HOKKAIDO UNIVERSITY

Title	Characteristics and components of poly-aluminum chloride coagulants that enhance arsenate removal by coagulation: Detailed analysis of aluminum species
Author(s)	Matsui, Yoshihiko; Shirasaki, Nobutaka; Yamaguchi, Takuro et al.
Citation	Water Research, 118, 177-186 https://doi.org/10.1016/j.watres.2017.04.037
Issue Date	2017-07
Doc URL	https://hdl.handle.net/2115/74829
Rights	© 2017, Elsevier. Licensed under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International
Rights(URL)	https://creativecommons.org/licenses/by-nc-nd/4.0/
Type	journal article
File Information	Characteristics and Components of Poly-aluminum Chloride Coagulants.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Paper submitted to Water Research

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

Yoshihiko Matsui [a]*, Nobutaka Shirasaki [a], Takuro Yamaguchi [b], Kenta Kondo [b], Kaori Machida [b], Taiga Fukuura [b], and Taku Matsushita [a]

a Faculty of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan

b Graduate School of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan

* Corresponding author. Tel./fax: +81-11-706-7280

E-mail address: matsui@eng.hokudai.ac.jp

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 ($Al_{30min-3h}$) fraction, had the highest arsenate sorption capacity, followed by a colloidal aluminum fraction ($Al_{>3h}$, which reacted with ferron at a time of >3 h). The $Al_{30min-3h}$ fraction was stable, and its arsenate sorption capacity did not decrease markedly with increasing pH. The $Al_{30min-3h}$ fraction did not correspond to the Keggin-type e-Al_{13} polycation or the δ-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 $Al_{30min-3h}$ fraction should be used for enhanced arsenate removal by coagulation. A high content of the e-Al_{13} polycation or the δ-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 e-Al_{13} polycation (Keggin-type e-Al_{13} polycation, $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$) is the active species responsible for arsenate removal by aluminum coagulants and that the e-Al_{13} 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 e-Al_{13} 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-Al_{30} polycation (specifically, the Keggin-type δ-Al_{30} polycation, $[Al_{30}O_8(OH)_{56}(H_2O)_{24}]^{18+}$) have a higher removal efficiency than PACls with a low δ-Al_{30} polycation content. Finally, higher arsenate removal by PACl than by conventional coagulants may be attributed to the e-Al_{13} polycation, the δ-Al_{30} 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 e-Al_{13} polycation, the δ-Al_{30} 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 e-Al_{13} 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 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-Cl_2/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 (~20°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 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-μm 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-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-Al_{13} polycation. Hu et al. (2012)

did not use a PACl with a high Alc content. Therefore, the e-Al_{13} polycation may remove arsenate more effectively than monomeric aluminum species, but other species may also be effective for arsenate removal.

Sulfated PACls are widely used in practice, particularly for treatment of raw water with low turbidity and low NOM concentrations, because sulfate suppresses charge reversal and accelerates the kinetics of aluminum hydroxide precipitation (Amirtharaja and O'Melia 1990). We also visually observed that larger floc particles were formed by sulfated PACls than by nonsulfated PACls. The effects of sulfate ion can be seen in Figure 6S by comparing PACl-70st-1 and PACl-70-3-1. The arsenate removal percentages were the same at pH 6–7.5, but PACl-70st-1, which contained sulfate ion, showed somewhat higher arsenate removal at a pH of >8. A similar trend was observed for PACls of 50% basicity (Figure 8S). In water, sulfate ion has a negligible or deleterious effect on As(V) removal by ferric chloride coagulants (Hering et al. 1997, Jain et al. 2009, Meng et al. 2000, Qiao et al. 2012). The deleterious effect is due to competitive adsorption of the divalent sulfate ion and arsenate (the divalent ion $HAsO_4^{2-}$ is present at pH 7–11) (Wilkie and Hering 1996). Therefore, the higher arsenate removal by the sulfated PACls would be related to aluminum species distribution. Compared with nonsulfated PACls of the same basicity, the sulfated PACls were low in monomeric aluminum species, which is less effective for arsenate removal than the other aluminum species, as will be discussed next.

3.2. PACl characteristics that affect arsenate removal

Arsenate removal percentages were clearly different depending on PACls at alkaline pH. As described above, differences in the Alb content in PACls did not explain differences in arsenate 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:

$$As\ removed = Coagulant\ dose \times q_S \qquad (1)$$

where q_S (μg-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:

$$q_S = \sum q_i\, f_i \qquad (2)$$

where q_i is the arsenate sorption capacity of aluminum species i (μg-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

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

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

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

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 corelations. 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 $Al_{30min-3h}$ 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 $Al_{>3h}$ fraction was the second highest, and that of the $Al_{<30min}$ fraction was the lowest. The arsenate sorption capacities of $Al_{>3h}$ and $Al_{<30min}$ decreased with increasing coagulation pH. In particular, the sorption capacity of $Al_{<30min}$ decreased by about 1/3 from pH 7.5 to 8.5. $Al_{<30min}$ 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 $Al_{30min-3h}$ and $Al_{>3h}$. 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 $Al_{30min-3h}$ was stable and did not decrease appreciably with increasing pH. Overall, a higher

346 percentage of the $Al_{30min-3h}$ fraction is key to better arsenate removal because the species in
347 this fraction have higher arsenate sorption capacity than other Al species and are stable even
348 under alkaline conditions.
349
350 In the first set of coagulation experiments, the PACls that exhibited high arsenate removal
351 percentages were PACl-70-1-1 and PACl-90-1-1. In the second set of experiments, 80%-
352 basicity PACls such as PACl-80-1-2 exhibited high arsenate removal percentages (Tables 5S
353 and 6S). The high arsenate removal percentages by PACl-70-1-1, PACl-80-1-2, and PACl-80-
354 4-2 were due to the high content of $Al_{30min-3h}$. The value of $f_{30min-3h}$ for these PACls was
355 ~26% and was higher than the $f_{30min-3h}$ values for all the other PACls. In contrast, the high
356 removal percentages achieved with PACl-90-1-1, PACl-80-2-2, and PACl-80-3-2 were due to
357 the high content of $Al_{>3h}$ ($f_{>3h}$ > 37%) as well as to the moderate content of $Al_{30min-3h}$
358 ($f_{30min-3h}$ > 18%). The high arsenate removal percentages achieved with PACl-80st-2 and
359 PACl-83t-2 were due mainly to the high content of $Al_{>3h}$ ($f_{>3h}$ > 82%), but the contribution of
360 $Al_{30min-3h}$ ($f_{30min-3h}$ ≈ 5%) was non-negligible. Therefore, there are two approaches for
361 developing PACls that exhibit high arsenate removal: one is to increase the percentage of the
362 $Al_{30min-3h}$, and the other is to increase the percentage of the $Al_{>3h}$ to at least approximately
363 80%. The percentage of the $Al_{30min-3h}$ in commercially available and commonly used PACls
364 (PACl-50st and PACl-70st) is low, 10% at most. PACl-70st showed better removal than PACl-
365 50st, and the difference was due to the moderately high content of $Al_{>3h}$.
366
367 ***3.3.3. Aluminum species by NMR analysis***
368
369 The $Al_{30min-3h}$ fraction includes a portion of Alb and a portion of Alc. The e-Al_{13} polycation is
370 treated as being equivalent to Alb, and Alc includes the δ-Al_{30} polycation (Chen et al. 2007,

