y (blue, red, pink, green, and light green lines, respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In Fig. 7, experimentally observed residual aluminum concentrations were compared with the solubility of amorphous aluminum hydroxide and gibbsite (Al(OH)₃). For pH < 6.5, residual aluminum concentrations exceeded the solubility limit of amorphous Al(OH)₃. The residual aluminum concentrations for PACI-70 were below the solubility limit of amorphous Al(OH)₃ at pH > 7, but they exceeded the solubility limit of gibbsite. The residual aluminum concentrations of PACI-85x, PACI-90by, and PACI-90y were much lower than the amorphous aluminum solubility and closely approached the solubility limit of gibbsite. In particular, residual aluminum concentrations of PACI-85x and PACI-90y at pH > 7.5 were close to or lower than the aluminum solubility. These PACls are highly prehydrolyzed aluminum salts that are obtained by neutralizing the acidic polymer with base. In particular, the pH value of PACI-90y is 5.5, and the solubility diagrams (dashed and solid black lines) suggest the dissolved aluminum concentration at pH 5.5 is in agreement with the Ala content in PACI-90y (Fig. 1). Therefore, the low concentration of dissolved aluminum contained in this PACl would lead to a very low residual aluminum concentration after its dosing.

4. Conclusions

1. The amount of Ala in PACl mainly determined the dissolved residual aluminum concentration after coagulation, whereas polymeric (Alb)/colloidal (Alc) ratio in PACl did not affect dissolved residual aluminum concentration at a given basicity.
2. PACls with Ala ≤ 0.5% and basicity ≥ 85% yielded residual aluminum concentrations < 0.007 mg/L at the optimum pH. Even at a wide pH range of 6.5–8.5 the concentration was always < 0.02 mg/L. Residual aluminum concentrations at pH > 7.5 were close to or lower than the gibbsite solubility limit. The very low monomeric aluminum content inherent

to these high-basidity PACls appears to have contributed to the very low residual aluminum concentration.

3. When coagulation was performed at pH > 6.5, dissolved residual aluminum concentration was reduced by using high-basidity PACls. For coagulation at pH < 6.5, the dissolved residual aluminum concentration was reduced by using sulfated PACls instead of non-sulfated PACls.
4. Dissolved residual aluminum was present in the fractions with MW ranges of 500 Da–3 kDa and 100 kDa–0.45 μm at pH 7.0, and aluminum was also present in the fraction with a MW range of 3–100 kDa at pH 7.5. The lower dissolved residual aluminum concentrations observed after treatment with PACl, compared with treatment with alum and AlCl₃, were due to the lower aluminum concentrations in the fractions at 100 kDa–0.45 μm. High-basidity PACls produced higher reductions in aluminum concentrations in the MW fractions at 500 Da–3 kDa, 3–100 kDa, and 100 kDa–0.45 μm.
5. The dissolved residual aluminum in the fraction with an MW range of 100 kDa–0.45 μm would have been dissolved aluminum–NOM complex formed from Ala (monomeric aluminum). The low dissolved residual aluminum concentrations observed after coagulation by high-basidity PACls may have been related partly to their low content of Ala, which tends to form dissolved aluminum–NOM complex.
6. Although increasing the dosage of normal-basidity PACls led to an increased dissolved residual aluminum concentration at pH 7.5, increasing the dosage of high-basidity PACls did not.
7. At higher raw water temperatures, the residual aluminum concentrations increased, yet the ability of high-basidity PACls to lower the residual aluminum concentration was maintained.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2013.01.037>.

