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Characteristics and Components of Poly-aluminum Chloride Coagulants that Enhance Arsenate Removal by Coagulation: Detailed Analysis of Aluminum Species

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Abstract

We evaluated 51 poly-aluminum chloride (PACl) coagulants to determine the coagulant characteristics that were responsible for effective arsenate removal from contaminated river water by means of experiments involving coagulation, settling, and microfiltration. Some of the high-basicity PACls exhibited high arsenate removal percentages, particularly under alkaline conditions, and we investigated various relevant properties and characteristics of these high-basicity PACls. Effective arsenate removal was correlated with the content of polymeric and colloidal aluminum species (Alb and Alc) in the PACls but was not well correlated with colloid charge or zeta potential. Multiple regression analysis revealed that a portion of Alb and Alc, which reacted with the ferron reagent during the period from 30 min to 3 h, that is, the ($\text{Al}_{30\text{min}-3\text{h}}$) fraction, had the highest arsenate sorption capacity, followed by a colloidal aluminum fraction ($\text{Al}_{>3\text{h}}$, which reacted with ferron at a time of >3 h). The $\text{Al}_{30\text{min}-3\text{h}}$ fraction was stable, and its arsenate sorption capacity did not decrease markedly with increasing pH. The $\text{Al}_{30\text{min}-3\text{h}}$ fraction did not correspond to the Keggin-type e-Al_{13} polycation or the $\delta\text{-Al}_{30}$ polycation; it is likely to be an aluminum polymer that is unobservable by ^{27}Al NMR spectroscopy. Our results suggest that PACls with a high proportion of the $\text{Al}_{30\text{min}-3\text{h}}$ fraction should be used for enhanced arsenate removal by coagulation. A high content of the e-Al_{13} polycation or the $\delta\text{-Al}_{30}$ polycation was not indispensable for effective arsenate removal.

Keywords: PACl; basicity; arsenic; ferron; NMR

1. Introduction

Arsenic, a carcinogenic metalloid, in drinking water sources is usually removed by means of coagulation with aluminum salts followed by sedimentation or filtration or both (Chen et al. 2002, Choong et al. 2007, Edwards 1994, Gregor 2001, Kartinen and Martin 1995, McNeill and Edwards 1995, Scott et al. 1995). If the arsenic is in the form of arsenite, As(III), which has little affinity for aluminum hydroxide formed from the aluminum salts during the coagulation process (Hering et al. 1997), oxidation to arsenate, As(V), prior to coagulation-settling-filtration is generally necessary for effective removal (Ghurye and Clifford 2004).

Enhancing coagulation by optimizing the coagulant dose effectively improves arsenic removal (Cheng et al. 1994). Adjusting the coagulation pH to approximately 6.5 is important because the efficiency of arsenate removal has been found to be maximized in the pH range of 6–7 (Bilici Baskan and Pala 2010). Coagulants other than aluminum salts have been tested in attempts to improve arsenic removal. In some studies, ferric coagulants have been shown to be as effective as aluminum sulfate on a molar basis because iron flocs and aluminum flocs have the same adsorption capacity (Edwards 1994, McNeill and Edwards 1997). In contrast, other studies have shown that ferric coagulants have higher adsorption capacity than alum (Lakshmanan et al. 2008). Electrocoagulation has also been studied. For example, electrocoagulation with steel and iron electrodes effectively removes arsenate (Balasubramanian et al. 2009, Balasubramanian and Madhavan 2001). However, electrocoagulation is inferior to conventional coagulation (Lakshmanan et al. 2010, Ratna Kumar et al. 2004). However, in situations in which the decrease in pH caused by the use of a high dose of coagulant during the coagulation process increases the solubility, and thus the removal efficiency, of arsenate compounds, electrocoagulation may be preferable to conventional coagulation (Lacasa et al. 2013).

Poly-aluminum chloride (PACl) is effective for controlling arsenate concentration than the above-mentioned coagulants because PACl removes more arsenate than do conventional coagulants, such as aluminum sulfate and chloride, at both acidic and alkaline pH, as well as at neutral pH (Fan et al. 2003). On the basis of a recent comparison between one alum and two PACls, Hu et al. (2012) proposed that the reasons for the superiority of PACls are that the ϵ -Al₁₃ polycation (Keggin-type ϵ -Al₁₃ polycation, $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$) is the active species responsible for arsenate removal by aluminum coagulants and that the ϵ -Al₁₃ polycation that is preformed in PACl is stable during coagulation and is present at high levels even during coagulation under acidic and alkaline conditions. However, the commercially available PACls that are in practical use for arsenate removal do not necessarily contain large amounts of the ϵ -Al₁₃ polycation (Fan et al. 2003, Kimura et al. 2013, Yan et al. 2007), but, in practice, PACls are better at arsenate removal than alum. Mertens et al. (2012) reported that PACls with a high content of the δ -Al₃₀ polycation (specifically, the Keggin-type δ -Al₃₀ polycation, $[\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{24}]^{18+}$) have a higher removal efficiency than PACls with a low δ -Al₃₀ polycation content. Finally, higher arsenate removal by PACl than by conventional coagulants may be attributed to the ϵ -Al₁₃ polycation, the δ -Al₃₀ polycation, or both. However, these findings were obtained by comparing a few PACls with a limited variety of characteristics. Therefore, the aluminum species in PACls that is most effective for arsenate removal remains unknown. In addition, whether or not the ϵ -Al₁₃ polycation, the δ -Al₃₀ polycation, or both are indispensable species for arsenate removal remains to be determined.

The pH range that is optimal for arsenate removal (pH 6–7) is also optimal for in situ formation of the ϵ -Al₁₃ polycation during coagulation with alum (Hu et al. 2012, Lin et al. 2008, Wang et al. 2004, Yan et al. 2008). If arsenate could be removed by coagulation at a nonoptimized pH,

such as $\text{pH} > 7.5$, this would be beneficial because the pH increase to control corrosion in water distribution networks would not be required. It would also be beneficial for small treatment facilities that have difficulty attaining the optimal pH because such facilities have limited access to the required expertise. In this study, we prepared and tested 51 PACls with various characteristics to investigate the aluminum species responsible for arsenate removal and to identify PACls that can readily control arsenic concentration even when the coagulation pH is ≥ 7.5 .

2. Materials and Methods

2.1. Preparation and characterization of coagulants

We prepared 14 aluminum-based coagulants for the first set of coagulation experiments (Table 1S). The PACls were given unique designations in which the first number indicates percent basicity, “s” indicates “sulfated,” “t” indicates a commercial PACl coagulant or a trial PACl product obtained from Taki Chemical Co. (Kakogawa, Japan), and the final number (1) indicates that the coagulant was used in the first set of coagulation experiments. For the second set of coagulation experiments, we prepared an additional 20 coagulants, 16 of which were analyzed by ^{27}Al NMR spectroscopy (Table 2S). An additional 17 coagulants were prepared specifically for NMR analysis and were also used in supplemental coagulation experiments (Table 3S). The preparation of the coagulants is described in Supplementary Material. The distributions of the aluminum species in the coagulants were analyzed by means of ferron colorimetry (Jia et al. 2004, Wang et al. 2004), and the aluminum species in the coagulants were characterized by ^{27}Al NMR spectroscopy (Chen et al. 2006, Chen et al. 2007, Gao et al. 2005). The charge densities

of the aluminum species in the coagulants were determined with a colloid titrator (Hiranuma Sangyo Co., Ibaraki, Japan). The zeta potentials of aluminum hydrolysis products were determined with an electrophoretic light-scattering spectrophotometer (Zetasizer Nano ZS, 532-nm green laser; Malvern Instruments, Malvern, Worcestershire, UK). The measurement procedures are described in detail in Supplementary Material.

2.2. Water samples

In the first and second sets of coagulation experiments, we used mainly Toyohira River samples (collected at 42°57'57"N, 141°16'06"E), which contained arsenate and a trace amount of arsenite; the arsenic concentrations in the water used for the two sets of experiments were 15.8 and 21.0 µg/L, respectively. Water from the Kotonai River (collected at 43°30'44"N, 144°37'18"E) was also used in the first set of coagulation experiments, and the arsenic concentration in this water was 11.2 µg/L. For supplementary coagulation experiment, we collected Toyohira River water collected at the above-described site and mixed it with Toyohira River water collected at a site further upstream (42°57'55"N, 141°9'45"E) in proportions such that the arsenic concentration in the mixture was the same as that in the Toyohira River water used for the second set of coagulation experiments (21.0 µg/L). The dissolved organic carbon (DOC) concentrations in all the water samples were ≤1.0 mg/L (Table 4S), and thus the effect of DOC on arsenate removal during coagulation was assumed to be small (Zhang et al. 2012). Before being used in the jar tests, water samples were pretreated with a small amount of chlorine (0.15 mg-Cl₂/L) to oxidize traces of arsenite (present at a concentration of ~0.5 µg/L) to arsenate; therefore, all the arsenic in the test water samples was in the form of arsenate.

2.3. Jar tests

Jar tests were performed with a jar test apparatus at room temperature ($\sim 20^{\circ}\text{C}$) as follows. Each raw water sample was transferred to a 1-L square plastic beaker, a predetermined volume of 0.1 N HCl or 0.1 N NaOH was added to bring the final coagulation pH to the target value, and a coagulant was injected into the water. The mixture was stirred rapidly for 1 min ($G = 190\text{ s}^{-1}$, 136 rpm), slowly for 10 min (19 s^{-1} , 29 rpm), and then allowed to stand for 1 h so that the generated aluminum floc particles would settle. Sample of the supernatant were taken from the beaker for the measurement of coagulation pH and turbidity. A portion of the sample was filtered through a $0.45\text{-}\mu\text{m}$ polytetrafluoroethylene microfilter (DISMIC-25HP; Toyo Roshi Kaisha, Tokyo), and the arsenic and aluminum concentrations in the filtrate were determined by means of inductively coupled plasma mass spectrometry (HP-7700, Agilent Technologies) after the addition of nitric acid. The rationale for the selection of the microfilter is described in Supplementary Material including Figure 1S. The filtrate was also analyzed for DOC (Sievers 900 TOC Analyzer, GE Analytical Instruments, Boulder, CO, USA) and ultraviolet absorbance at 260 nm (UV-1700, Shimadzu Co.).

3. Results and Discussion

3.1. Arsenate removal in jar tests

First, we conducted jar tests with 14 PACls and evaluated residual arsenate concentrations as a function of coagulation pH after coagulation, settling, and microfiltration. The results for five PACls are depicted in Figure 2S to illustrate the general trend for the variation of arsenate concentration with pH (the data for the other nine PACls are shown in Figure 3S). Residual

turbidity values are shown in Figures 4S and 5S. Arsenate removal percentages were highest at pH 6.5–7 (that is, the residual arsenate concentrations were lowest in this pH range). This range is consistent with values reported previously: for example, Hu et al. (2012) reported pH 5–7 as the optimum pH range, and Baskan and Pala (2009) reported an optimum range of pH 6–8. At pH > 9, arsenate was not removed by any of the PACls. For all the tested coagulants, the residual arsenate concentration increased substantially as the coagulation pH was increased from neutral to alkaline. Variations in residual arsenate concentration among the PACls were observed, particularly at pH 7.5–8.5 and ~5.5. Turbidity removal was high at pH 7.0–8.5. This result is reasonable given that sweep coagulation, which is effective for low-turbidity water such as the water tested in this study, is conducted at pH 7–8 (Amirtharaja and O'Melia 1990, Letterman 2011). Our results also indicate that when the coagulation pH was >7.5, residual arsenate concentration decreased with increasing PACl basicity, which reduced the monomeric aluminum species content in the coagulant (Table 1S). However, the correlation between arsenate removal percentage and PACl basicity was not very strong (as will be discussed in the section 3.2).

Four different PACls with a basicity of 70% were tested (Figures 6S and 7S). Compared to the other three PACls, PACl-70-1-1 was the most effective at lowering the residual arsenate concentration at pH 6–8.5, which covers the pH range conventionally employed in real-world coagulation processes. The high arsenate removal by PACl-70-1-1, which had a higher Alb content (80.7%) than the other 70%-basicity PACls, is in accordance with previous indications that the $e\text{-Al}_{13}$ polycation, which is believed to correspond to Alb measured by means of the ferron method, is the active species responsible for arsenate removal (Hu et al. 2012). However, the residual arsenate concentrations achieved with PACl-70-2-1 (Alb 68.2%) and PACl-70-3-1 (Alb 7.1%) did not differ substantially. Therefore, the arsenate removal performance by aluminum coagulants may not be due solely to Alb or to the $e\text{-Al}_{13}$ polycation. Hu et al. (2012)

197 did not use a PACl with a high Alc content. Therefore, the e-Al₁₃ polycation may remove arsenate
198 more effectively than monomeric aluminum species, but other species may also be effective for
199 arsenate removal.