371 Parker and Bertsch 1992). Therefore, the high arsenate sorption capacity of $Al_{30min-3h}$ might
372 have been related to the e-Al_{13} polycation, the δ-Al_{30} polycation, or both. We evaluated the areas
373 of the e-Al_{13} and δ-Al_{30} polycation peaks in the NMR spectra, and correlate the areas with the
374 percentages of aluminum fractions determined by means of ferron analysis.
375
376 There was a strong correlation between the peak area of the e-Al_{13} polycation and the percentage
377 of Alb ($Al_{0.5min-2h}$) (R^2 = 0.703, Table 7S), which is in agreement with previous observations
378 (Parker and Bertsch 1992, Sposito 1995). However, when the aluminum was separated at
379 different ferron reaction cut-off times, the highest correlation was observed for the percentage of
380 $Al_{0.5min-1h}$ (R^2 = 0.735, Figure 11S, Table 7S), followed by the percentages of $Al_{0.5-30min}$ (R^2
381 = 0.722), $Al_{3-30min}$ (R^2 = 0.721), and $Al_{3\ min-1h}$ (R^2 = 0.717). The $Al_{0.5-30min}$, $Al_{3-30min}$, and
382 $Al_{3min-1h}$ fractions are subfractions of the $Al_{0.5min-1h}$ fraction. Therefore, the data indicate that
383 the e-Al_{13} polycation corresponds more closely to the $Al_{0.5min-1h}$ fraction than to the $Al_{0.5min-2h}$
384 fraction in the ferron protocol that we employed. This result is in accordance with the result of
385 Bertsch et al. (1986), who partitioned Alb into a rapidly reacting fraction (≤1 h) and a slowly
386 reacting fraction (>1 h) and reported that the rapidly reacting fraction corresponded to the amount
387 of Al_{13} polymers as determined by NMR spectroscopy.
388
389 More important is that $Al_{0.5min-1h}$ was close to and partially overlapping with $Al_{30min-3h}$,
390 which was the fraction with the highest arsenate sorption capacity. The correlation between the
391 percentage of the $Al_{30min-3h}$ fraction and the e-Al_{13} polycation peak area was low (R^2 = 0.173,
392 Figure 12S, Table 8S). These results suggest that the e-Al_{13} polycation may be active for arsenate
393 removal but that it is not the most active substance in PACl. To verify this possibility, we
394 compared the arsenate removal percentages of two selected PACls: one PACl (PACl-80-1-3)
395 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-Al_{13} polycation (by NMR), as shown in the uppermost panels of Figure 3. Despite the difference in the amounts of the e-Al_{13} 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-Al_{13} polycation was not indispensable for high arsenate removal, although it was one of the active substances.

Next we focused on the δ-Al_{30} polycation. The NMR signals corresponding to the δ-Al_{30} polycation were not sharp but rather were broad, low humps, as previously reported (Allouche et al. 2000). The areas of the δ-Al_{30} 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-Al_{30} 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-Al_{30} 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-Al_{30} 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-Al_{30} polycation, whereas the other (PACl-90-1-3) did not have the δ-Al_{30} 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-Al_{30} polycation in PACls was not a strongly active species for arsenate removal.

Some recent studies have suggested that polymeric aluminum species (e-Al_{13} and δ-Al_{30}

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

(3) Neither the e-Al_{13} polycation nor the δ-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 $Al_{30min-3h}$ fraction (26%) or those in which the proportion of the $Al_{>3h}$ fraction was >80%. The percentages of $Al_{30min-3h}$ 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.

Acknowledgements

This study was supported by Grants-in-Aid for Scientific Research S (24226012 and 16H06362) from the Japan Society for the Promotion of Science and a by Health and Labour Sciences Research Grant (Research on Health Security Control) of Japan.

Appendix. Supplementary Information

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

References

Allouche, L., Gérardin, C., Loiseau, T., Férey, G. and Taulelle, F. (2000) Al30: A Giant Aluminum Polycation. Angewandte Chemie International Edition 39(3), 511-514.

Amirtharaja, A. and O'Melia, C.R. (1990) Water Quality & Treatment 4th ed. Pontius, F.W. (ed), McGraw-Hill.

Balasubramanian, N., Kojima, T., Basha, C.A. and Srinivasakannan, C. (2009) Removal of arsenic from aqueous solution using electrocoagulation. Journal of Hazardous Materials 167(1-3), 966-969.

Balasubramanian, N. and Madhavan, K. (2001) Arsenic removal from industrial effluent through electrocoagulation. Chemical Engineering & Technology 24(5), 519-521.

Baskan, M.B. and Pala, A. (2009) Determination of arsenic removal efficiency by ferric ions

using response surface methodology. Journal of Hazardous Materials 166(2-3), 796-801.
Batchelor, B., McEwen, J.B. and Perry, R. (1986) Kinetics of aluminum hydrolysis: measurement and characterization of reaction products. Environmental Science & Technology 20(9), 891-894.
Bersillon, J.L., Hsu, P.H. and Fiessinger, F. (1980) Characterization of Hydroxy-Aluminum Solutions1. Soil Sci. Soc. Am. J. 44(3), 630-634.
Bertsch, P.M., Layton, W.J. and Barnhisel, R.I. (1986) Speciation of Hydroxy-Aluminum Solutions by Wet Chemical and Aluminum-27 NMR Methods1. Soil Science Society of America Journal 50(6), 1449-1454.
Bilici Baskan, M. and Pala, A. (2010) A statistical experiment design approach for arsenic removal by coagulation process using aluminum sulfate. Desalination 254(1–3), 42-48.
Casey, W.H., Phillips, B.L. and Furrer, G. (2001) Aqueous aluminum polynuclear complexes and nanoclusters: A review. Nanoparticles and the Environment 44, 167-190.
Chen, A.S.C., Fields, K.A., Sorg, T.J. and Wang, L.L. (2002) Field evaluation of As removal by conventional plants. Journal American Water Works Association 94(9), 64-77.
Chen, Z., Fan, B., Peng, X., Zhang, Z., Fan, J. and 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. and 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.
Cheng, R.C., Wang, H.C. and Beuhler, M.D. (1994) Enhanced coagulation for arsenic removal. Journal American Water Works Association 86(9), 79-90.
Choong, T.S.Y., Chuah, T.G., Robiah, Y., Gregory Koay, F.L. and Azni, I. (2007) Arsenic

toxicity, health hazards and removal techniques from water: an overview. Desalination 217(1–3), 139-166.

