

Modified ferron assay for speciation characterization of hydrolyzed Al(III): a precise k value based judgment

Ye Changqing, Wang Dongsheng, Wu Xiaohong, Qu Jiuwei and John Gregory

ABSTRACT

The speciation of Al-OH complexes in terms of Al_a , Al_b and Al_c could be achieved by traditional ferron assay and Al_b is generally considered as Al_{13} , however, the inherent correlation between them remains an enigma. This paper presents a modified ferron assay to get precise determination of Al_{13} using nonlinear least squares analysis, and to clarify the correlation between Al_b and Al_{13} . Two parallel reactions conforming to pseudo-first-order kinetics can simulate the complicate reactions between polynuclear complexes and ferron successfully. Four types of experimental kinetic constant (k value) of Al-OH complexes can be observed by this method when investigating three typical aluminium solutions. Comparing with the results of ^{27}Al NMR, the species with moderate kinetics around 0.001 s^{-1} can be confirmed to resemble to Al_{13} polycation. The other types of kinetics are also well-regulated in partially neutralized aluminium solutions with various OH/Al ratios (b values) in the range $0 \sim 2.5$. It would provide potential means to trace the in-situ formation of Al_{13} in dilute solutions such as coagulation with Al-based coagulants

Key words | Al_{13} , coagulation, ferron assay, hydrolyzed Al(III), speciation characterization

Ye Changqing

Yantai Institute of Coastal Zone Research for Sustainable Development, Chinese Academy of Sciences, Yantai 264003, China
E-mail: cqye@yic.ac.cn

Ye Changqing Wang Dongsheng Wu Xiaohong Qu Jiuwei

State Key Lab of Environmental Aquatic Chemistry, RCEES, Chinese Academy of Sciences, Beijing 100085, China
E-mail: wgds@rcees.ac.cn;
wu_sherry@126.com;
jqqu@rcees.ac.cn

John Gregory

Department of Civil and Environmental Engineering, University of College London, WC1E 6BT London, UK

INTRODUCTION

Alum and polyaluminium chloride (PACl) are widely used as coagulants (Wang *et al.* 2002; Jiménez *et al.* 2007; Li *et al.* 2008). The tridecameric Al polycation, $Al_{13}(O_4)(OH)_{24}^{7+}$ known as Al_{13} , is suggested to be the dominant species in PACls and plays a crucial role in coagulation (Bottero *et al.* 1980; Hu *et al.* 2006; Ye *et al.* 2007). Al_{13} is also applied in catalyst, ceramics, pharmaceutical and cosmetic products (Bertsch 1989a). With the wide application of aluminium salts and possible mobilization of soil Al by acid deposition, there arise an impetus for discerning the basic relationships between Al speciation and biological responses (Tang *et al.* 2004).

It is more generally accepted that polynuclear Al-OH complexes are metastable intermediate in the precipitation of $Al(OH)_3$. However, the structures of those intermediate species have not been well identified, and disparate models

of core-links and cage-like are proposed to interpret the hydrolysis of Al(III) (Bi *et al.* 2004). Generally, in the core-links model various possible species are proposed to be formed continuously (Bersillon *et al.* 1980), whereas in the cage-like model the polymers are deemed to distribute not in a row, but in a combination with a minimum of species, such as dimer $Al_2(OH)_2^{4+}$, trimer $Al_3(OH)_4^{5+}$, Al_{13} and Al_{30} in the hydrolysis process (Bottero *et al.* 1980). The latter model is more popular among environmental researchers since those limited polymers, especially the tridecamer (Al_{13}) and Al_{30} , can be characterized by ^{27}Al NMR (Bottero *et al.* 1987; Allouche & Taulelle 2003; Shafran *et al.* 2004). There are various well defined empirical techniques that can assist in providing reasonable estimates of the distribution of Al species (Parker & Bertsch 1992; Clarke *et al.* 1996). Most are not suitable for analysis of short-lived reaction products,

because they require too much time for sample preparation or analysis. Perhaps more common method is the timed spectrophotometric technique originally developed for quantitative analysis of Al. The timed colorimetric procedure can be started within several seconds of sampling and is suitable to analyze the metastable intermediate products that will change to other forms in minutes during the hydrolysis.