REFERENCES

- Amirtharaja, A., O'Melia, C.R., 1990. Coagulation processes: destabilization, mixing, and flocculation. In: Pontius, F.W. (Ed.), *Water Quality & Treatment*, fourth ed. McGraw-Hill.
- Chen, Z., Fan, B., Peng, X., Zhang, Z., Fan, J., Luan, Z., 2006. Evaluation of Al₃₀ polynuclear species in polyaluminum solutions as coagulant for water treatment. *Chemosphere* 64 (6), 912–918.
- Chen, Z., Luan, Z., Fan, J., Zhang, Z., Peng, X., Fan, B., 2007. Effect of thermal treatment on the formation and transformation of Keggin Al₁₃ and Al₃₀ species in hydrolytic polymeric aluminum solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 292 (2–3), 110–118.
- Chen, Z., Luan, Z., Jia, Z., Li, X., 2009. Study on the hydrolysis/precipitation behavior of Keggin Al₁₃ and Al₃₀ polymers in polyaluminum solutions. *Journal of Environmental Management* 90 (8), 2831–2840.
- Driscoll, C.T., Letterman, R.D., 1995. Factors regulating residual aluminum concentrations in treated waters. *Environmetrics* 6 (3), 287–309.
- Flaten, T.P., 2001. Aluminium as a risk factor in Alzheimer's disease, with emphasis on drinking water. *Brain Research Bulletin* 55 (2), 187–196.
- Gao, B.-Y., Chu, Y.-B., Yue, Q.-Y., Wang, B.-J., Wang, S.-G., 2005. Characterization and coagulation of a polyaluminum chloride (PAC) coagulant with high Al₁₃ content. *Journal of Environmental Management* 76 (2), 143–147.
- Gupta, V.B., Anitha, S., Hegde, M.L., Zecca, L., Garruto, R.M., Ravid, R., Shankar, S.K., Stein, R., Shanmugavelu, P., Jagannatha Rao, K.S., 2005. Aluminium in Alzheimer's disease: are we still at a crossroad? *Cellular and Molecular Life Sciences* 62 (2), 143–158.
- Itoh, Y., Sato, K., 1995. Production of Sulfate-containing Basic Al Chloride. Japanese Patent, Application number 1993-181638, Publication number 1995-033432 (information available at: the web of Japan Patent Office, http://www.ipdl.inpit.go.jp/homepg_e.ipdl).
- Jekel, M.R., Henizmann, B., 1989. Residual aluminum in drinking water treatment. *Journal of Water Supply: Research & Technology AQUA* 38, 281–288.
- Jekel, M.R., 1991. Removal of aluminium in coagulation and acidic raw waters. Special Subject: aluminium in water: how can it be removed? Use of aluminium salts in treatment. In: Proc. IWSA (International Water Supply Association) 18th International Water Supply Conference and Exhibition. Copenhagen, Denmark, pp. SS8:1–SS8:4.
- Jia, Z., He, F., Liu, Z., 2004. Synthesis of polyaluminum chloride with a membrane reactor: operating parameter effects and reaction pathways. *Industrial & Engineering Chemistry Research* 43 (1), 12–17.
- Licsko, I., Szakal, F., 1988. Possibility of lowering the aluminium concentration in drinking water from water works drawing on surface water in Hungary. In: Astruc, M. (Ed.), *Heavy Metal in the Hydrological Cycle*. Selper Ltd, United Kingdom, pp. 631–636.
- Lin, J.-L., Huang, C., Pan, J.R., Wang, D., 2008. Effect of Al(III) speciation on coagulation of highly turbid water. *Chemosphere* 72 (2), 189–196.
- Miller, R.G., Kopfler, F.C., Kelty, K.C., Stober, J.A., Ulmer, N.S., 1984. The occurrence of aluminum in drinking water. *Journal of the American Water Works Association* 76 (1), 84–91.
- Matsukawa, S., Itoho, S., Habuthu, S., Aizawa, T., 2006. An approach to residual aluminium control at Nisiya purification plant, Water Works Bureau, Yokohama. *Water Science & Technology: Water Supply* 6 (4), 67–74.
- Ohno, K., Kadota, E., Matsui, Y., Kondo, Y., Matsushita, T., Magara, Y., 2009. Plant capacity affects some basic indices of treated water quality: multivariate statistical analysis of drinking water treatment plants in Japan. *Journal of Water Supply: Research & Technology-AQUA* 58 (7), 476–487.
- Parthasarathya, N., Buffle, J., 1985. Study of polymeric aluminium(III) hydroxide solutions for application in waste water treatment. Properties of the polymer and optimal conditions of preparation. *Water Research* 19 (1), 25–36.
- Pernitsky, D.J., Edzwald, J.K., 2003. Solubility of polyaluminium coagulants. *Journal of Water Supply: Research & Technology-AQUA* 52 (6), 395–406.
- Sato, F., Matsuda, S., 2009. Novel Basic Aluminum Chloride, Its Manufacturing Method and Its Application. Japanese Patent, Application number 2008-047932, Publication number 2009-203125 (information available at: the web of Japan Patent Office, http://www.ipdl.inpit.go.jp/homepg_e.ipdl).
- Shen, Y.-H., Dempsey, B.A., 1998. Synthesis and speciation of polyaluminum chloride for water treatment. *Environment International* 24 (8), 899–910.
- Simpson, A.M., Hatton, W., Brokbank, M., 1988. Aluminum, its use and control, in potable water. *Environmental Technology* 9 (9), 907–916.
- Van Benschoten, J.E., Edzwald, J.K., 1990. Measuring aluminum during water treatment: methodology and application. *Journal of the American Water Works Association* 82 (5), 71–78.
- Van Benschoten, J.E., Jensen, J.N., Rahman, Md.A., 1994. Effects of temperature and pH on residual aluminum in alkaline waters. *Journal of Environmental Engineering-ACSE* 120 (3), 543–559.
- Wang, D., Tang, H., Gregory, J., 2002. Relative importance of charge neutralization and precipitation on coagulation of kaolin with PAC: Effect of sulfate ion. *Environmental Science & Technology* 36 (8), 1815–1820.
- Wang, W.-Z., Hsu, P.H., 1994. The nature of polynuclear OH-Al complexes in laboratory-hydrolyzed and commercial hydroxyaluminum solutions. *Clays and Clay Minerals* 42 (3), 356–368.
- Wang, D., Suna, W., Xua, Y., Tang, H., Gregory, J., 2004. Speciation stability of inorganic polymer flocculant–PACl. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 243 (1–3), 1–10.
- World Health Organization, 2004. *Guidelines for Drinking – Water Quality*. World Health Organization, Geneva, Switzerland, pp. 301–303.
- Yan, M., Wang, D., Qu, J., He, W., Chow, C.W.K., 2007. Relative importance of hydrolyzed Al(III) species (Ala, Alb, and Alc) during coagulation with polyaluminum chloride: a case study with the typical micro-polluted source waters. *Colloid and Interface Science* 316 (2), 482–489.
- Yan, M., Wang, D., Ni, J., Qu, J., Chow, C.W.K., Liu, H., 2008a. Mechanism of natural organic matter removal by polyaluminum chloride: effect of coagulant particle size and hydrolysis kinetics. *Water Research* 42 (13), 3361–3370.
- Yan, M., Wang, D., Yu, J., Ni, J., Edwards, M., Qu, J., 2008b. Enhanced coagulation with polyaluminum chlorides: role of pH/Alkalinity and speciation. *Chemosphere* 71 (9), 1665–1673.
- Yang, Z., Gao, B., Cao, B., Xu, W., Yue, Q., 2011. Effect of OH⁻/Al³⁺ ratio on the coagulation behavior and residual aluminum speciation of polyaluminum chloride (PAC) in surface water treatment. *Separation and Purification Technology* 80 (1), 59–66.