Edwards, M. (1994) CHEMISTRY OF ARSENIC REMOVAL DURING COAGULATION AND FE-MN OXIDATION. Journal American Water Works Association 86(9), 64-78.

Fan, M.H., Brown, R.C., Sung, S.W., Huang, C.P., Ong, S.K. and van Leeuwen, J. (2003) Comparisons of polymeric and conventional coagulants in arsenic(V) removal. Water Environment Research 75(4), 308-313.

Gao, B.-Y., Chu, Y.-B., Yue, Q.-Y., Wang, B.-J. and Wang, S.-G. (2005) Characterization and coagulation of a polyaluminum chloride (PAC) coagulant with high Al13 content. J Environ Manage 76(2), 143-147.

Ghurye, G. and Clifford, D. (2004) As(III) oxidation using chemical and solid-phase oxidants. Journal American Water Works Association 96(1), 84-96.

Gregor, J. (2001) Arsenic removal during conventional aluminium-based drinking-water treatment. Water Research 35(7), 1659-1664.

Hering, J.G., Chen, P.Y., Wilkie, J.A. and Elimelech, M. (1997) Arsenic removal from drinking water during coagulation. Journal of Environmental Engineering-Asce 123(8), 800-807.

Hu, C., Liu, H., Chen, G. and Qu, J. (2012) Effect of aluminum speciation on arsenic removal during coagulation process. Separation and Purification Technology 86, 35-40.

Jain, A., Sharma, V.K. and Mbuya, O.S. (2009) Removal of arsenite by Fe(VI), Fe(VI)/Fe(III), and Fe(VI)/Al(III) salts: effect of pH and anions. J Hazard Mater 169(1-3), 339-344.

Jia, He, F. and Liu (2004) Synthesis of Polyaluminum Chloride with a Membrane Reactor: Operating Parameter Effects and Reaction Pathways. Industrial & Engineering Chemistry Research 43(1), 12-17.

Kartinen, E.O. and Martin, C.J. (1995) An overview of arsenic removal processes. Desalination

547 103(1-2), 79-88.
548 Kimura, M., Matsui, Y., Kondo, K., Ishikawa, T.B., Matsushita, T. and Shirasaki, N. (2013)
549 Minimizing residual aluminum concentration in treated water by tailoring properties of
550 polyaluminum coagulants. Water Research 47(6), 2075-2084.
551 Lacasa, E., Saez, C., Canizares, P., Fernandez, F.J. and Rodrigo, M.A. (2013) Arsenic Removal
552 from High-Arsenic Water Sources by Coagulation and Electrocoagulation. Separation Science
553 and Technology 48(3), 508-514.
554 Lakshmanan, D., Clifford, D. and Samanta, G. (2008) Arsenic removal by coagulation - With
555 aluminum, iron, titanium, and zirconium. Journal American Water Works Association 100(2),
556 76-+.
557 Lakshmanan, D., Clifford, D.A. and Samanta, G. (2010) Comparative study of arsenic removal
558 by iron using electrocoagulation and chemical coagulation. Water Research 44(19), 5641-5652.
559 Letterman, R.D. (2011) Water Quality & Treatment: A Handbook on Drinking Water, Sixth
560 Edition. American Water Works, A. and James, E. (eds), McGraw Hill Professional, Access
561 Engineering.
562 Lin, J.L., Huang, C., Pan, J.R. and Wang, D. (2008) Effect of Al(III) speciation on coagulation
563 of highly turbid water. Chemosphere 72(2), 189-196.
564 McNeill, L.S. and Edwards, M. (1995) Soluble arsenic removal at water treatment plants.
565 Journal American Water Works Association 87(4), 105-113.
566 McNeill, L.S. and Edwards, M. (1997) Predicting as removal during metal hydroxide
567 precipitation. Journal American Water Works Association 89(1), 75-86.
568 Meng, X., Bang, S. and Korfiatis, G.P. (2000) Effects of silicate, sulfate, and carbonate on
569 arsenic removal by ferric chloride. Water Research 34(4), 1255-1261.
570 Mertens, J., Casentini, B., Masion, A., Pöthig, R., Wehrli, B. and Furrer, G. (2012)
571 Polyaluminum chloride with high Al30 content as removal agent for arsenic-contaminated well

572 water. Water Research 46(1), 53-62.
573 Mertens, J., Rose, J., Wehrli, B. and Furrer, G. (2016) Arsenate uptake by Al nanoclusters and
574 other Al-based sorbents during water treatment. Water Research 88, 844-851.
575 Pallier, V., Feuillade-Cathalifaud, G., Serpaud, B. and Bollinger, J.-C. (2010) Effect of organic
576 matter on arsenic removal during coagulation/flocculation treatment. Journal of Colloid and
577 Interface Science 342(1), 26-32.
578 Parker, D.R. and Bertsch, P.M. (1992) Identification and quantification of the "Al13"
579 tridecameric aluminum polycation using ferron. Environmental Science & Technology 26(5),
580 908-914.
581 Qiao, J., Jiang, Z., Sun, B., Sun, Y., Wang, Q. and Guan, X. (2012) Arsenate and arsenite
582 removal by FeCl3: Effects of pH, As/Fe ratio, initial As concentration and co-existing solutes.
583 Separation and Purification Technology 92(0), 106-114.
584 Ratna Kumar, P., Chaudhari, S., Khilar, K.C. and Mahajan, S.P. (2004) Removal of arsenic
585 from water by electrocoagulation. Chemosphere 55(9), 1245-1252.
586 Scott, K.N., Green, J.F., Do, H.D. and McLean, S.J. (1995) Arsenic Removal by Coagulation.
587 Journal American Water Works Association 87(4), 114-126.
588 Sposito, G. (1995) The Environmental Chemistry of Aluminum, Second Edition, Taylor &
589 Francis.
590 Wang, D., Sun, W., Xu, Y., Tang, H. and Gregory, J. (2004) Speciation stability of inorganic
591 polymer flocculant–PACl. Colloids and Surfaces A: Physicochemical and Engineering Aspects
592 243(1-3), 1-10.
593 Wang, W.Z. and Hsu, P.H. (1994) The nature of polynuclear OH-AL complexes in laboratory-
594 hydrolyzed and commercial hydroxyaluminum solutions. Clays and Clay Minerals 42(3), 356-
595 368.
596 Wilkie, J.A. and Hering, J.G. (1996) Adsorption of arsenic onto hydrous ferric oxide: effects of

adsorbate/adsorbent ratios and co-occurring solutes. Colloids and Surfaces A: Physicochemical and Engineering Aspects 107(0), 97-110.