The timed colorimetric is established based on different reaction rates between various hydrolyzed Al(III) species and colorimetric reagent. Different dissolution rates may arise from differences in the nature and size of the species. The most commonly used colorimetric reagent is ferron (8-hydroxy-7-iodo-5-quinoline-sulfonic acid). Al speciation in partially neutralized solutions can be achieved according to the different reaction kinetics with ferron. However, due to the absence of accurate reaction kinetic data, the traditional classification is operationally separated into three fractions: (i) the mononuclear Al, defined as Al_a ; (ii) the reactive polynuclear Al, defined as Al_b ; and (iii) the inert or colloidal Al, defined as Al_c , the difference between the total Al content (Al_T) and $Al_a + Al_b$. Al_a is labile due to the random cut-off time in the range 30–90 s (Bersillon *et al.* 1980; Parker & Bertsch 1992) selected to determine this fraction. Al_b is experientially deemed as Al_{13} . Batchelor *et al.* (1986) have defined four types of aluminium species (instantaneously, rapidly, moderately, and slowly dissolving aluminium) from timed colorimetric experiments. Duffy & van Loon (1994) have characterized the amorphous aluminium hydroxide by the ferron method. Bersillon *et al.* (1980) have combined sulfate precipitation, resin treatment, and ferron method to group the soluble Al species into at least four categories. Despite the ubiquity of these operational speciation methods, the polynuclear Al species mentioned above are mostly determined from the cutoff time but not based on the kinetic constants. The polynuclear Al fraction exhibiting a moderate reaction rate with ferron are suggested to be Al_{13} (Bottero *et al.* 1980; Bertsch *et al.* 1986). Parker & Bertsch (1992) have concluded that the apparent rate constant of Al_b reaction with ferron is diagnostic for Al_{13} and suggested that the ferron method could be used to quantify Al_{13} at concentrations below practical detection limits of ^{27}Al NMR.

However, there are scarce consistent and reliable rate constants used for Al speciation due to the presence of

various polynuclear Al complexes with unclear structures, the composition of ferron work solution and the absence of analysis standard of kinetics model (Bertsch 1989b; Parker & Bertsch 1992). When buffered with NaOAc and $NH_2OH \cdot HCl$ with constant pH value of 5.2–5.4 and aged for 5 days, the ferron work solution remains stable within 25 days and exhibits consistent kinetic reactions (Jardine & Zelazny 1986; Wang *et al.* 2004). The reaction of polynuclear hydroxy-Al with ferron is deemed to conform to pseudo first-order kinetics (Bersillon *et al.* 1980; Parker & Bertsch 1992). With complicated and stepwise treatment of experimental data, Jardine & Zelazny (1986) have employed two simultaneous first-order reactions to quantify mononuclear Al, and thus arbitrary cutoff times is avoided. They later use two simultaneous pseudo second-order reactions to described mixed monomer-polymer solutions during the first 250 s (Jardine & Zelazny 1987). In fact, the reaction time is so short that the insightful information concerning polynuclear Al species would be masked. Another nonlinear congress analyses has been used elsewhere (Batchelor *et al.* 1986), but the rate constants are not regulated due to the same reason. It has been reported that consistent rate of Al_b (or Al_{13}) could be obtained using linearized first-order model (Parker & Bertsch 1992), where the selection and separation of ferron- Al_b reaction is required for the extrapolative quantification of Al_{13} , which is a pivotal and arduous work due to the easy overlapping of the parallel reactions.