201 Sulfated PACls are widely used in practice, particularly for treatment of raw water with low
202 turbidity and low NOM concentrations, because sulfate suppresses charge reversal and
203 accelerates the kinetics of aluminum hydroxide precipitation (Amirtharaja and O'Melia 1990).
204 We also visually observed that larger floc particles were formed by sulfated PACls than by
205 nonsulfated PACls. The effects of sulfate ion can be seen in Figure 6S by comparing PACl-70st-
206 1 and PACl-70-3-1. The arsenate removal percentages were the same at pH 6–7.5, but PACl-
207 70st-1, which contained sulfate ion, showed somewhat higher arsenate removal at a pH of >8. A
208 similar trend was observed for PACls of 50% basicity (Figure 8S). In water, sulfate ion has a
209 negligible or deleterious effect on As(V) removal by ferric chloride coagulants (Hering et al.
210 1997, Jain et al. 2009, Meng et al. 2000, Qiao et al. 2012). The deleterious effect is due to
211 competitive adsorption of the divalent sulfate ion and arsenate (the divalent ion HAsO₄²⁻ is
212 present at pH 7–11) (Wilkie and Hering 1996). Therefore, the higher arsenate removal by the
213 sulfated PACls would be related to aluminum species distribution. Compared with nonsulfated
214 PACls of the same basicity, the sulfated PACls were low in monomeric aluminum species, which
215 is less effective for arsenate removal than the other aluminum species, as will be discussed next.

217 ***3.2. PACl characteristics that affect arsenate removal***

219 Arsenate removal percentages were clearly different depending on PACls at alkaline pH. As
220 described above, differences in the Alb content in PACls did not explain differences in arsenate
221 removal percentage. To determine the PACl characteristics that influenced arsenate removal, we

conducted single regression analysis of data obtained at pH 7.5, 8.0, and 8.5 (Figure 1). Arsenate removal percentages at a fixed pH value were obtained by interpolation because the final coagulation pH rarely coincided with the target value; for example, a removal percentage value for pH 8 was obtained by interpolation of the results for two pH ranges (7.6–7.9 and 8.1–8.4) surrounding the target pH value. Correlations between arsenate removal and colloid charge and zeta potential were poor, even though aluminum hydroxide precipitates that have high positive colloid charge and high zeta potential can be expected to have surface sites for the sorption of the arsenate anion. The fairly good correlation between arsenate removal and PACl basicity (Figure 1, top row) suggests that selecting a high-basicity PACl is a good strategy for enhancing arsenate removal. However, not all of the high-basicity PACls showed high arsenate removal. A slightly better correlation was attained for Alb+Alc content. This result suggests that monomeric aluminum in PACls is less effective than polymeric and colloidal aluminum. However, Alb+Alc comprises a broad range of aluminum species in PACls. We investigated the Alb+Alc aluminum species that were highly effective for arsenate removal by using ferron and NMR analyses.

3.3. Aluminum species effective for arsenate removal

3.3.1. Multiple regression analysis of ferron colorimetry data

To determine the aluminum species that were effective for arsenate removal, we modified the ferron speciation by changing the cut-off times for absorbance measurement in ferron colorimetry. Although it is assumed that monomeric aluminum reacts with ferron instantaneously, a cut-off time between 0.5 and 1.5 min is generally used (Bersillon et al. 1980, Parker and Bertsch 1992). In this study, we used a cut-off time of 0.5 min, which was the shortest workable time, for Ala (monomeric aluminum), as was done in previous studies (e.g., Wang et

al. 2004). The usual cut-off time for Alb is 120 min, but Alb may consist of various polynuclear aluminum complexes with unclear structures; some of the complexes react rapidly with ferron, whereas others react with moderate speed (Batchelor et al. 1986). Therefore, in this study, we measured absorbances at 0.5, 3, 10, and 30 min and 1, 2, and 3 h, and we then separated the aluminum into three fractions on the basis of various cut-off times (Table 1).

When the main mechanism of arsenate removal is sorption (Mertens et al. 2016, Pallier et al. 2010), the following equation holds:

$$As\ removed = Coagulant\ dose \times q_s \quad (1)$$

where q_s ($\mu\text{g-As/mg-Al}$) is the overall arsenate sorption capacity of the aluminum species formed from PACl.

Sorption capacity (q_s) varies with coagulant dose, the type of coagulant, the coagulation conditions, and the water characteristics. For the same water being treated at a constant PACl dose, q_s depends on the characteristics of the PACl. The q_s of a PACl depends on the distribution of the aluminum species in the PACl. We assumed that the aluminum species in a PACl formed hydrolytic aluminum species with different sorption capacities for arsenate and that there were no synergetic effects between the species with regard to arsenate sorption. Under these assumptions, the overall sorption capacity of the system is given by the sum of the capacities of all the aluminum species:

$$q_s = \sum q_i f_i \quad (2)$$

where q_i is the arsenate sorption capacity of aluminum species i ($\mu\text{g-As/mg-Al}$) and f_i is the ratio of the mass of aluminum species i to the total mass of aluminum species in the coagulant (mg-Al/mg-Al) and where

$$\sum f_i = 1 \quad (3)$$

When the aluminum in PACl is separated into three fractions, combining equations (1)–(3) yields equation (4):

$$\frac{\text{As removed}}{\text{Coagulant dose}} = q_{21}f_2 + q_{31}f_3 + q_1 \quad (4)$$

where q_{21} is $q_2 - q_1$, and q_{31} is $q_3 - q_1$.

We determined the values of q_1 , q_{21} , and q_{31} by multiple regression analysis using equation (4). In this analysis, the dependent variable was mass of arsenate removed per mass of coagulant, and the independent variables were the percentages of aluminum fractions 2 and 3 (f_2 and f_3). The arsenate sorption capacities of the aluminum fractions (q_1 , q_2 , and q_3) were known after the values of q_1 , q_{21} , and q_{31} were determined. The ultimate objective of the regression analysis was to determine the species that effectively removed arsenate, by comparing the values of q_1 , q_2 , and q_3 . Note that the equation obtained by regression analysis may not be useful for predicting arsenate removal from water samples with different water qualities. The prediction ability of the equation can be expected to be improved by inclusion of additional data on how sorption capacity depends on arsenate concentration, coagulant dose, and concentrations of co-existing ions and natural organic matter. For example, the effect of initial arsenate concentration,

coagulant dose, and pH on arsenate removal by iron coagulation has been studied by means of a response surface method involving a second-degree polynomial (Baskan and Pala 2009, Bilici Baskan and Pala 2010).

Initially, we conducted multiple regression analyses by using data from the first set of coagulation experiments (Table 5S). Aluminum species were classified into three fractions on the basis of ferron reaction time, as shown in Table 1. Table 1 also shows the R^2 and p values of regression analysis models obtained with different cut-off times; note that the cut-off times for the various fractions were not always the same. For T1 water at pH 7.5, the largest R^2 values with the p values of the model parameters <0.05 was obtained for models S1-35, S1-36, and S1-45, although the R^2 values for these three models did not differ substantially from one another. For T1 water at pH 8.0, models S1-35, S1-36, and S1-46 showed the largest R^2 values; and at pH 8.5, models S1-36 and S1-46 showed the largest R^2 values. For K water, correlations with a p value of <0.05 were not obtained, but S1-35 and S1-36 were arguably the best models by virtue of having relatively low p values and high R^2 values. Overall, the experimental data indicate that model S1-36 (for which the cut-off times were 30 min and 3 h) gave the highest correlations. The correlation between the experimental removal percentages and the percentages predicted by model S1-36 is shown in Figure 9S.

It should be noted, however, that 3 h was the longest observation time in the ferron assays for the coagulants tested in the first set of experiments; that is, absorbance was not measured after 3 h of reaction time. Therefore, a cut-off time of >3 h might have been more appropriate than a cut-off time of 3 h for characterization of arsenate removal. In the ferron assays for the second set of coagulation experiments, absorbance was measured until 7 days, and aluminum species in the PACls were categorized into three fractions according to two cut-off times selected from

among the times of 0.5, 3, and 30 min and 1, 2, 3, 6, and 12 h (Table 2). At pH 7.5 and 8.0, the largest R^2 values were obtained with model S2-36 (for which the cut-off times were 30 min and 3 h). At pH 8.5, model S2-36 gave the third largest R^2 values, but the difference between the three largest R^2 values was small. These two sets of coagulation experiments indicated that aluminum fractionation by means of ferron assay results obtained at 30 min and 3 h was the best method for describing differences in arsenate removal percentages by various PACls. The correlation between the experimental removal percentages and the removal percentages predicted by model S2-36 is shown in Figure 10S.

3.3.2. Aluminum fractions effective for arsenate removal

In the best model for each of the two sets of coagulation experiments (S1-36 and S2-36, respectively), the aluminum in PACl was separated into three fractions at cut-off times of 30 min and 3 h. Among the three aluminum fractions, the $Al_{30\text{min}-3\text{h}}$ fraction (that is, the fraction that reacted with ferron during the period from 30 min to 3 h) showed the largest q_i value, meaning the highest sorption capacity (Figure 2). The arsenate sorption capacity of the $Al_{>3\text{h}}$ fraction was the second highest, and that of the $Al_{<30\text{min}}$ fraction was the lowest. The arsenate sorption capacities of $Al_{>3\text{h}}$ and $Al_{<30\text{min}}$ decreased with increasing coagulation pH. In particular, the sorption capacity of $Al_{<30\text{min}}$ decreased by about 1/3 from pH 7.5 to 8.5. $Al_{<30\text{min}}$ includes aluminum monomers, dimers, and low-molecular-weight polymer species. Such species hydrolyze faster at higher pH, and hydrolysis results in decreased arsenate sorption. The effect of pH on sorption capacity was small for $Al_{30\text{min}-3\text{h}}$ and $Al_{>3\text{h}}$. This result is in accordance with the understanding that polymeric and colloidal species are more stable and less amenable to hydrolysis than monomeric species (Wang et al. 2004). In particular, the sorption capacity of $Al_{30\text{min}-3\text{h}}$ was stable and did not decrease appreciably with increasing pH. Overall, a higher

percentage of the $Al_{30min-3h}$ fraction is key to better arsenate removal because the species in this fraction have higher arsenate sorption capacity than other Al species and are stable even under alkaline conditions.

In the first set of coagulation experiments, the PACls that exhibited high arsenate removal percentages were PACl-70-1-1 and PACl-90-1-1. In the second set of experiments, 80%-basicity PACls such as PACl-80-1-2 exhibited high arsenate removal percentages (Tables 5S and 6S). The high arsenate removal percentages by PACl-70-1-1, PACl-80-1-2, and PACl-80-4-2 were due to the high content of $Al_{30min-3h}$. The value of $f_{30min-3h}$ for these PACls was $\sim 26\%$ and was higher than the $f_{30min-3h}$ values for all the other PACls. In contrast, the high removal percentages achieved with PACl-90-1-1, PACl-80-2-2, and PACl-80-3-2 were due to the high content of $Al_{>3h}$ ($f_{>3h} > 37\%$) as well as to the moderate content of $Al_{30min-3h}$ ($f_{30min-3h} > 18\%$). The high arsenate removal percentages achieved with PACl-80st-2 and PACl-83t-2 were due mainly to the high content of $Al_{>3h}$ ($f_{>3h} > 82\%$), but the contribution of $Al_{30min-3h}$ ($f_{30min-3h} \approx 5\%$) was non-negligible. Therefore, there are two approaches for developing PACls that exhibit high arsenate removal: one is to increase the percentage of the $Al_{30min-3h}$, and the other is to increase the percentage of the $Al_{>3h}$ to at least approximately 80%. The percentage of the $Al_{30min-3h}$ in commercially available and commonly used PACls (PACl-50st and PACl-70st) is low, 10% at most. PACl-70st showed better removal than PACl-50st, and the difference was due to the moderately high content of $Al_{>3h}$.

3.3.3. Aluminum species by NMR analysis

The $Al_{30min-3h}$ fraction includes a portion of Alb and a portion of Alc. The e- Al_{13} polycation is treated as being equivalent to Alb, and Alc includes the δ - Al_{30} polycation (Chen et al. 2007,

Parker and Bertsch 1992). Therefore, the high arsenate sorption capacity of $Al_{30min-3h}$ might have been related to the e- Al_{13} polycation, the δ - Al_{30} polycation, or both. We evaluated the areas of the e- Al_{13} and δ - Al_{30} polycation peaks in the NMR spectra, and correlate the areas with the percentages of aluminum fractions determined by means of ferron analysis.