Yan, M., Wang, D., Qu, J., He, W. and Chow, C.W. (2007) Relative importance of hydrolyzed Al(III) species (Al(a), Al(b), and Al(c)) during coagulation with polyaluminum chloride: a case study with the typical micro-polluted source waters. J Colloid Interface Sci 316(2), 482-489.

Yan, M., Wang, D., Yu, J., Ni, J., Edwards, M. and Qu, J. (2008) Enhanced coagulation with polyaluminum chlorides: Role of pH/Alkalinity and speciation. Chemosphere 71(9), 1665-1673.

Zhang, G., Li, X., Wu, S. and Gu, P. (2012) Effect of source water quality on arsenic (V) removal from drinking water by coagulation/microfiltration. Environmental Earth Sciences 66(4), 1269-1277.

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

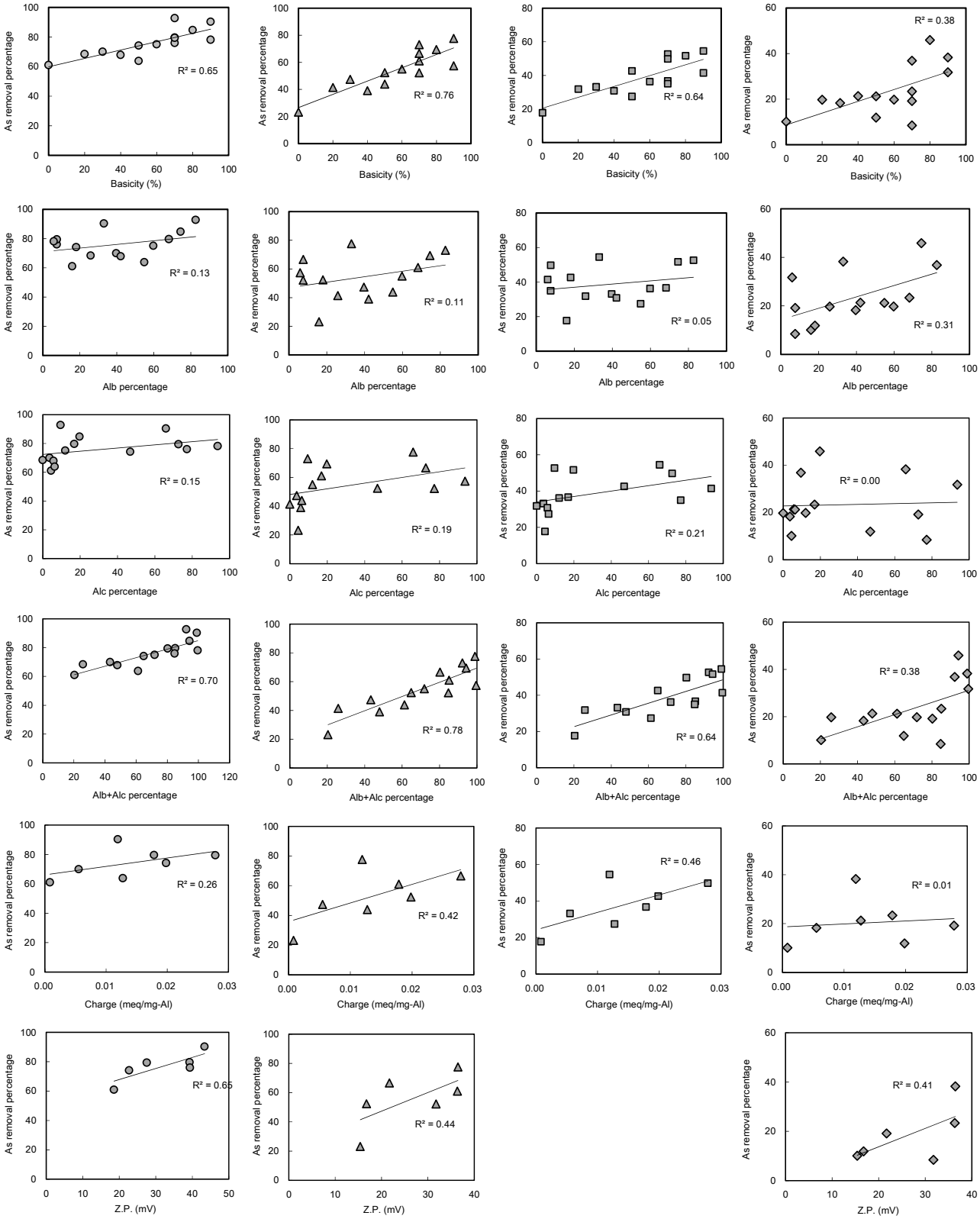


Figure 1. Plots of arsenate removal percentage against PACl's basicity, colloid charge, zeta potential, Alb content, Alc content, and Alb+Alc content (the leftmost, second, and third left panels are of coagulation pH 7.5, 8.0, and 8.5, respectively, using T1 water with the initial As concentration 15.8 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).