Considering the increasing interests on Al phytotoxicity and PACl application, a convenient method for more precise speciation is basically required. The objectives of this research are (i) to evaluate the kinetics of the reactions between the ferron reagent and polynuclear Al using purified Al_{13} polycation, (ii) to investigate the consistence of the kinetic constants of aluminium species reactions with ferron, (iii) to develop a new speciation method based on their kinetic constants and (iv) to clarify the ambiguous correlation between Al_b and Al_{13} .

MATERIALS AND METHODS

Sample preparation

All reagents were of analytical grade or higher purity. Deionized water was used throughout, all glassware and containers

were acid-washed to prevent contamination. Except for brief residence in volumetric flasks as needed, all solutions and reagents were prepared and stored in plastic ware. Aluminium samples were derived from 0.5 M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (AC) or $\text{Al}_2(\text{SO}_4)_3$ (AS) stock solution. The pH of the stock solution was below 3.0 and thus pre-acidified was not adopted. Furthermore, the self-hydrolysis was concerned in the preparations of nominal mononuclear Al solutions and this effect on further neutralization could be ignored. Total Al content (Al_T) of the stock solution was determined by comparison with standards prepared from pure Al wire using ICP-AES. Solutions were made to their final volume of 200 ml and purged of CO_2 by bubbling with pre-purified N_2 gas for 2 h.

Four nominal mononuclear Al solutions were derived from direct dilution of AC or AS stock solutions using deionized water, representing an array of 1 mM AC, 50 mM AC, 1 mM AS, and 100 mM AS in Al.

Ten partially neutralized Al solutions, i.e. polyaluminium chloride (PACls), were prepared by the slow (0.1 ml min^{-1}) injection of standardized NaOH (0.25 M) using a peristaltic pump under a rapid stirring condition. The amount of NaOH varied with the target basicity ($[\text{OH}]/[\text{Al}]$ molar ratio, b value). The chosen b values of ten PACls ranged from 0 to 2.5. All PACls were prepared within 1 hour and were made to their final volume of 200 ml and concentration of 0.1 M in Al. All samples were aged for a week before analyses.

Al_{13} stock solution (0.20 M) was prepared by dissolving the solid phase of Al_{13} , which was purified through sulfate precipitation and nitrate metathesis (Shi *et al.* 2007)

Larger polymeric Al solutions were derived from both aging of Al_{13} solution and forced hydrolysis Al solution. For the former, Al_{13} solution was aged for 1 year under room temperature and became solid gel due to the loss of water, part of the gel was dissolved in deionized water and was filtered to get transparent solution of gel, the final solution was 0.02 M in Al; for the latter, the forced hydrolysis Al solution was first prepared by the addition of AC stock to a bicarbonate solution, which was stirred at 200 rpm by a paddle stirrer. With target b value of 2.2, the final solution (1 mM) was dominated by larger polymeric Al species after 8 months aging.

Samples were capped and sealed, thoroughly mixed, and stored overnight at 25°C prior to the initiation of

analyses. Concurrently, the final pH of each solution was measured using a pH meter.

Methods

^{27}Al NMR analyses

The ^{27}Al NMR methods were used to quantitatively analyze samples for the Al_{13} polycation and mononuclear Al. Spectra were obtained at 52.14 MHz using a VARIANUNITY INOVA (500 MHz) spectrometer in the Fourier transform mode. The instrumental setting parameters were: temperature 293 K; number of scan 128; pulse width $0.8 \mu\text{s}$. 0.2 M NaAlO_2 solution diluted with D_2O was used as inner standard of deuterium lock and Al quantification. The probe diameter was 5 mm, and either 8,000 or 10,000 acquisitions per sample were obtained. Mononuclear standards were run for both spectral calibration and quantification. The resonance corresponding to the mononuclear Al hexaaquo ion, $\text{Al}(\text{H}_2\text{O})_6^{3+}$, was assigned a chemical shift of 0 ppm, as established in the literature (Bertsch *et al.* 1986). The resonance at 62.5 ± 0.5 ppm downfield corresponds to the tetrahedrally coordinated Al in the center of the Al_{13} polycation. The integrated intensity of this peak was compared with the hexaaquo ion peaks of at least three acidified standards to obtain a quantitative estimate and multiplied by 13 to obtain the molar concentration of atomic Al present as the Al_{13} species (Parker & Bertsch 1992). The undetectable Al (Al_U) was obtained from the remainder of the Al_T .