There was a strong correlation between the peak area of the e- Al_{13} polycation and the percentage of Alb ($Al_{0.5min-2h}$) ($R^2 = 0.703$, Table 7S), which is in agreement with previous observations (Parker and Bertsch 1992, Sposito 1995). However, when the aluminum was separated at different ferron reaction cut-off times, the highest correlation was observed for the percentage of $Al_{0.5min-1h}$ ($R^2 = 0.735$, Figure 11S, Table 7S), followed by the percentages of $Al_{0.5-30min}$ ($R^2 = 0.722$), $Al_{3-30min}$ ($R^2 = 0.721$), and $Al_{3min-1h}$ ($R^2 = 0.717$). The $Al_{0.5-30min}$, $Al_{3-30min}$, and $Al_{3min-1h}$ fractions are subfractions of the $Al_{0.5min-1h}$ fraction. Therefore, the data indicate that the e- Al_{13} polycation corresponds more closely to the $Al_{0.5min-1h}$ fraction than to the $Al_{0.5min-2h}$ fraction in the ferron protocol that we employed. This result is in accordance with the result of Bertsch et al. (1986), who partitioned Alb into a rapidly reacting fraction (≤ 1 h) and a slowly reacting fraction (> 1 h) and reported that the rapidly reacting fraction corresponded to the amount of Al_{13} polymers as determined by NMR spectroscopy.

More important is that $Al_{0.5min-1h}$ was close to and partially overlapping with $Al_{30min-3h}$, which was the fraction with the highest arsenate sorption capacity. The correlation between the percentage of the $Al_{30min-3h}$ fraction and the e- Al_{13} polycation peak area was low ($R^2 = 0.173$, Figure 12S, Table 8S). These results suggest that the e- Al_{13} polycation may be active for arsenate removal but that it is not the most active substance in PACl. To verify this possibility, we compared the arsenate removal percentages of two selected PACls: one PACl (PACl-80-1-3) with a large amount of the e- Al_{13} polycation (as indicated by NMR) and another PACl (PACl-

80-8-3) with a small amount of the e-Al₁₃ polycation (by NMR), as shown in the uppermost panels of Figure 3. Despite the difference in the amounts of the e-Al₁₃ polycation, the arsenate removal percentages achieved with these two PACls did not differ greatly at either pH 7.5 or 8.0 (Figure 3, lowermost panels). Therefore, our data indicate that the e-Al₁₃ polycation was not indispensable for high arsenate removal, although it was one of the active substances.

Next we focused on the δ -Al₃₀ polycation. The NMR signals corresponding to the δ -Al₃₀ polycation were not sharp but rather were broad, low humps, as previously reported (Allouche et al. 2000). The areas of the δ -Al₃₀ polycation signals were calculated, and correlation between the peak areas and the percentage of aluminum fractions based on the ferron reaction times were examined. The percentage of the Al_{4-7d} fraction showed the best correlation with the δ -Al₃₀ polycation peak area ($R^2 = 0.182$, Figure 13S, Table 8S), followed by the percentage of the Al_{12h-1d} fraction ($R^2 = 0.140$). Even the higher R^2 values were low. However, a plot of the correlation indicates that the PACls with strong δ -Al₃₀ polycation signals had high percentages of Al_{4-7d}. These PACls did not exhibit high percentages of the Al_{30min-3h} fraction, which was the most active fraction for arsenate removal ($R^2 = -2.23$, Figure 14S). These results suggest that the δ -Al₃₀ polycation was not the most active species for arsenate removal. To verify this possibility, we selected two PACls and compared their arsenate removal percentages: the NMR spectrum of one of the two PACls (PACl-70-6-3) exhibited a small but clear hump for the δ -Al₃₀ polycation, whereas the other (PACl-90-1-3) did not have the δ -Al₃₀ polycation hump (Fig. 4, uppermost panels). However, the arsenate removal percentage achieved with PACl-70-6-3 was not higher than that achieved with PACl-90-1-3 (Figure 4, lowermost panel). Therefore, the δ -Al₃₀ polycation in PACls was not a strongly active species for arsenate removal.

Some recent studies have suggested that polymeric aluminum species (e-Al₁₃ and δ -Al₃₀

polycations) are active for arsenate removal during aluminum coagulation (Hu et al. 2012, Mertens et al. 2012). However, these studies used a few coagulants that included alum, and the investigators concluded that the fact that arsenate removal by PACls was high compared to removal by non-prepolymerized coagulants (alum or AlCl_3) was attributable to the polymeric species in the PACls. Our data also show that compared with non-prepolymerized coagulants, PACls exhibited high arsenate removal, as was previously reported. This result could be attributed to the polymeric species in some PACls. However, the e-Al_{13} and $\delta\text{-Al}_{30}$ polycations are not the only active substances in PACls used for coagulation (Wang and Hsu 1994). In fact, we did not observe peaks for either the e-Al_{13} polycation or the $\delta\text{-Al}_{30}$ polycation in the NMR spectra of the commercial PACl coagulants, although these are widely accepted as being useful coagulants for arsenate as well as for turbidity removal. The presence of aluminum species that are unobservable by ^{27}Al NMR has been inferred by means of a ferron speciation method (Sposito 1995). For example, the presence of a flat aluminum tridecamer Al_{13} species has been suggested (Casey et al. 2001). This species can be distinguished from the e-Al_{13} and $\delta\text{-Al}_{30}$ polycations because it has octahedral coordination of the central aluminum, whereas the e-Al_{13} and $\delta\text{-Al}_{30}$ polycations have tetrahedral coordination. A polymer with a hexameric ring morphology has been suggested as the slowly reacting fraction (>1 h) of Alb and a portion of Alc (Bertsch et al. 1986). The $\text{Al}_{30\text{min-3h}}$ fraction may have such a morphology. Although our experiments indicate that a high content of the e-Al_{13} or $\delta\text{-Al}_{30}$ polycation is not necessary for effective arsenate removal and suggest that the $\text{Al}_{30\text{min-3h}}$ fraction is the most effective fraction, these results may be specific to the water samples we tested in our experiments. Aluminum polymerization reactions are influenced by water quality, such as DOC concentration. A different aluminum fraction might be effective for arsenate removal from water with a high DOC concentration, for example. Clearly, further study is required, but our regression analysis method should be effective for elucidating the aluminum fraction that is effective for arsenate removal.

4. Conclusions

(1) Colloidal (Alc) and polymeric (Alb) aluminum species in PACls were responsible for efficient arsenate removal by coagulation at alkaline pH (>7); whereas at neutral pH, arsenate removal percentages by PACls and non-prepolymerized aluminum coagulants did not differ substantially. The percentage of colloidal and polymeric aluminum species increased with increasing PACl basicity, and therefore arsenate removal was generally enhanced by using a high-basicity PACl.

(2) Among colloidal and polymeric aluminum species, a subfraction of Alb and Alc (that is, the $\text{Al}_{30\text{ min}-3\text{ h}}$ fraction) appeared to be the most effective active species for arsenate removal under alkaline coagulation conditions, and the next most effective fraction was $\text{Al}_{>3\text{ h}}$. The arsenate sorption capacity of $\text{Al}_{30\text{ min}-3\text{ h}}$ was stable and did not decrease markedly with increasing pH.

(3) Neither the e-Al_{13} polycation nor the $\delta\text{-Al}_{30}$ polycation was the only important active species for effective arsenate removal.

(4) In this study, the PACls that showed the highest arsenate removal percentages were those that had a high proportion of the $\text{Al}_{30\text{ min}-3\text{ h}}$ fraction (26%) or those in which the proportion of the $\text{Al}_{>3\text{ h}}$ fraction was $>80\%$. The percentages of $\text{Al}_{30\text{ min}-3\text{ h}}$ in the commercially available and commonly used PACls (basicity 50–70%) that were evaluated in this study were low, $<10\%$. The enhanced arsenate removal observed for these PACls compared with that for AlCl_3 were

due to the high proportion of the Al_{>3h} fraction.

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Appendix. Supplementary Information

Supplementary Information including Figure 1S–14S and Table 1S–8S is available in the online version.

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608

Table 1. Regression analysis for the first set of coagulation experiment (T1 and K waters. The coagulant dose was 0.98 mg-Al/L).

T1 water (pH 7.5)	Ferron reaction time			R^2	p		
	Al ₁	Al ₂	Al ₃		q_1	q_{21}	q_{31}
S1-13	0 – 0.5 min	0.5 – 30 min	> 30 min	0.68	0.000	0.002	0.000
S1-14	0 – 0.5 min	0.5 – 1 h	> 1 h	0.68	0.000	0.001	0.000
S1-15	0 – 0.5 min	0.5 – 2 h	> 2 h	0.68	0.000	0.001	0.000
S1-16	0 – 0.5 min	0.5 – 3 h	> 3 h	0.69	0.000	0.000	0.000
S1-23	0 – 3 min	3 – 30 min	> 30 min	0.67	0.000	0.001	0.001
S1-24	0 – 3 min	3 min – 1 h	> 1 h	0.67	0.000	0.001	0.001
S1-25	0 – 3 min	3 min – 2 h	> 2 h	0.68	0.000	0.001	0.001
S1-26	0 – 3 min	3 min – 3 h	> 3 h	0.69	0.000	0.000	0.001
S1-34	0 – 30 min	30 min – 1 h	> 1 h	0.69	0.000	0.001	0.001
S1-35	0 – 30 min	30 min – 2 h	> 2 h	0.74	0.000	0.000	0.001
S1-36	0 – 30 min	30 min – 3 h	> 3 h	0.76	0.000	0.000	0.002
S1-45	0 – 1 h	1 h – 2 h	> 2 h	0.75	0.000	0.000	0.008
S1-46	0 – 1 h	1 h – 3 h	> 3 h	0.76	0.000	0.000	0.066

T1 water (pH 8.0)	Ferron reaction time			R^2	p		
	Al ₁	Al ₂	Al ₃		q_1	q_{21}	q_{31}
S1-13	0 – 0.5 min	0.5 – 30 min	> 30 min	0.75	0.017	0.001	0.000
S1-14	0 – 0.5 min	0.5 – 1 h	> 1 h	0.76	0.013	0.000	0.000
S1-15	0 – 0.5 min	0.5 – 2 h	> 2 h	0.76	0.012	0.000	0.000
S1-16	0 – 0.5 min	0.5 – 3 h	> 3 h	0.76	0.012	0.000	0.000
S1-23	0 – 3 min	3 – 30 min	> 30 min	0.74	0.000	0.001	0.000
S1-24	0 – 3 min	3 min – 1 h	> 1 h	0.75	0.000	0.000	0.000
S1-25	0 – 3 min	3 min – 2 h	> 2 h	0.75	0.000	0.000	0.000
S1-26	0 – 3 min	3 min – 3 h	> 3 h	0.76	0.000	0.000	0.000
S1-34	0 – 30 min	30 min – 1 h	> 1 h	0.78	0.000	0.000	0.000
S1-35	0 – 30 min	30 min – 2 h	> 2 h	0.81	0.000	0.000	0.000
S1-36	0 – 30 min	30 min – 3 h	> 3 h	0.83	0.000	0.000	0.000
S1-45	0 – 1 h	1 h – 2 h	> 2 h	0.78	0.000	0.000	0.003
S1-46	0 – 1 h	1 h – 3 h	> 3 h	0.80	0.000	0.000	0.026

T1 water (pH 8.5)	Ferron reaction time			R^2	p		
	Al ₁	Al ₂	Al ₃		q_1	q_{21}	q_{31}
S1-13	0 – 0.5 min	0.5 – 30 min	> 30 min	0.57	0.022	0.018	0.001
S1-14	0 – 0.5 min	0.5 – 1 h	> 1 h	0.57	0.020	0.006	0.001
S1-15	0 – 0.5 min	0.5 – 2 h	> 2 h	0.57	0.019	0.004	0.001
S1-16	0 – 0.5 min	0.5 – 3 h	> 3 h	0.58	0.020	0.004	0.001
S1-23	0 – 3 min	3 – 30 min	> 30 min	0.57	0.000	0.019	0.002
S1-24	0 – 3 min	3 min – 1 h	> 1 h	0.57	0.000	0.007	0.002
S1-25	0 – 3 min	3 min – 2 h	> 2 h	0.57	0.000	0.004	0.003
S1-26	0 – 3 min	3 min – 3 h	> 3 h	0.58	0.000	0.004	0.003
S1-34	0 – 30 min	30 min – 1 h	> 1 h	0.64	0.000	0.002	0.001
S1-35	0 – 30 min	30 min – 2 h	> 2 h	0.66	0.000	0.001	0.002
S1-36	0 – 30 min	30 min – 3 h	> 3 h	0.70	0.000	0.001	0.002
S1-45	0 – 1 h	1 h – 2 h	> 2 h	0.61	0.000	0.003	0.013
S1-46	0 – 1 h	1 h – 3 h	> 3 h	0.71	0.000	0.000	0.040

K water (pH 8.0)	Ferron reaction time			R^2	p		
	Al ₁	Al ₂	Al ₃		q_1	q_{21}	q_{31}
S1-13	0 – 0.5 min	0.5 – 30 min	> 30 min	0.45	0.984	0.006	0.017
S1-14	0 – 0.5 min	0.5 – 1 h	> 1 h	0.47	0.917	0.004	0.022
S1-15	0 – 0.5 min	0.5 – 2 h	> 2 h	0.48	0.875	0.003	0.028
S1-16	0 – 0.5 min	0.5 – 3 h	> 3 h	0.49	0.885	0.003	0.031
S1-23	0 – 3 min	3 – 30 min	> 30 min	0.43	0.127	0.008	0.076
S1-24	0 – 3 min	3 min – 1 h	> 1 h	0.44	0.130	0.005	0.080
S1-25	0 – 3 min	3 min – 2 h	> 2 h	0.47	0.121	0.004	0.096
S1-26	0 – 3 min	3 min – 3 h	> 3 h	0.47	0.126	0.004	0.110
S1-34	0 – 30 min	30 min – 1 h	> 1 h	0.58	0.144	0.003	0.077
S1-35	0 – 30 min	30 min – 2 h	> 2 h	0.59	0.095	0.001	0.111
S1-36	0 – 30 min	30 min – 3 h	> 3 h	0.57	0.108	0.001	0.221
S1-45	0 – 1 h	1 h – 2 h	> 2 h	0.69	0.011	0.000	0.500
S1-46	0 – 1 h	1 h – 3 h	> 3 h	0.56	0.027	0.001	0.754

Table 2. Regression analysis for the second set of coagulation experiment (T2 water. The coagulant dose was 2.1 mg-Al/L).