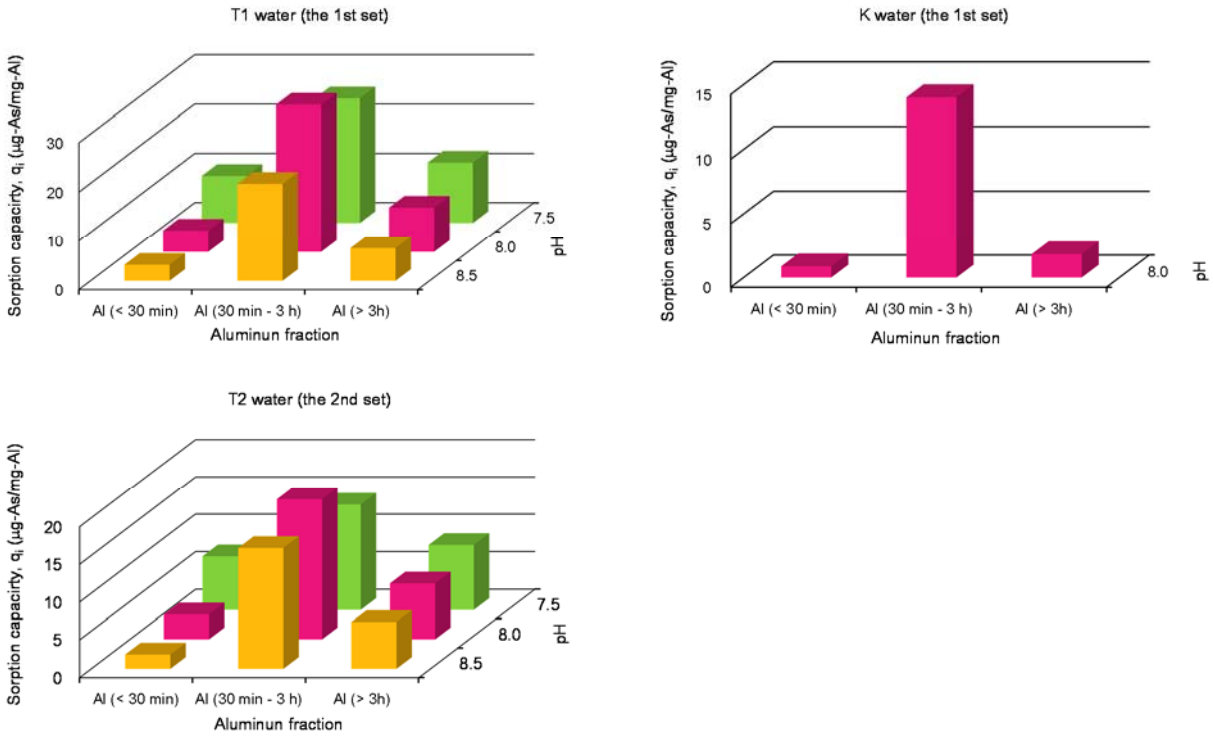


Figure 2. Arsenate sorption capacities of aluminum fractions

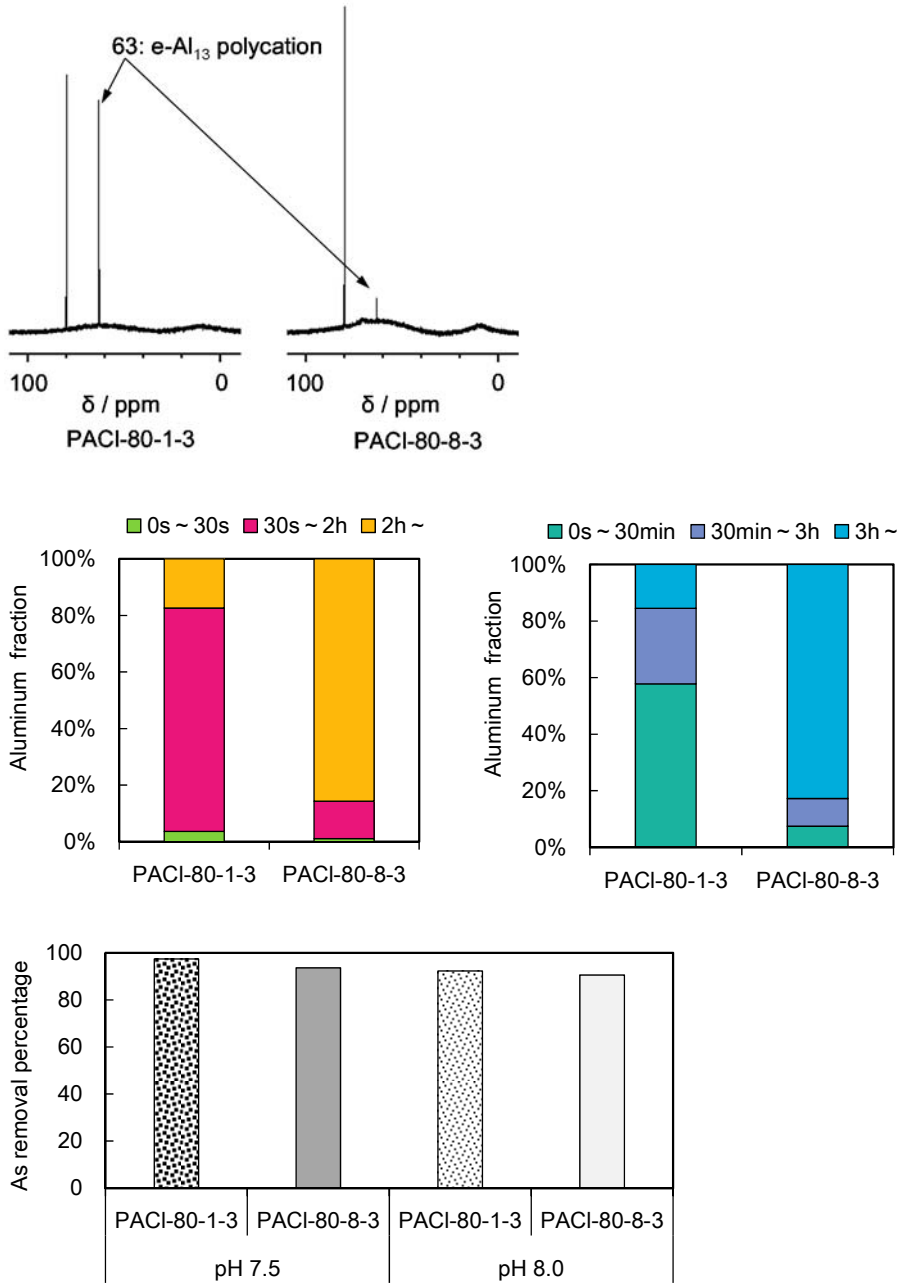
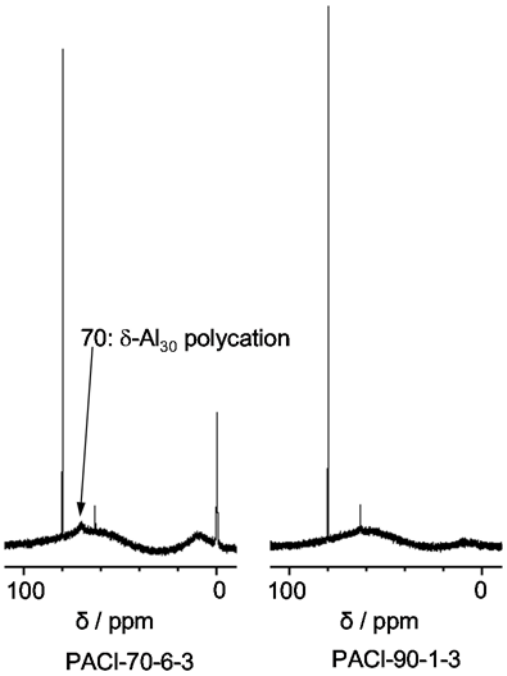
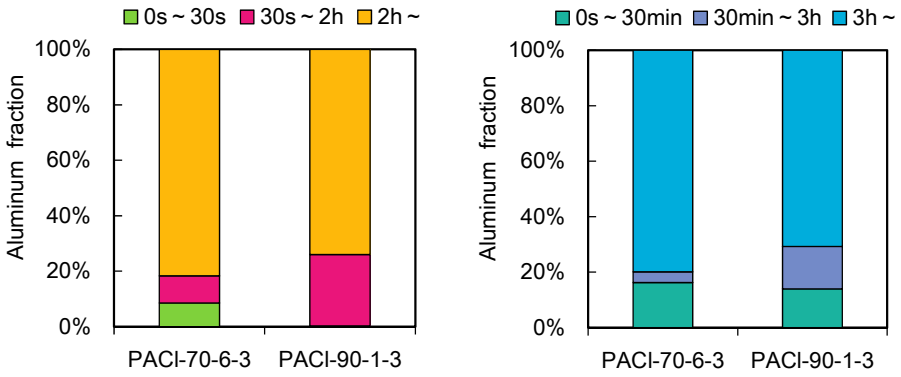