Ferron analyses

The speciation by traditional ferron method has been described in some detail previously (Wang *et al.* 2004), where three fractions (Al_a , Al_b , Al_c) were operationally defined; key features are restated here due to the pivotal role in the current study. Briefly, three stock solutions described previously were prepared, filtered, and combined to yield the mixed, working ferron reagent with the following composition: 2.07 mM ferron; 111 mM sodium acetate; 218 mM HCl; with a final pH of 5.2–5.3. The working solution was prepared frequently such that a 5–7-day-old batch was always available for use. Volumes of

sample and mixed ferron reagent were selected such that the ferron/ Al_T molar ratio kept a value > 10 .

The reaction between sample and ferron was carried out in a 25 ml graduated glass tube and the reaction temperature was maintained at $25 \pm 3^\circ C$ throughout. The procedure was outlined below: 5.50 ml of the mixed working ferron were transferred into the glass tube and diluted to certain volume with distilled water, and then a certain amount of the sample was added into the glass tube to get the graduation. Seconds mixing later, a subsample was transferred to a 1 cm glass cuvette and measured in the DU650 Beckman UV-Visible spectrophotometer immediately. Consequently, kinetics scan at 366 nm was initiated and the start delay last 30–60 s with precise recording.

Absorbance increases were monitored for 2 hrs ensuring a complete complexation between Al species and ferron agent. Traditionally, three fractions could be operationally defined: the first 1 min absorbance as Al_a ; 1 min to 2 hr as Al_b ; and then Al_c was obtained by Al_T minus Al_a and Al_b , corresponding to nominal “mononuclear Al”, “reactive polynuclear Al”, and “unreactive Al”, respectively (Smith & Hem 1972; Wang *et al.* 2004).

It is assumed that the mononuclear Al and ferron react instantaneously (Smith & Hem 1972). This assumption is accepted in this study and the mononuclear Al is regarded to contribute the whole absorbance at $t = 0$. The following increases of absorbance result from the reactions between the polynuclear Al and ferron. Those reactions are analyzed on the basis of the following generalized kinetic model

$$-(d[Al_{px}]/dt) = k_{px}[\text{ferron}]^m [Al_{px}]^n \quad (1)$$

where $[Al_{px}]$ ($x = 1, 2, \dots$) is the molar concentration of certain kind of polynuclear Al species at any time. The absorbance increases resulting from the Al-ferron complexes are assumed to be parallel the reaction directly. If the $[\text{ferron}]/[Al_T]$ molar ratio is sufficiently high, $[\text{ferron}]$ is effectively constant, and an apparent rate coefficient can be defined as

$$k_x = k_{px}[\text{ferron}]^m \quad (2)$$

Previous research has shown that the reaction is approximately of first order with respect to $[Al_{px}]$ (i.e., $n = 1$), such that Equation (1) and (2) can be combined to

yield a pseudo-first-order reaction. Therefore, the integrated rate expression is expressed

$$C_t - C_0 = \sum_x C_x (1 - \exp(-k_x t)) \quad (3)$$

where C_t is the molar concentration of formation of ferron-Al complex at any time, C_0 is the initial concentration of mononuclear Al; C_x ($x = 1, 2, \dots$) is the initial concentration of certain kind of polynuclear Al species, and k_x is the first-order rate constants for its reaction with ferron.