T2 water (pH 7.5)	Ferron reaction time			R^2	p		
	Al ₁	Al ₂	Al ₃		q_1	q_{21}	q_{31}
S2-13	0 – 0.5 min	0.5 – 30 min	> 30 min	0.685	0.000	0.000	0.000
S2-14	0 – 0.5 min	0.5 min – 1 h	> 1 h	0.686	0.000	0.000	0.000
S2-15	0 – 0.5 min	0.5 min – 2 h	> 2 h	0.689	0.000	0.000	0.000
S2-16	0 – 0.5 min	0.5 min – 3 h	> 3 h	0.691	0.000	0.000	0.000
S2-17	0 – 0.5 min	0.5 min – 6 h	> 6 h	0.693	0.000	0.000	0.000
S2-18	0 – 0.5 min	0.5 min – 12 h	> 12 h	0.695	0.000	0.000	0.000
S2-23	0 – 3 min	3 – 30 min	> 30 min	0.674	0.000	0.000	0.000
S2-24	0 – 3 min	3 min – 1 h	> 1 h	0.676	0.000	0.000	0.000
S2-25	0 – 3 min	3 min – 2 h	> 2 h	0.679	0.000	0.000	0.000
S2-26	0 – 3 min	3 min – 3 h	> 3 h	0.681	0.000	0.000	0.000
S2-27	0 – 3 min	3 min – 6 h	> 6 h	0.684	0.000	0.000	0.000
S2-28	0 – 3 min	3 min – 12 h	> 12 h	0.687	0.000	0.000	0.000
S2-34	0 – 30 min	30 min – 1 h	> 1 h	0.685	0.000	0.000	0.000
S2-35	0 – 30 min	30 min – 2 h	> 2 h	0.699	0.000	0.000	0.000
S2-36	0 – 30 min	30 min – 3 h	> 3 h	0.701	0.000	0.000	0.000
S2-37	0 – 30 min	30 min – 6 h	> 6 h	0.685	0.000	0.000	0.002
S2-38	0 – 30 min	30 min – 12 h	> 12 h	0.645	0.000	0.000	0.132
S2-45	0 – 1 h	1 h – 2 h	> 2 h	0.697	0.000	0.000	0.000
S2-46	0 – 1 h	1 h – 3 h	> 3 h	0.655	0.000	0.000	0.003
S2-47	0 – 1 h	1 h – 6 h	> 6 h	0.489	0.000	0.002	0.463
S2-48	0 – 1 h	1 h – 12 h	> 12 h	0.330	0.000	0.031	0.987

T2 water (pH 8.0)	Ferron reaction time			R^2	p		
	Al ₁	Al ₂	Al ₃		q_1	q_{21}	q_{31}
S2-13	0 – 0.5 min	0.5 – 30 min	> 30 min	0.813	0.000	0.000	0.000
S2-14	0 – 0.5 min	0.5 min – 1 h	> 1 h	0.814	0.000	0.000	0.000
S2-15	0 – 0.5 min	0.5 min – 2 h	> 2 h	0.815	0.000	0.000	0.000
S2-16	0 – 0.5 min	0.5 min – 3 h	> 3 h	0.815	0.000	0.000	0.000
S2-17	0 – 0.5 min	0.5 min – 6 h	> 6 h	0.816	0.000	0.000	0.000
S2-18	0 – 0.5 min	0.5 min – 12 h	> 12 h	0.817	0.000	0.000	0.000
S2-23	0 – 3 min	3 – 30 min	> 30 min	0.838	0.000	0.000	0.000
S2-24	0 – 3 min	3 min – 1 h	> 1 h	0.839	0.000	0.000	0.000
S2-25	0 – 3 min	3 min – 2 h	> 2 h	0.841	0.000	0.000	0.000
S2-26	0 – 3 min	3 min – 3 h	> 3 h	0.842	0.000	0.000	0.000
S2-27	0 – 3 min	3 min – 6 h	> 6 h	0.844	0.000	0.000	0.000
S2-28	0 – 3 min	3 min – 12 h	> 12 h	0.844	0.000	0.000	0.000
S2-34	0 – 30 min	30 min – 1 h	> 1 h	0.853	0.000	0.000	0.000
S2-35	0 – 30 min	30 min – 2 h	> 2 h	0.860	0.000	0.000	0.000
S2-36	0 – 30 min	30 min – 3 h	> 3 h	0.862	0.000	0.000	0.000
S2-37	0 – 30 min	30 min – 6 h	> 6 h	0.852	0.000	0.000	0.000
S2-38	0 – 30 min	30 min – 12 h	> 12 h	0.806	0.000	0.000	0.003
S2-45	0 – 1 h	1 h – 2 h	> 2 h	0.841	0.000	0.000	0.000
S2-46	0 – 1 h	1 h – 3 h	> 3 h	0.804	0.000	0.000	0.000
S2-47	0 – 1 h	1 h – 6 h	> 6 h	0.654	0.000	0.000	0.089
S2-48	0 – 1 h	1 h – 12 h	> 12 h	0.489	0.000	0.017	0.559

T2 water (pH 8.5)	Ferron reaction time			R^2	p		
	Al ₁	Al ₂	Al ₃		q_1	q_{21}	q_{31}
S2-13	0 – 0.5 min	0.5 – 30 min	> 30 min	0.713	0.131	0.004	0.000
S2-14	0 – 0.5 min	0.5 min – 1 h	> 1 h	0.711	0.139	0.000	0.000
S2-15	0 – 0.5 min	0.5 min – 2 h	> 2 h	0.710	0.143	0.000	0.000
S2-16	0 – 0.5 min	0.5 min – 3 h	> 3 h	0.710	0.145	0.000	0.000
S2-17	0 – 0.5 min	0.5 min – 6 h	> 6 h	0.710	0.149	0.000	0.000
S2-18	0 – 0.5 min	0.5 min – 12 h	> 12 h	0.709	0.151	0.000	0.000
S2-23	0 – 3 min	3 – 30 min	> 30 min	0.738	0.003	0.002	0.000
S2-24	0 – 3 min	3 min – 1 h	> 1 h	0.738	0.003	0.000	0.000
S2-25	0 – 3 min	3 min – 2 h	> 2 h	0.738	0.003	0.000	0.000
S2-26	0 – 3 min	3 min – 3 h	> 3 h	0.738	0.003	0.000	0.000
S2-27	0 – 3 min	3 min – 6 h	> 6 h	0.738	0.004	0.000	0.000
S2-28	0 – 3 min	3 min – 12 h	> 12 h	0.739	0.004	0.000	0.000
S2-34	0 – 30 min	30 min – 1 h	> 1 h	0.755	0.001	0.000	0.000
S2-35	0 – 30 min	30 min – 2 h	> 2 h	0.756	0.001	0.000	0.000
S2-36	0 – 30 min	30 min – 3 h	> 3 h	0.754	0.001	0.000	0.000
S2-37	0 – 30 min	30 min – 6 h	> 6 h	0.744	0.001	0.000	0.000
S2-38	0 – 30 min	30 min – 12 h	> 12 h	0.714	0.001	0.000	0.004
S2-45	0 – 1 h	1 h – 2 h	> 2 h	0.729	0.001	0.000	0.000
S2-46	0 – 1 h	1 h – 3 h	> 3 h	0.697	0.001	0.000	0.000
S2-47	0 – 1 h	1 h – 6 h	> 6 h	0.585	0.001	0.004	0.047
S2-48	0 – 1 h	1 h – 12 h	> 12 h	0.474	0.000	0.039	0.331

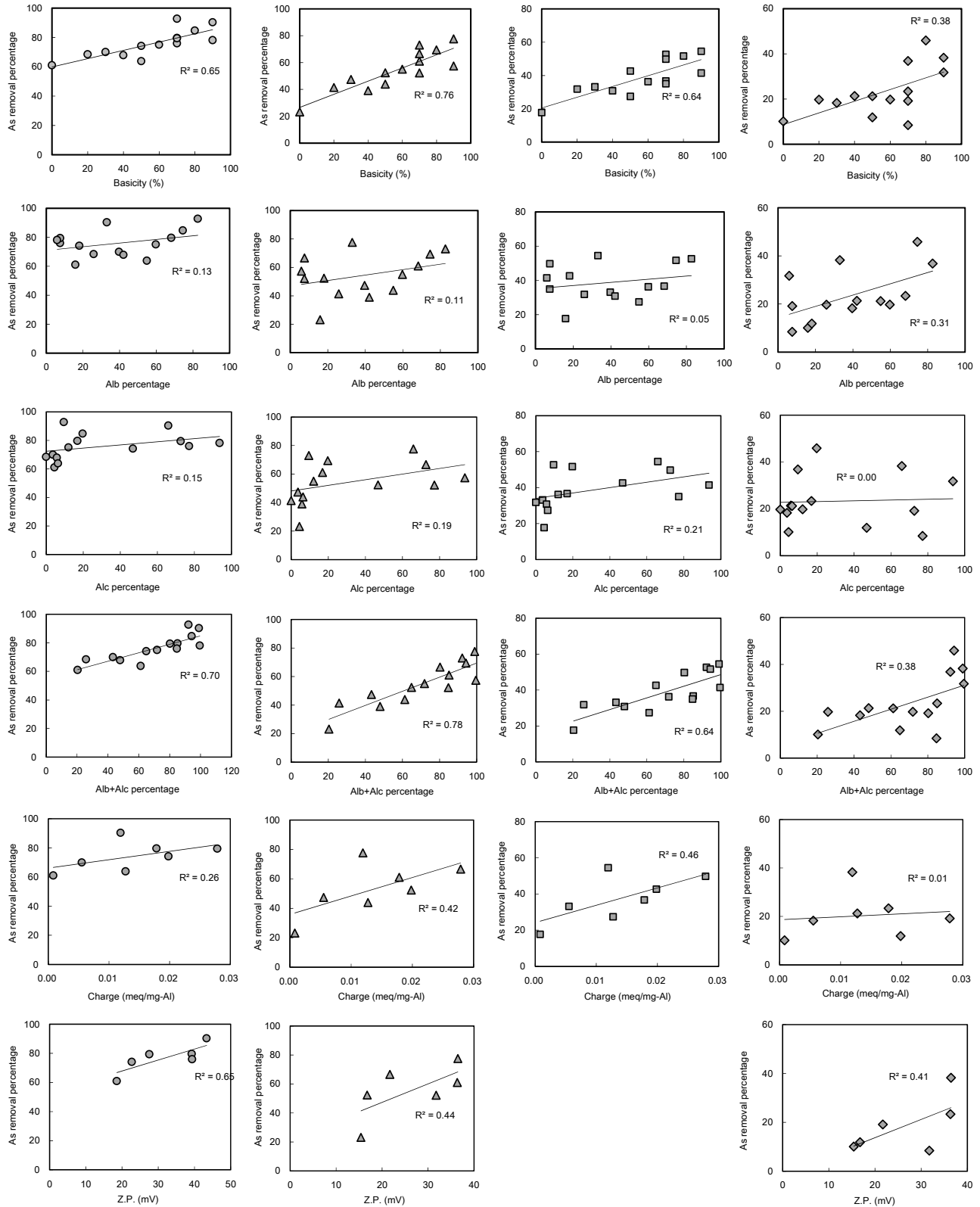
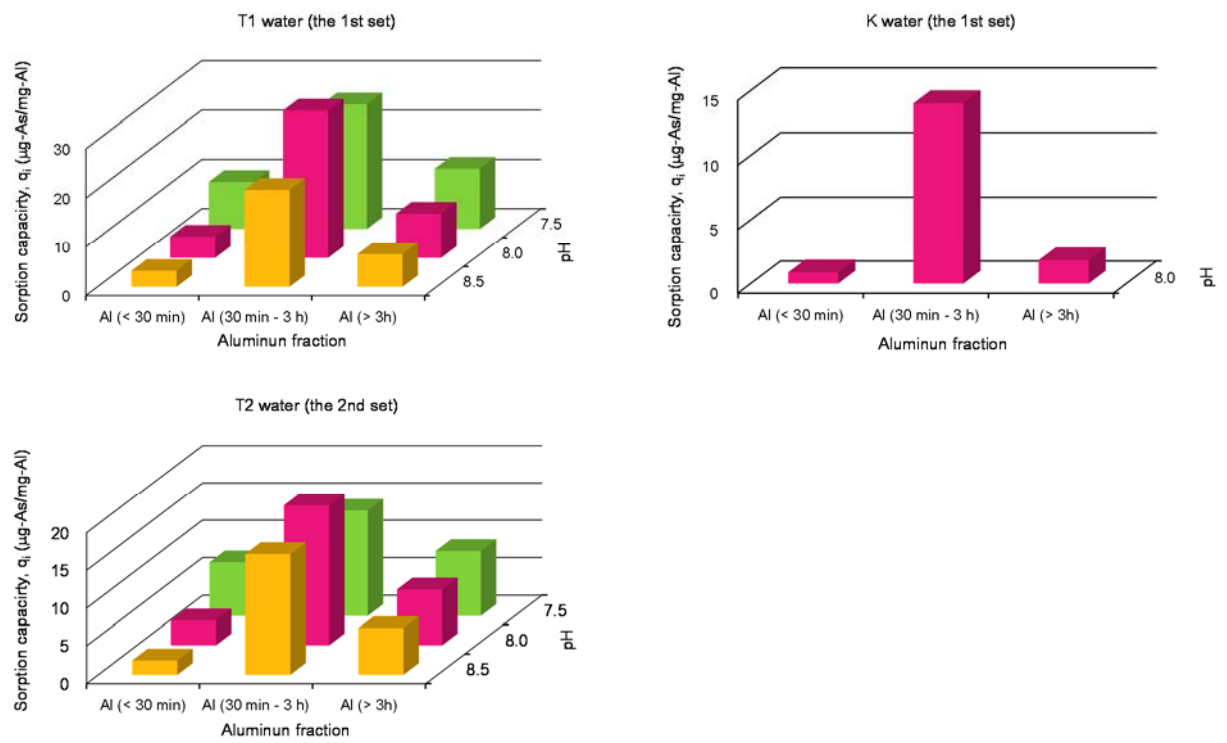