Figure 3. Comparison of NMR spectra, Al fractions, and arsenate removals by using two coagulants (TM water was used for the coagulation experiment. Coagulant dose was 2.1 mg-Al/L)





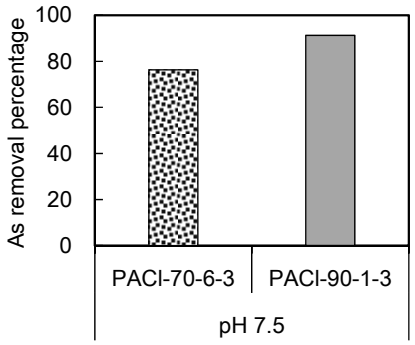


Figure 4. Comparison of NMR spectra, Al fractions, and arsenate removals by using two coagulants (TM water was used for the coagulation experiment. Coagulant dose was 2.1 mg-Al/L).

Supplementary Material

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

Yoshihiko Matsui [a]*, Nobutaka Shirasaki [a], Takuro Yamaguchi [b], Kenta Kondo [b], Kaori Machida [b], Taiga Fukuura [b], and Taku Matsushita [a]

a Faculty of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan
b Graduate School of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan

* Corresponding author. Tel./fax: +81-11-706-7280
E-mail address: matsui@eng.hokudai.ac.jp

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 $Al(OH)_3$ 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 $AlCl_3 \cdot 6H_2O$ (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 AlCl3 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 $Al(OH)_3$ (Wako) in HCl solution at 165 °C ("h" indicates $Al(OH)_3$ 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 e-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 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.

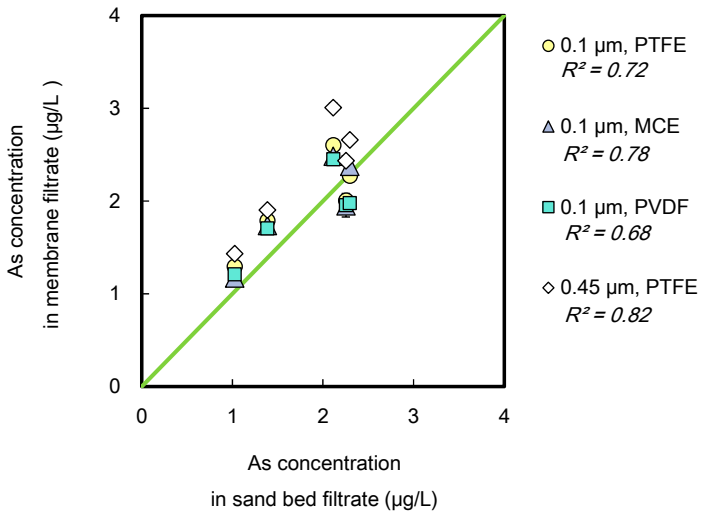


Figure 1S. Correlation between As concentrations in filtrates from membrane microfiltration and sand bed filtration [Moiwa Water Treatment Plant, raw water total organic carbon = 1.1–1.5 mg/L, coagulant dose = 1.2–3.4 mg-Al/L, pH 7.3–7.5, water temperature = 7–12 °C, PTFE: Polytetrafluoroethylene, MCE: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

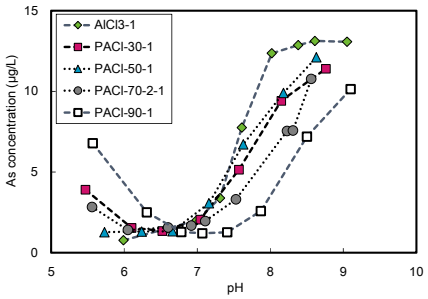


Figure 2S. As concentration after coagulation, settling, and microfiltration for five PACls (T1 water [see water designations in Table 4S], initial As concentration = 15.8 µg/L, coagulant dose = 0.98 mg-Al/L).

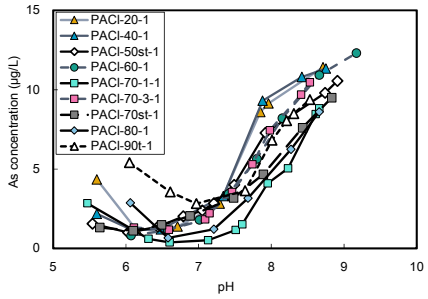


Figure 3S. As concentration after coagulation, settling, and microfiltration for nine PACls (T1 water [see water designations in Table 4S], initial As concentration = 15.8 µg/L, coagulant dose = 0.98 mg-Al/L)

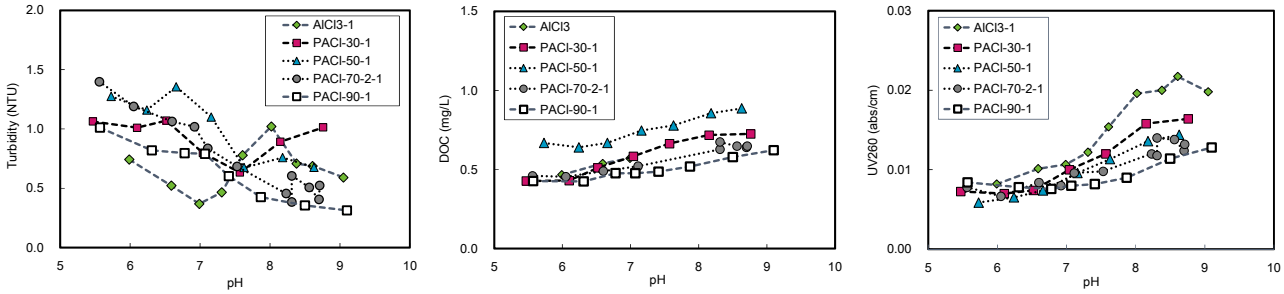


Figure 4S. Residual turbidity, dissolved organic carbon (DOC), and ultraviolet absorbance (260 nm) observed after coagulation and settling under experimental conditions matching those described for Figure 2S.