Figure 1. Plots of arsenate removal percentage against PACI's basicity, colloid charge, zeta potential, Alb content, Alc content, and Alb+Alc content (the leftmost, second, and third left panels are of coagulation pH 7.5, 8.0, and 8.5, respectively, using T1 water with the initial As concentration 15.8 µg/L. The rightmost is of coagulation pH 8.0 using K water with the initial As concentration 11.2 µg/L. Coagulant dose is 0.98 mg-Al/L).

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Figure 2. Arsenate sorption capacities of aluminum fractions

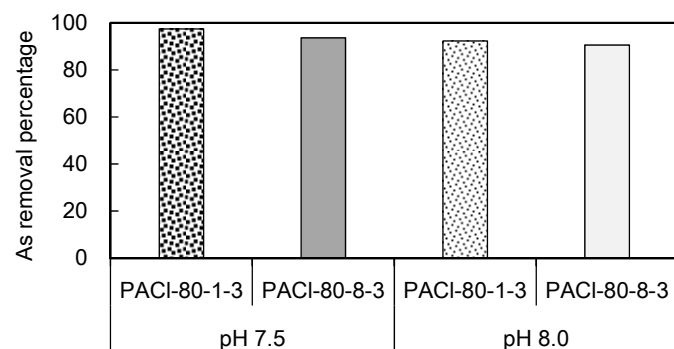
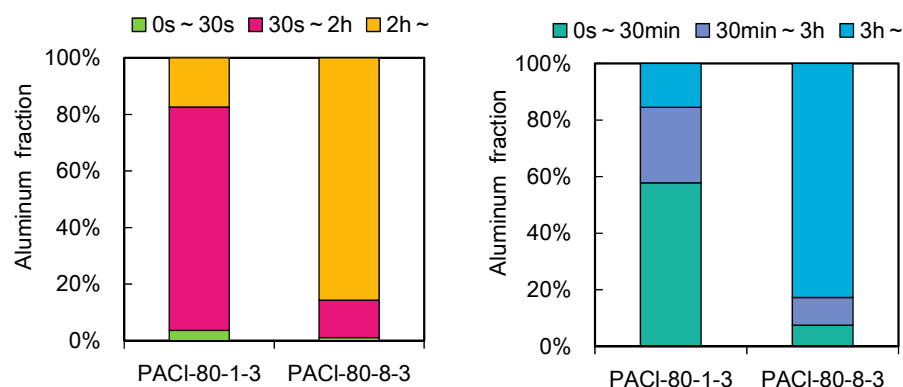
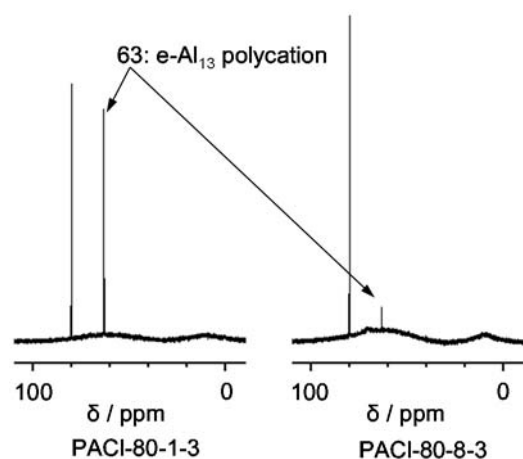


Figure 3. Comparison of NMR spectra, Al fractions, and arsenate removals by using two coagulants (TM water was used for the coagulation experiment. Coagulant dose was 2.1 mg-Al/L)

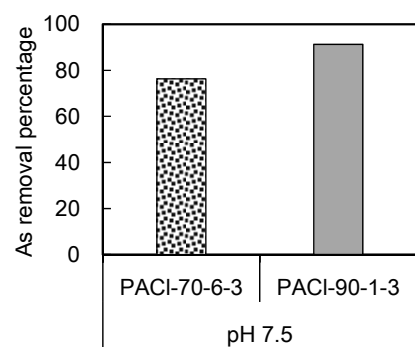
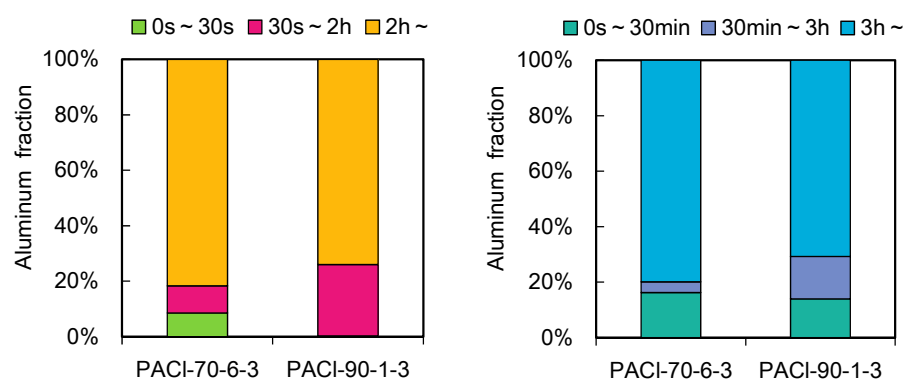
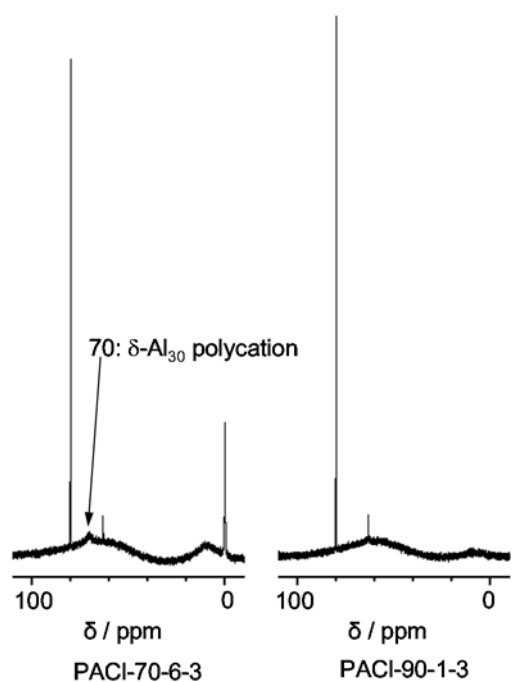


Figure 4. Comparison of NMR spectra, Al fractions, and arsenate removals by using two coagulants (TM water was used for the coagulation experiment. Coagulant dose was 2.1 mg-Al/L).

Supplementary Material

Characteristics and Components of Poly-aluminum Chloride Coagulants that Enhance Arsenate Removal by Coagulation: Detailed Analysis of Aluminum Species

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Preparation and characterization of coagulants

Fourteen PACls were prepared for the first set of coagulation experiments (Table 1S). All the PACls used in this study were given unique designations in which the first number indicates percent basicity, “s” indicates “sulfated,” “t” indicates a commercial PACl or a trial PACl product obtained from Taki Chemical Co. (Kakogawa, Japan), and the final number (1) indicates that the coagulant was used in the first set of coagulation experiments. The number in the middle indicate serial number. The PACls obtained from Taki Chemical Co. were produced by dissolving $\text{Al}(\text{OH})_3$ solids in hydrochloric and sulfuric acid as described by, for example, (Itoh and Sato, 1995; Sato and Matsuda, 2009). The other PACls were prepared in our laboratory by a base titration method described in the literature (Shen and Dempsey, 1998; Yan et al., 2008b; Kimura et al., 2013). Specifically, PACl-20-1, 30-1, 40-1, 50-1, 60-1, 70-1-1, 70-2-1, and 80-1-1 were prepared as follows. An AlCl_3 solution (0.5 M, 80 mL) in a 500-mL Erlenmeyer flask was titrated with 0.3 M NaOH by means of a peristaltic pump at a rate of 4 mL/min to achieve the target basicity. During the titration, a combined hot plate/magnetic stirrer was used to agitate the solution in the flask and maintain the temperature at 85–90 °C. The same materials and procedure were used to prepare PACl-90-1-1, except that the solution was heated at 85–90 °C for 2 h after the titration. To prepare PACl-70-3-1, we first titrated a 1.5 M AlCl_3 solution with 0.9 M NaOH, and then we heated the resulting solution at 85–90 °C for 12 h (Shafran and Perry, 2005).

Alum was obtained as a solution from Taki Chemical Co. The PACls and alum were used in jar tests immediately after dilution with Milli-Q water (Milli-Q Advantage, Nihon Millipore, Tokyo, Japan). An 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; this solution was considered as a reference PACl having a basicity of zero (Yan et al., 2008a).

The 20 coagulants used in the second set of coagulation experiments (Table 2S) were prepared as described above for the first set of experiments, with the following exceptions. PACl-70-4-2 was prepared by titration of a 1.0 M AlCl_3 solution with 0.6 M NaOH and heating the resulting solution for 3 h at 85–90 °C. For PACl-80-2-2 and 80-3-2, 1.0 M AlCl_3 solution were titrated with 0.6 M NaOH, and the resulting solutions were heated for 1 and 2.5 h, respectively, at 85–90 °C. For PACl-80-4-2, 0.15 M NaOH and 0.25 M AlCl_3 were used in the titration. Sixteen of the 20 coagulants were analyzed by means of ^{27}Al nuclear magnetic resonance (NMR) spectroscopy.

Another 17 coagulants were prepared for ^{27}Al NMR analysis and supplemental coagulation experiments (Table 3S). PACl-70-1-3, 70-4-3, 80-1-3, 80-2-3, and 90-1-3 were prepared by the procedures described for PACl-70-1-1, 70-4-2, 80-1-2, 80-2-2, and 90-1-1, respectively. PACl-80-5-3 was prepared by heating PACl-80-1-3 for 24 h at 85–90 °C. PACl-80-6-3 and 80-7-3 were prepared by heating PACl-80-2-3 for 0.5 and 1.5 h, respectively, at 90–95 °C. PACl-70-5-3 and 80-8-3 were prepared by titrating 1.5 M AlCl_3 with 0.9 M NaOH and heating the resulting solutions at 90–95 °C for 24 h. PACl-70-6-3 was prepared by titrating 0.5 M AlCl_3 with 0.3 M NaOH and heating the resulting solution for 72 h at 90–95 °C. For PACl-90-2-3, 0.15 M NaOH and 0.25 M AlCl_3 were used for the titration. PACl-83st-2-3 and 83st-3-3 were prepared by heating a PACl-83st-1-2 solution for 72 h at 90–95 °C after dilution with Milli-Q water. PACl-30h-3, 40h-3, and 50h-3 were prepared by dissolving reagent-grade $\text{Al}(\text{OH})_3$ (Wako) in HCl solution at 165 °C (“h” indicates $\text{Al}(\text{OH})_3$ as a raw material).

The distributions of aluminum species in the coagulants were analyzed by means of ferron colorimetry. On the basis of their reaction rates with the ferron reagent (8-hydroxy-7-iodo-5-quinoline sulfonic acid; Wako), the aluminum species were classified into three groups: Ala, Alb, and Alc. Ala denotes species that reacted with ferron instantaneously (within 0.5 min). Alb denotes species that reacted during the period from 0.5 min to 2 h. Alc denotes species that did not react by 2h. These three groups are assumed to correspond to monomeric, polymeric, and colloidal aluminum species, respectively (Wang et al., 2004). Ferron analyses were conducted immediately (1–2 min) after dilution of coagulants with Milli-Q water to 0.1 M (Jia et al., 2004; Wang et al., 2004). Dilution reportedly has little effect on the ferron speciation distribution of PACls (Wang et al., 2004; Kimura et al., 2013). For the PACls used in the first set of coagulation experiments, the ferron reagent was added to the diluted coagulant, the mixture was immediately shaken, and then the absorbance at 366 nm was measured in a 1-cm cell (UV-1700, Shimadzu Co., Kyoto, Japan) at 3, 10, 30, 60, and 180 min as well as at the customary times of 0.5 and 120 min. For the PACls used in the second set of coagulation experiments and in the ^{27}Al NMR analysis, the time period for the absorbance measurement was extended to 7 days: that is, absorbances were measured at 0.5, 1, 3, and 30 min; 1, 2, 3, 6, and 12 h; and 1, 2, 4, and 7 days. Between measurements, the mixtures of ferron and coagulant were kept at 20 °C in the dark.

^{27}Al NMR spectroscopy was also used to characterize some of the aluminum species in the coagulants after dilution with Milli-Q water to 0.1–9.5 M-Al (Tables 2S and 3S). On the basis of chemical shift differences, aluminum species were detected: monomeric species, dimeric and

trimeric species, the ϵ - Al_{13} polycation, and the δ - Al_{30} polycation (Gao et al., 2005; Chen et al., 2006; Chen et al., 2007). For NMR analysis, deuterium oxide (75% v/v, Wako) was added to the diluted coagulant, and the resulting solution was placed in a 5-mm NMR tube. A 3-mm coaxial capillary filled with a diluted solution of sodium aluminate (Wako) was further diluted with Milli-Q water to 0.01 M-Al, and then deuterium oxide (75% v/v) was added. The coaxial capillary was used as an internal standard for Al content and as the deuterium lock. NMR spectra were measured at 70 °C with a JEOL JNM-ECA 600 spectrometer (JEOL, Tokyo, Japan) by means of a single-pulse method (field strength 14.09 T, resonance frequency 156.39 MHz, pulse width 5.0 μs , repetition time 1.13 s, number of scans 8000, X-sweep 78.25 kHz). The reference chemical shift (0 ppm) was adjusted with AlCl_3 solution (0.1 M-Al) mixed with deuterium oxide (75% v/v) prepared by the procedure described above.

The charge densities of the aluminum species in the coagulants were determined with a colloid titrator (Hiranuma Sangyo Co., Ibaraki, Japan). Diluted coagulant solution (150 mL, 1–2 mg-Al/L) was transferred to a titration vessel. After 0.1% (v/v) toluidine blue (0.3 mL, Wako) was added as an indicator, the solution was titrated with 1 mN potassium polyvinyl sulfate (Wako) at a rate of 10 mL/min by means of a pump. The contents of the vessel were magnetically stirred during the titration, and the absorbance at a wavelength of 630 nm was recorded continuously until there was little change in the absorbance. The charge was determined from the amount of potassium polyvinyl sulfate solution that corresponded to the half-height of the descending slope of the absorbance curve.

The zeta potentials of aluminum hydrolysis products were determined with an electrophoretic light-scattering spectrophotometer (Zetasizer Nano ZS, 532-nm green laser, Malvern Instruments, Malvern, Worcestershire, UK) at 25 °C and at a 17° measurement angle. Milli-Q water was buffered with NaHCO_3 to give the equivalent of 20 mg- CaCO_3 /L of alkalinity (buffered Milli-Q water). The buffered Milli-Q water was supplemented with 200-nm latex microparticles (Micromer plain, Corefront Corp., Tokyo, Japan) at 0.1 mg/L. After a predetermined volume of 0.1 N HCl or 0.1 N NaOH was added to bring the final coagulation pH to the target value, a coagulant was injected into the water sample. The mixture was stirred rapidly for 1 min ($G = 190 \text{ s}^{-1}$, 136 rpm) and then sampled. The electrophoretic mobility of aluminum hydrolysis products containing latex particles was measured to determine the zeta potential. The addition of latex particles enabled the detection of the aluminum hydrolysis products; the co-existing latex particles did not affect the zeta potential values, which indicates that the zeta potentials measured were those of aluminum hydrolysis products alone, with no influence from the zeta potential of latex.

Selection of membrane filter

Removal of arsenic by means of coagulation in jar tests is usually assessed in terms of the arsenic concentration measured after the coagulated/settled water is filtered through a membrane filter; whereas in actual conventional water treatment plants, arsenic removal is assessed after coagulation, settling and sand filtration. Membrane filters with a pore size of 0.1–0.45 μm have traditionally been used to separate soluble materials. However, the concentrations of metals in filtrates may be decreased when smaller-pore-size filters are used (Kennedy et al., 1974; Wagemann and Brunskill, 1975; Hydes and Liss, 1977). Therefore, removal of arsenic species by coagulation might have been affected by the pore size of the membrane filter used for the separation process. Therefore, in this study, we evaluated the effect of membrane pore size and membrane material on the arsenate concentration in the filtrate by comparing the arsenate

concentration after jar tests with that after sand filtration conducted at a full-scale water treatment plant, as described below.

Water samplings were conducted primarily at the Moiwa Water Treatment Plant (Sapporo, Japan), where drinking water is produced by coagulation by PACl, settling, chlorination, and rapid sand filtration. Details of the procedure are described elsewhere (Matsui et al., 2013). Water that had been subjected to coagulation and settling was sampled, and the sample was immediately filtered through the membrane filters. Water that had been treated by rapid sand filtration was also sampled, 15 minutes (the detention time of the rapid sand filtration process) after the coagulated-and-settled water was sampled. The arsenate concentrations in the samples were analyzed. The results are shown in Figure 1S. Arsenate concentrations were more or less the same regardless of membrane pore size and material, although the PTFE (polytetrafluoroethylene) membrane with a pore size a 0.45 μm showed slightly higher arsenate concentration than the 0.1- μm membrane. Because the arsenate concentrations in the filtrates obtained with the 0.45- μm PTFE membrane showed the strongest correlation to the concentrations in filtrates from sand filtration, we used mainly 0.45- μm PTFE membranes in the jar tests.

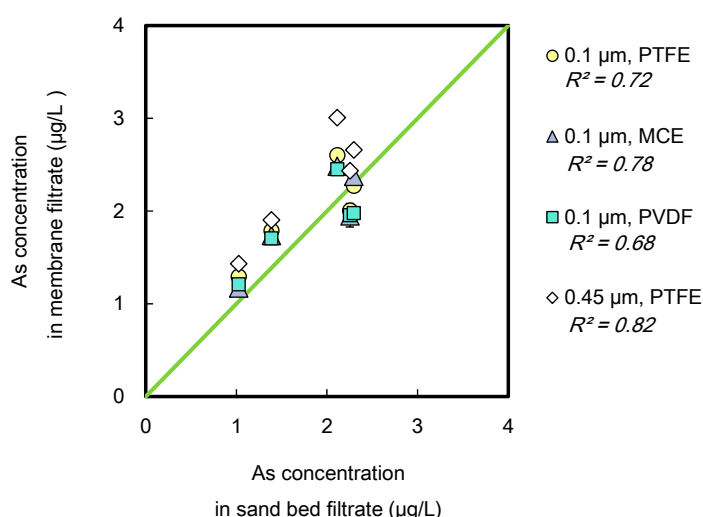


Figure 1S. Correlation between As concentrations in filtrates from membrane microfiltration and sand bed filtration [Moiwa Water Treatment Plant, raw water total organic carbon = 1.1–1.5 mg/L, coagulant dose = 1.2–3.4 mg-Al/L, pH 7.3–7.5, water temperature = 7–12 $^{\circ}\text{C}$, PTFE: Polytetrafluoroethylene, MCE: mixed cellulose ester, PVDF: poly(vinylidene fluoride)].

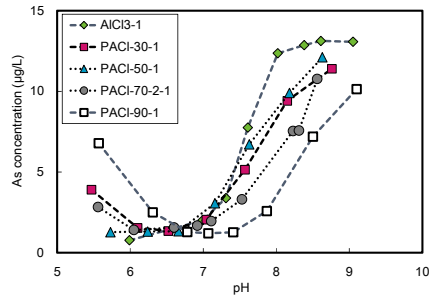


Figure 2S. As concentration after coagulation, settling, and microfiltration for five PACIs (T1 water [see water designations in Table 4S], initial As concentration = 15.8 µg/L, coagulant dose = 0.98 mg-Al/L).

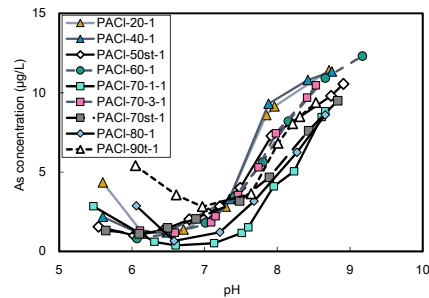


Figure 3S. As concentration after coagulation, settling, and microfiltration for nine PACIs (T1 water [see water designations in Table 4S], initial As concentration = 15.8 µg/L, coagulant dose = 0.98 mg-Al/L)

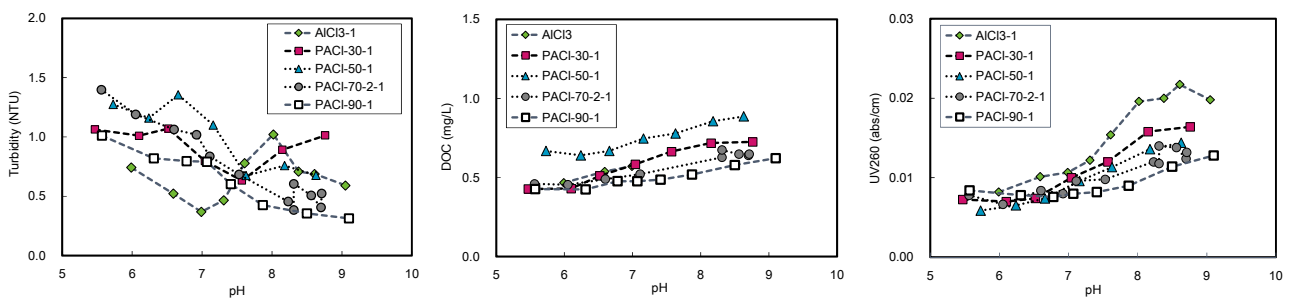


Figure 4S. Residual turbidity, dissolved organic carbon (DOC), and ultraviolet absorbance (260 nm) observed after coagulation and settling under experimental conditions matching those described for Figure 2S.

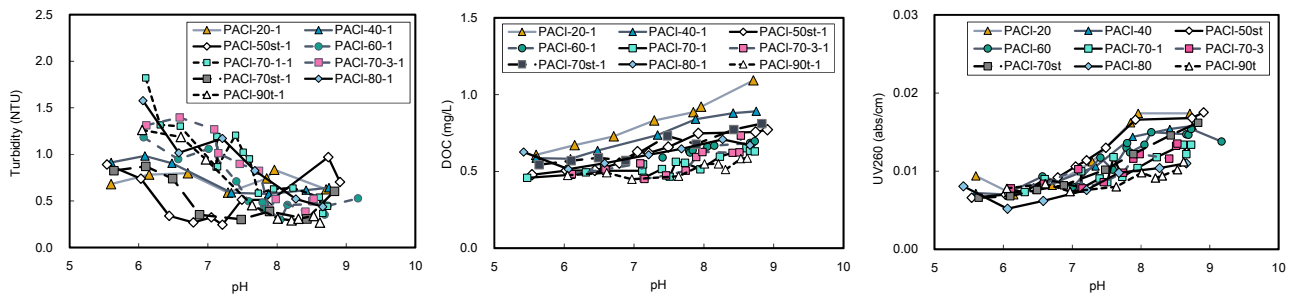


Figure 5S. Residual turbidity, dissolved organic carbon (DOC), and ultraviolet absorbance (260 nm) observed after coagulation and settling under experimental conditions matching those described for Figure 3S.