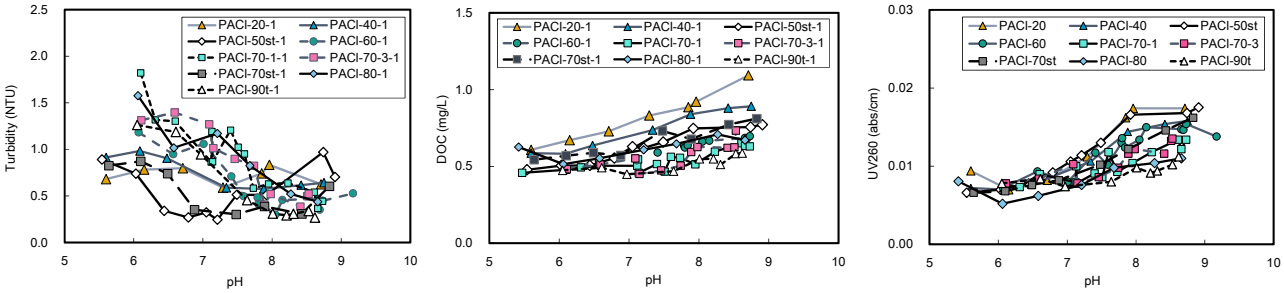


Figure 5S. Residual turbidity, dissolved organic carbon (DOC), and ultraviolet absorbance (260 nm) observed after coagulation and settling under experimental conditions matching those described for Figure 3S.

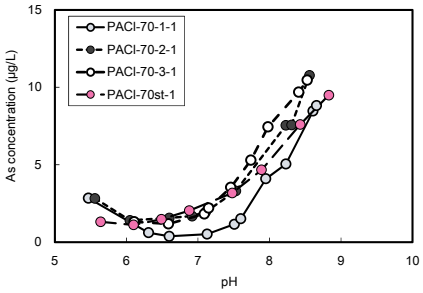


Figure 6S. As concentration after coagulation, settling, and microfiltration for 70%-basicity PACls (T1 water [see designations in Table 4S], initial As concentration = 15.8 µg/L, coagulant dose = 0.98 mg-Al/L).

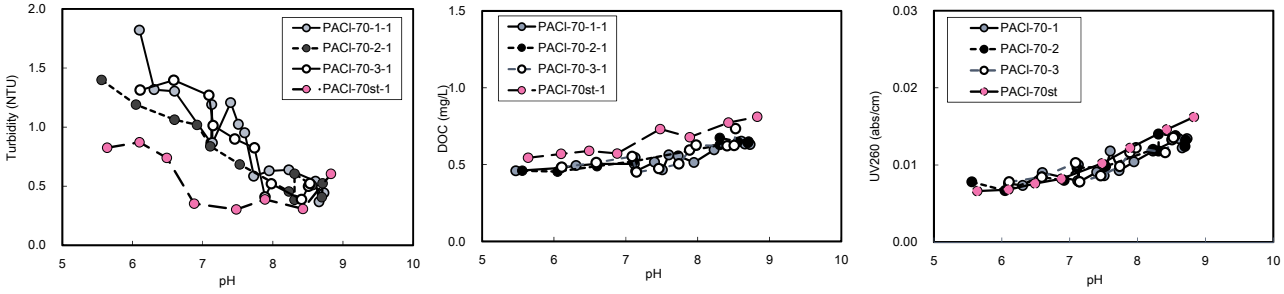


Figure 7S. Residual turbidity, dissolved organic carbon (DOC), and ultraviolet absorbance (260 nm) observed after coagulation and settling under experimental conditions matching those described for Figure 6S.

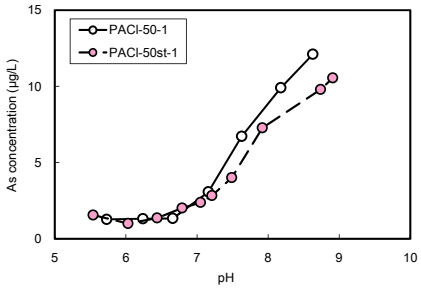


Figure 8S. As concentration after coagulation, settling, and microfiltration for 50%-basicity PACls (T1 water [see designations in Table 4S], initial As concentration = 15.8 µg/L, coagulant dose = 0.98 mg-Al/L).

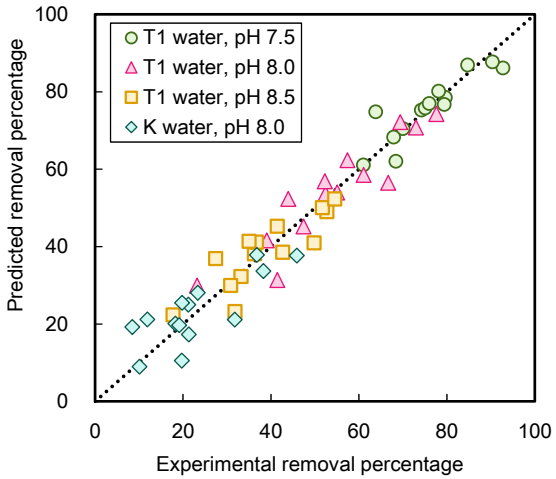


Figure 9S. Correlation between arsenate removal percentages obtained by experiments and predicted by regression analysis model S1-36.

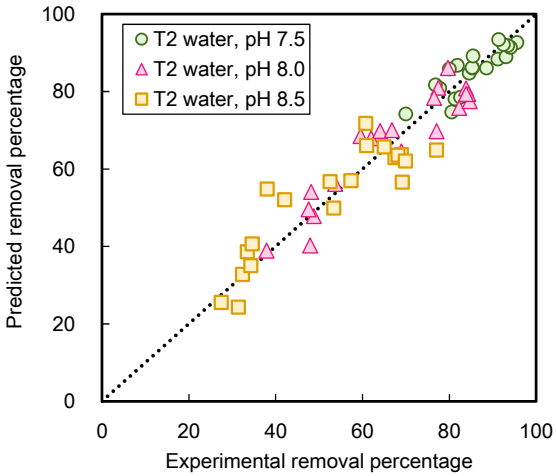


Figure 10S. Correlation between arsenate removal percentages obtained by experiments and predicted by regression analysis model S2-36.

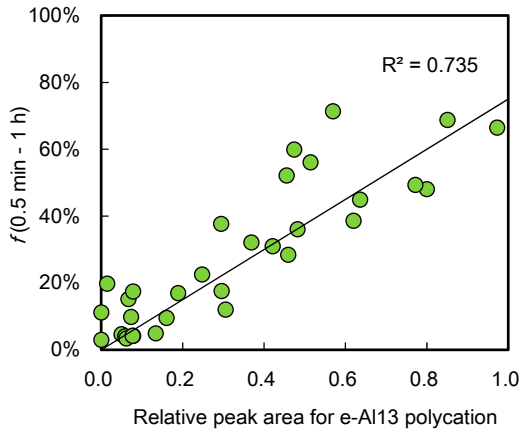


Figure 11S. Correlation between the relative ^{27}Al NMR peak area for the e-Al_{13} polycation (the peak areas are relative to the area for an internal standard) and $f_{0.5\mathrm{min}-1\mathrm{h}}$ (the percentage of $Al_{0.5\mathrm{min}-1\mathrm{h}}$ fraction, that is, the fraction that reacted with ferron during the period from 0.5 min to 1 h). The R^2 values were determined from 1 – SSreg/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).

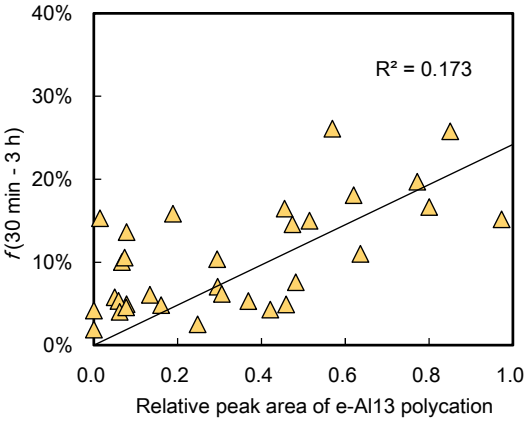


Figure 12S. Correlation between the relative ^{27}Al NMR peak area for the e-Al_{13} polycation (the peak areas are relative to the area for an internal standard) and $f_{30\mathrm{min}-3\mathrm{h}}$ (the percentage of $Al_{30\mathrm{min}-3\mathrm{h}}$ fraction, that is, the fraction that reacted with ferron during the period from 30 min to 3 h). The R^2 values were determined from 1 – SSreg/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).

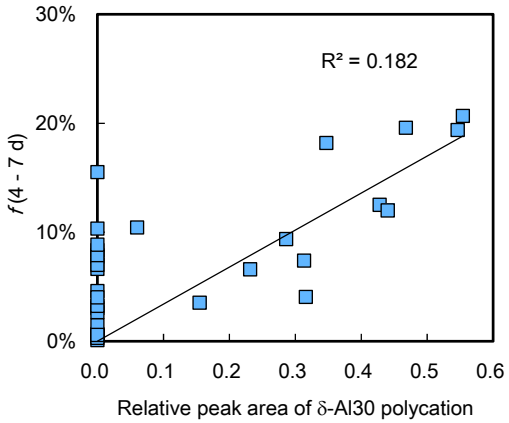


Figure 13S. Correlation between the relative ^{27}Al NMR peak area for the δ-Al_{30} polycation (the peak areas are relative to the area for an internal standard) and $f_{4-7\mathrm{d}}$ (the percentage of $Al_{4-7\mathrm{d}}$ fraction, that is, the fraction that reacted with ferron during the period from 4 to 7 days). The R^2 values were determined from 1 – SSreg/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).

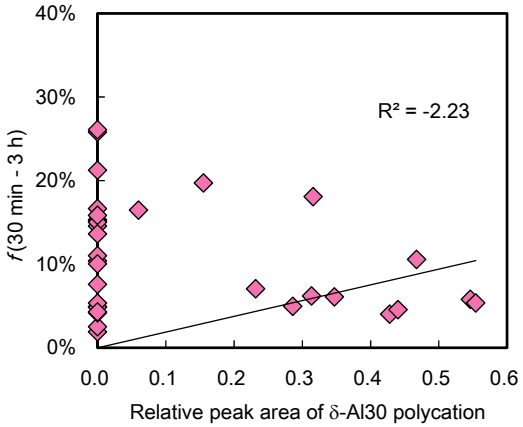


Figure 14S. Correlation between the relative ^{27}Al NMR peak area for the δ-Al_{30} polycation (the peak areas are relative to the area for an internal standard) and $f_{30\mathrm{min}-3\mathrm{h}}$ (the percentage of $Al_{30\mathrm{min}-3\mathrm{h}}$ fraction, that is, the fraction that reacted with ferron during the period from 30 min to 3 h). The R^2 values were determined from 1 – SSreg/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_2O_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_2O_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_2O_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 ^{27}Al 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 (Sievers 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)	$f_{<30\text{min}}$	$f_{30\text{min}-3h}$	$f_{>3\text{h}}$
$AlCl_3$-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 – SSreg/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 δ-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 – SSreg/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												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											

References

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, 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, 110-118.

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, 143-147.

Hydes, D.J., Liss, P.S., 1977. The behaviour of dissolved aluminium in estuarine and coastal waters. Estuarine and Coastal Marine Science 5, 755-769.

Itoh, Y., Sato, K., 1995. Production of Sulfate-containing Basic Al Chloride. in: Office, J.P. (Ed.), Japan.

Jia, He, F., Liu, 2004. Synthesis of Polyaluminum Chloride with a Membrane Reactor: Operating Parameter Effects and Reaction Pathways. Industrial & Engineering Chemistry

Research 43, 12-17.

Kennedy, V.C., Zellweger, G.W., Jones, B.F., 1974. Filter pore-size effects on the analysis of Al, Fe, Mn, and Ti in water. Water Resources Research 10, 785-790.

Kimura, M., Matsui, Y., Kondo, K., Ishikawa, T.B., Matsushita, T., Shirasaki, N., 2013. Minimizing residual aluminum concentration in treated water by tailoring properties of polyaluminum coagulants. Water Res 47, 2075-2084.

Matsui, Y., Ishikawa, T.B., Kimura, M., Machida, K., Shirasaki, N., Matsushita, T., 2013. Aluminum concentrations of sand filter and polymeric membrane filtrates: a comparative study. Separation and Purification Technology 119, 58-65.

Motulsky, H., Christopoulos, A., 2004. Fitting Models to Biological Data Using Linear and Nonlinear Regression: A Practical Guide to Curve Fitting. Oxford University Press.

Sato, F., Matsuda, S., 2009. Novel basic aluminum chloride, its manufacturing method and its application. in: Office, J.P. (Ed.), Japan.

Shafran, K.L., Perry, C.C., 2005. A systematic investigation of aluminium ion speciation at high temperature. Part 1. Solution studies. Dalton transactions, 2098-2105.

Shen, Y.H., Dempsey, B.A., 1998. Synthesis and speciation of polyaluminum chloride for water treatment. Environment International 24, 899-910.

Wagemann, R., Brunskill, G.J., 1975. The Effect of Filter Pore-Size on Analytical Concentrations of Some Trace Elements in Filtrates of Natural Water. International Journal of Environmental Analytical Chemistry 4, 75-84.

Wang, D., Sun, W., Xu, Y., Tang, H., Gregory, J., 2004. Speciation stability of inorganic polymer flocculant–PACl. Colloids and Surfaces A: Physicochemical and Engineering Aspects 243, 1-10.

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 Res 42, 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, 1665-1673.