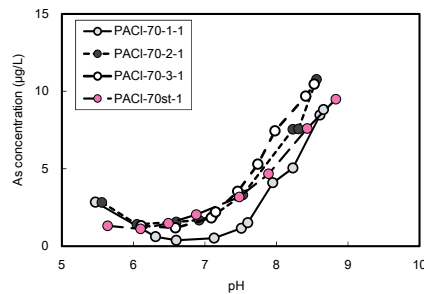


Figure 6S. As concentration after coagulation, settling, and microfiltration for 70%-basicity PACls (T1 water [see designations in Table 4S], initial As concentration = 15.8 μg/L, coagulant dose = 0.98 mg-Al/L).

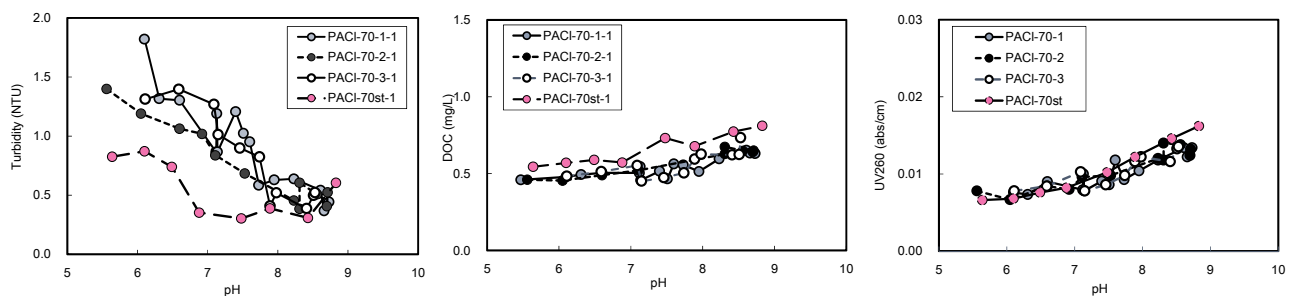


Figure 7S. Residual turbidity, dissolved organic carbon (DOC), and ultraviolet absorbance (260 nm) observed after coagulation and settling under experimental conditions matching those described for Figure 6S.

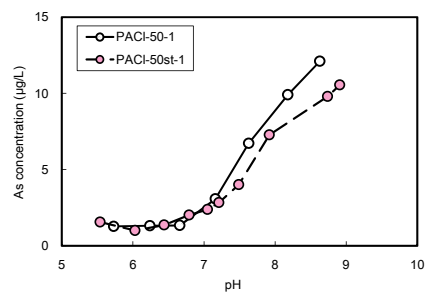


Figure 8S. As concentration after coagulation, settling, and microfiltration for 50%-basicity PACls (T1 water [see designations in Table 4S], initial As concentration = 15.8 µg/L, coagulant dose = 0.98 mg-Al/L).

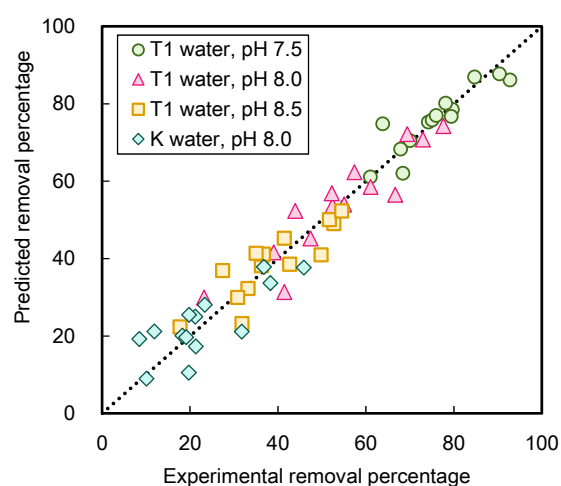


Figure 9S. Correlation between arsenate removal percentages obtained by experiments and predicted by regression analysis model S1-36.

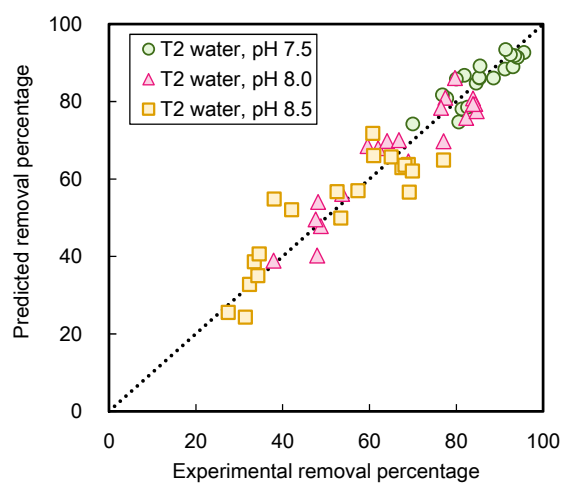


Figure 10S. Correlation between arsenate removal percentages obtained by experiments and predicted by regression analysis model S2-36.

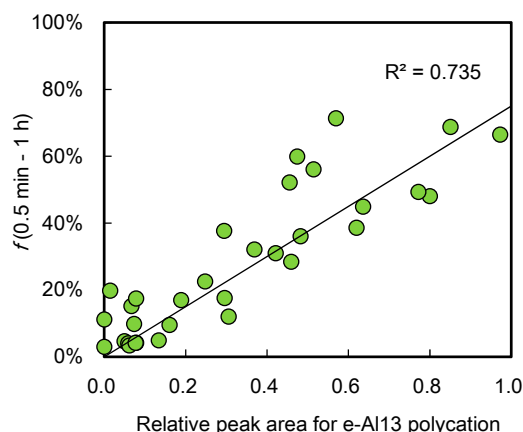


Figure 11S. Correlation between the relative ^{27}Al NMR peak area for the e- Al_{13} polycation (the peak areas are relative to the area for an internal standard) and $f_{0.5\text{min}-1\text{h}}$ (the percentage of $\text{Al}_{0.5\text{min}-1\text{h}}$ fraction, that is, the fraction that reacted with ferron during the period from 0.5 min to 1 h). The R^2 values were determined from $1 - \text{SSreg}/\text{SStot}$, where SSreg is the sum of squares of the residuals around the regression line with an intercept of 0, and SStot is the sum of squares of the residuals around a horizontal line representing the mean absorbance value for this dataset (Motulsky and Christopoulos, 2004).

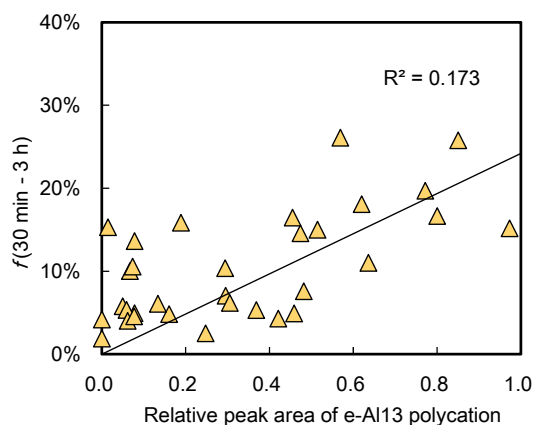


Figure 12S. Correlation between the relative ^{27}Al NMR peak area for the e- Al_{13} polycation (the peak areas are relative to the area for an internal standard) and $f_{30\text{min}-3\text{h}}$ (the percentage of $\text{Al}_{30\text{min}-3\text{h}}$ fraction, that is, the fraction that reacted with ferron during the period from 30 min to 3 h). The R^2 values were determined from $1 - \text{SSreg}/\text{SStot}$, where SSreg is the sum of squares of the residuals around the regression line with an intercept of 0, and SStot is the sum of squares of the residuals around a horizontal line representing the mean absorbance value for this dataset (Motulsky and Christopoulos, 2004).

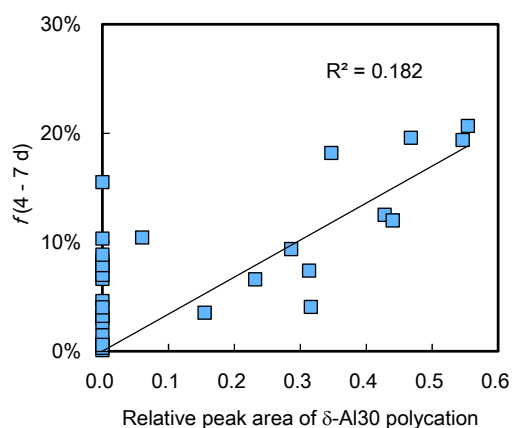


Figure 13S. Correlation between the relative ^{27}Al NMR peak area for the $\delta\text{-Al}_{30}$ polycation (the peak areas are relative to the area for an internal standard) and $f_{4-7\text{d}}$ (the percentage of $\text{Al}_{4-7\text{d}}$ fraction, that is, the fraction that reacted with ferron during the period from 4 to 7 days). The R^2 values were determined from $1 - \text{SSreg}/\text{SStot}$, where SSreg is the sum of squares of the residuals around the regression line with an intercept of 0, and SStot is the sum of squares of the residuals around a horizontal line representing the mean absorbance value for this dataset (Motulsky and Christopoulos, 2004).

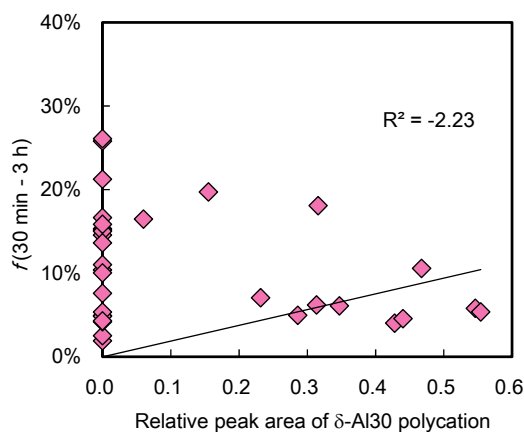


Figure 14S. Correlation between the relative ^{27}Al NMR peak area for the $\delta\text{-Al}_{30}$ polycation (the peak areas are relative to the area for an internal standard) and $f_{30\text{min}-3\text{h}}$ (the percentage of $\text{Al}_{30\text{min}-3\text{h}}$ fraction, that is, the fraction that reacted with ferron during the period from 30 min to 3 h). The R^2 values were determined from $1 - \text{SSreg}/\text{SStot}$, where SSreg is the sum of squares of the residuals around the regression line with an intercept of 0, and SStot is the sum of squares of the residuals around a horizontal line representing the mean absorbance value for this dataset (Motulsky and Christopoulos, 2004).

Table 1S. Properties of coagulants used in the first set of coagulation experiments.

Designation	Basicity (%)	Aluminum concentration	Sulfate concentration (% [w/w])	Density	Aluminum species percentage			Colloid charge (meq/g-Al)	Zeta potential (mV)			
					Ala	Alb	Alc		pH 6.5	pH 7.0	pH 7.5	pH 8.0
AlCl ₃ -1	0	13.5 g-Al/L	0	1.0	79.6	16.6	3.8	0.8	36.0	24.4	18.6	15.4
PACl-20-1	20	6.8 g-Al/L	0	1.0	74.1	25.8	0.1	NM	NM	NM	NM	NM
PACl-30-1	30	5.4 g-Al/L	0	1.0	56.7	38.2	5.1	5.5	NM	NM	NM	NM
PACl-40-1	40	4.5 g-Al/L	0	1.0	52.1	42.1	5.8	NM	NM	NM	NM	NM
PACl-50-1	50	3.9 g-Al/L	0	1.0	38.8	54.9	6.4	12.7	NM	NM	NM	NM
PACl-50st-1	50	10% (w/w) as Al ₂ O ₃	3	1.2	35.1	18.4	46.5	19.8	35.2	29.0	22.7	16.8
PACl-60-1	60	3.4 g-Al/L	0	1.0	28.1	59.8	12.1	NM	NM	NM	NM	NM
PACl-70-1-1	70	3.0 g-Al/L	0	1.0	7.8	80.7	11.6	NM	NM	NM	NM	NM
PACl-70-2-1	70	3.0 g-Al/L	0	1.0	14.9	68.2	16.9	17.8	47.7	44.1	39.3	36.4
PACl-70-3-1	70	9.0 g-Al/L	0	1.0	15.3	7.1	78	NM	49.9	47.6	39.4	31.8
PACl-70st-1	70	10% (w/w) as Al ₂ O ₃	2	1.2	19.8	7.7	72.7	27.9	39.7	33.9	27.6	21.7
PACl-80-1-1	80	2.7 g-Al/L	0	1.0	5.7	74.5	19.7	NM	NM	NM	NM	NM
PACl-90-1-1	90	2.5 g-Al/L	0	1.0	1.0	33.0	65.9	11.9	49.3	49.7	43.4	36.5
PACl-90t-1-1	90	1% (w/w) as Al ₂ O ₃	0	1.0	0.5	5.9	93.6	NM	NM	NM	NM	NM

Abbreviations: NM, not measured; Ala, Al species that reacted instantaneously with ferron (within 0.5 min); Alb, Al species that reacted during the period from 0.5 min to 2 h; Alc, species that did not react by 2h.

Table 2S. Properties of coagulants used in the second set of coagulation experiments.

Designation	Basicity (%)	Aluminum concentration (g-Al/L)	Sulfate concentration (% [w/w])	Density	Aluminum species percentage		
					Ala	Alb	Alc
AlCl ₃ -2*	0	13.5	0	1.0	81.0	11.9	7.1
PACl-20-2*	20	6.8	0	1.0	68.8	23.4	7.8
PACl-30-2	30	5.4	0	1.0	58.2	30.3	11.5
PACl-40-2*	40	4.5	0	1.0	46.7	40.4	12.9
PACl-50-2*	50	3.9	0	1.0	37.8	47.8	14.4
PACl-50st-2*	50	65.1	3	1.2	39.3	19.3	41.4
PACl-50t-2*	50	65.4	0	1.2	47.8	30.2	21.9
PACl-60-2*	60	3.4	0	1.0	23.9	53.0	23.1
PACl-70-3-2	70	3.0	0	1.0	13.0	14.8	72.2
PACl-70st-2*	70	65.4	2	1.2	16.7	11.4	72.0
PACl-70t-2*	70	64.5	0	1.2	18.5	20.3	61.2
PACl-70-4-2	70	6.0	0	1.0	12.9	14.2	72.9
PACl-80-1-2*	80	2.7	0	1.0	3.5	76.2	20.3
PACl-80st-2	80	64.7	2	1.2	5.5	10.0	84.6
PACl-83t-1-2*	83	163.5	0	1.3	3.0	6.1	90.9
PACl-80-2-2*	80	5.4	0	1.0	4.8	55.5	39.7
PACl-80-3-2*	80	5.4	0	1.0	5.1	44.8	50.1
PACl-80-4-2*	80	1.4	0	1.0	4.8	79.3	16.0
PACl-90-1-2*	90	2.5	0	1.0	0.3	25.6	74.0
PACl-90t-2-2*	90	5.4	0	1.0	0.1	4.7	95.2

Abbreviations: Ala, Al species that reacted with ferron instantaneously (<0.5 min); Alb, Al species that reacted during the period from 0.5 min to 2 h; Alc, species that did not react by 2h.

* Coagulant was analyzed by ²⁷Al NMR spectroscopy.

Table 3S. Properties of coagulants analyzed by ^{27}Al NMR spectroscopy.

Designation	Basicity (%)	Aluminum concentration (g-Al/L)	Sulfate concentration (% [w/w])	Density	Aluminum species percentage		
					Ala	Alb	Alc
PACl-30h-3	34	71.3	0	1.2	61.6	34.0	4.4
PACl-40h-3	36	61.6	0	1.2	56.7	38.4	4.9
PACl-50h-3	35	46.4	0	1.2	60.4	31.4	8.3
PACl-70-4-3	70	6.0	0	1.0	13.5	14.4	72.1
PACl-70-5-3	70	9.0	0	1.0	11.1	6.3	82.6
PACl-70-6-3	70	3.0	0	1.0	10.5	7.0	82.5
PACl-80-1-3	70	2.7	0	1.0	3.6	62.1	34.3
PACl-80-5-3	80	2.7	0	1.0	2.8	7.4	89.8
PACl-80-8-3	80	8.1	0	1.0	0.9	13.6	85.4
PACl-80-2-3	80	5.4	0	1.0	3.9	63.9	32.1
PACl-80-6-3	80	5.4	0	1.0	4.0	60.4	35.6
PACl-80-7-3	80	5.4	0	1.0	1.5	57.7	40.8
PACl-83t-2-3	83	130.0	0	1.2	1.6	4.9	93.5
PACl-83t-3-3	83	75.1	0	1.1	1.1	6.0	93.0
PACl-70-1-3	70	3.0	0	NM	13.6	70.4	16.0
PACl-90-2-3	90	1.2	0	NM	0.2	22.7	77.1
PACl-90-1-3	90	2.5	0	NM	0.3	23.4	76.3

Abbreviations: NM, not measured; Ala, Al species that reacted instantaneously with ferron (within 0.5 min); Alb, Al species that reacted during the period from 0.5 min to 2 h; Alc, species that did not react by 2h.

Table 4S. Characteristics of the water samples used in the coagulation tests.

Water designation		T1	K	T2	TM	Analytical method
Water source		Toyohira River	Kotonai River	Toyohira River	Mixture of Toyohira River water collected from two locations	
Objective		First set of coagulation experiments	First set of coagulation experiments	Second set of coagulation experiments	Additional coagulation experiments	
Water quality	pH	7.3	7.5	7.4	7.5	Glass electrode
	Turbidity (NTU)	1.5	0.41	7	1.2	Light scattering
	UV absorbance at 260 nm (cm ⁻¹)	0.024	0.004	0.028	0.024	Light absorbance
	DOC (mg/L)	0.82	0.23	1.0	0.85	Conductometric detection after UV and chemical oxidation (Sieves 900 TOC Analyzer, GE Analytical Instruments, Boulder, CO, USA)
	As (μg/L)	15.8	11.2	21.0	21.0	Inductively coupled plasma mass spectrometry (HP-7700, Agilent Technologies)
	Na ⁺ (mg/L)	11.8	na	9.8	6.5	Ion chromatography (Dionex DX-120, ICS-1000, Thermo Fisher Scientific)
	K ⁺ (mg/L)	2.0		1.6	1.6	
	Mg ⁺ (mg/L)	1.9		1.6	0.2	
	Ca ²⁺ (mg/L)	7.1		6.5	0.8	
	Cl ⁻ (mg/L)	16.0		10.2	17.8	
	NO ₃ ⁻ (mg-N/L)	0.96		0.21	0.2	
	SO ₄ ²⁻ (mg/L)	13.2		11.8	14.6	
	Coagulant dose (mg-Al/L)	0.98	0.98	2.1	2.1	

Abbreviation: DOC, dissolved organic carbon; na, not applicable.

Table 5S. Arsenate removal percentages in the first set of coagulation experiments.

	Arsenate removal percentage ^a				Aluminum species percentage		
	T1 water (pH 7.5)	T1 water (pH 8.0)	T1 water (pH 8.5)	K water (pH 8.0)	$f_{<30\text{min}}$	$f_{30\text{min}-3\text{h}}$	$f_{>3\text{h}}$
AlCl ₃ -1	61.0	23.2	17.7	10.1	95.5	0.9	3.6
PACl-20-1	68.4	41.4	31.8	19.7	97.5	2.5	0
PACl-30-1	70.0	47.4	33.2	18.3	85.8	10.5	3.6
PACl-40-1	67.9	39.0	30.8	21.3	87.1	8.1	4.8
PACl-50-1	63.8	43.9	27.4	21.2	79.9	14.7	5.4
PACl-50st-1	74.2	52.4	42.7	11.9	48.7	8.7	42.6
PACl-60-1	75.1	55.0	36.3	19.8	74.0	14.6	11.3
PACl-70-1-1	92.8	73.0	52.7	36.8	64.9	25.6	9.6
PACl-70-2-1	79.6	61.0	36.7	23.4	66.8	16.5	16.6
PACl-70-3-1	76.0	52.2	35.0	8.4	19.1	4.5	76.3
PACl-70st-1	79.4	66.7	49.8	19.1	24.1	5.3	70.6
PACl-80-1-1	84.7	69.4	51.7	45.9	56.8	24.8	18.4
PACl-90-1-1	90.3	77.6	54.5	38.3	20.1	18.1	61.8
PACl-90t-1-1	78.1	57.4	41.5	31.7	2.6	5.0	92.4

^a See Table 4S for water sample designations.

Table 6S. Arsenate removal percentages in the second set of coagulation experiments.

	Arsenate removal percentage ^a			Aluminum species percentage		
	T2 water (pH 7.5)	T2 water (pH 8.0)	T2 water (pH 8.5)	$f_{<30\text{min}}$	$f_{30\text{min}-3\text{h}}$	$f_{>3\text{h}}$
AlCl ₃ -2	70.0	37.9	31.4	91.5	1.9	6.6
PACl-20-2	80.6	48.0	27.5	90.1	2.5	7.4
PACl-30-2	81.3	48.8	32.4	82.8	6.6	10.6
PACl-40-2	77.8	48.2	33.5	78.1	10.4	11.5
PACl-50-2	76.8	53.7	34.6	74.9	11.0	14.1
PACl-50st-2	84.6	69.0	53.4	51.7	10.0	38.3
PACl-50t-2	82.6	47.6	34.3	74.0	4.9	21.1
PACl-60-2	81.9	62.0	42.1	61.7	16.7	21.6
PACl-70-3-2	88.6	64.1	52.6	24.5	4.8	70.7
PACl-70st-2	85.4	77.1	69.2	24.8	4.9	70.3
PACl-70t-2	80.0	59.6	38.1	33.9	7.0	59.1
PACl-70-4-2	85.3	66.8	57.4	23.9	4.8	71.4
PACl-80-1-2	95.6	83.9	69.0	55.7	25.8	18.5
PACl-80st-2	91.2	82.3	67.5	12.0	5.5	82.5
PACl-83t-1-2	93.1	84.7	77.1	6.3	5.0	88.8
PACl-80-2-2	94.1	84.4	68.2	42.4	19.7	37.8
PACl-80-3-2	93.5	77.5	65.0	34.0	18.1	48.0
PACl-80-4-2	92.5	83.9	69.9	60.1	26.1	13.8
PACl-90-1-2	91.4	79.7	60.8	14.0	15.3	70.7
PACl-90t-2-2	85.5	76.5	61.0	2.0	4.2	93.8

^a See Table 4S for water sample designations.

Table 7S. Coefficient of determination (R^2) values for correlations between the relative ^{27}Al NMR peak area for the e- Al_{13} polycation and the percentage of the aluminum fraction that reacted with ferron during the period from time t_1 to time t_2 . The R^2 values were determined from $1 - \text{SSreg}/\text{SStot}$, where SSreg is the sum of squares of the residuals around the regression line with an intercept of 0, and SStot is the sum of squares of the residuals around a horizontal line representing the mean absorbance value for this dataset (Motulsky and Christopoulos, 2004).

t_1	4 d												-1.060
	2 d											-1.570	-1.438
	1 d										-1.297	-1.517	-1.492
	12 h									-1.130	-1.248	-1.446	-1.462
	6 h								-1.166	-1.172	-1.272	-1.442	-1.466
	3 h							-1.676	-1.373	-1.297	-1.353	-1.494	-1.512
	2 h						-1.458	-2.028	-1.599	-1.435	-1.443	-1.560	-1.567
	1 h					-0.275	-1.054	-2.429	-2.268	-1.889	-1.742	-1.780	-1.754
	30 min				0.622	0.423	0.173	-0.889	-2.491	-2.678	-2.359	-2.249	-2.154
	3 min			0.721	0.717	0.683	0.644	0.489	0.022	-1.014	-2.206	-2.802	-2.891
	0.5 min		-0.112	0.722	0.735	0.703	0.662	0.495	-0.029	-1.429	-3.527	-4.552	-4.552
	0 s	-0.305	-0.313	-0.061	0.041	0.027	-0.033	-0.273	-0.929	-2.834	-10.130	-66.397	-796.658
		0.5 min	3 min	30 min	1 h	2 h	3 h	6 h	12 h	1 d	2 d	4 d	7 d
		t_2											

Table 8S. Coefficient of determination (R^2) values for correlation between the relative ^{27}Al NMR peak area for the $\delta\text{-Al}_{30}$ polycation and the percentage of the aluminum fraction that reacted with ferron during the period from time t_1 to time t_2 . The R^2 values were determined from $1 - \text{SSreg}/\text{SS}_{\text{tot}}$, where SSreg is the sum of squares of the residuals around the regression line with an intercept of 0, and SS_{tot} is the sum of squares of the residuals around a horizontal line representing the mean absorbance value for this dataset (Motulsky and Christopoulos, 2004).

t_1	4 d												0.182
	2 d											-0.450	-0.163
	1 d										-0.002	-0.237	-0.112
	12 h									0.140	0.066	-0.120	-0.049
	6 h								-0.077	0.049	0.030	-0.115	-0.055
	3 h							-0.579	-0.244	-0.059	-0.040	-0.159	-0.096
	2 h						-2.096	-1.065	-0.458	-0.177	-0.118	-0.219	-0.147
	1 h					-2.441	-3.009	-2.819	-1.435	-0.678	-0.430	-0.458	-0.345
	30 min				-1.352	-1.779	-2.230	-3.432	-3.657	-2.230	-1.345	-1.113	-0.867
	3 min			-1.129	-1.207	-1.373	-1.537	-2.034	-2.998	-4.213	-4.523	-4.054	-3.400
	0.5 min		-1.536	-1.714	-1.718	-1.900	-2.104	-2.769	-4.246	-6.822	-8.536	-7.772	-6.367
	0 s	-0.666	-0.843	-1.973	-2.272	-2.581	-2.824	-3.552	-5.265	-9.662	-24.411	-127.027	-1322.281
		0.5 min	3 min	30 min	1 h	2 h	3 h	6 h	12 h	1 d	2 d	4 d	7 d
		t_2											

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