Molar concentrations were converted to raw data of absorbance based on an appropriate standard curve for acidified mononuclear standards, such that Equation (3) can be converted to Equation (4)

$$A_t = A_0 + \sum_x (A_x - c)(1 - \exp(-k_x t)) \quad (4)$$

where A_t and A_0 = absorbance measured at any time, at time equal to zero, respectively. A_x ($x = 1, 2, \dots$) is the absorbance that would be measured at infinite time if only the certain kind of polynuclear Al species is present, and c is a constant value, depending on experiment system. It should be noted that the maximum value of x is let to be 2, which is confirmed to be big enough to fit the plot of absorbance-time perfectly. Two k values (k_1 and k_2 , letting $k_1 > k_2$) are sufficient to describe the reactions between ferron and aluminium species in a practical analyses. After the coefficients (A_0, A_1, A_2, k_1, k_2) are determined, two types of species with k_1 and k_2 , respectively, as well as the mononuclear Al with infinitely rapid kinetics can be identified, and their fractions, i.e., f_m for mononuclear Al, f_1 for the relatively rapid (k_1) Al, and f_2 for the relatively slow dissolving polynuclear Al can be calculated. Furthermore, the precise assignment of the species can be obtained by careful comparison of the rate constants, which will be discussed later on.

Noting that, if there is only one kind of polynuclear Al in the sample (eg., Al_{13} solution), Equation (5) could be derived from Equation (3) after conversion to common logarithms

$$\log Alp = \log Alp_0 - (k_p/2.303)t \quad (5)$$

where Alp , Alp_0 is the remainder concentration and initial concentration of this kind of polynuclear Al species, respectively.

RESULTS AND DISCUSSION

Kinetic model

The reaction between ferron and the sample mainly consisting of Al_{13} polycation with $Al_b\% > 93\%$ ($Al_{13}\% = 93\%$, Table 1) was studied. Under this condition the solution was simply regarded as consisting of only one type of species, and the theoretical Equation (5) could be used to describe the reaction. The experiment was conducted to verify the assumption that the solely Al-OH complex species (Al_{13} herein) reaction with ferron conforming to pseudo first-order kinetics. The data from timed colorimetric experiment were plotted in Figure 1 according to Equation (5). As expressed in Equation (5), the plot should exhibit a linearly shape if the reaction between solely Al-OH complex species (Al_{13} herein) and ferron conforms to pseudo first-order kinetics. As shown in Figure 1, such a linear plot could be found, and the first-order kinetic model was confirmed reasonable to describe the Al-OH complex-ferron reactions (Parker & Bertsch 1992).

The purified Al_{13} was used to avoid the disturbance of other species. However, other species such as ca. 3% Al_c were still contained in the Al_{13} solution (Table 1), and they may influence the results greatly. For Al_c uncorrected, where Al_c was not excluded in the content of un-reacted Al_p (denoting Al_{13} herein) in Equation (5), the plot was tailed

Table 1 | Speciation distribution in three typical Al solutions by traditional ferron assay

Sample	Al_a (%)	Al_b (%)	Al_c (%)	Al_{13} (%) [†]	pH
Mononuclear Al solutions [†]					
1 mM AC	86.44	8.00	5.56	ND	4.02
0.05 M AC	81.96	15.29	2.76	ND	3.67
1 mM AS	90.00	4.00	6.00	ND	3.96
0.1 M AS	85.83	6.94	7.22	ND	3.24
Al_{13} solution [‡]					
Al_{13}	4.62	93.05	2.33	93	5.08
Larger polynuclear Al solutions [§]					
Gel	13.61	5.13	81.26	–	5.13
Al_{fh22}	9.73	4.12	86.15	–	4.38

[†] Al_{13} (%), percentage of tridecamer detected by ²⁷Al NMR; ND, not determined.

[‡]Solutions containing predominant monomeric species, prepared by direct dissolution of aluminium salt.

[§] Al_{13} solution, derived by purified Al_{13} dissolved with concentration of 0.20M.

[§]Solutions containing predominant large polycations, gel refers to 0.02 M Al_{13} gel solution; Al_{fh22} refers to forced-hydrolyzed products with $b = 2.2$ and 1 mM in Al.

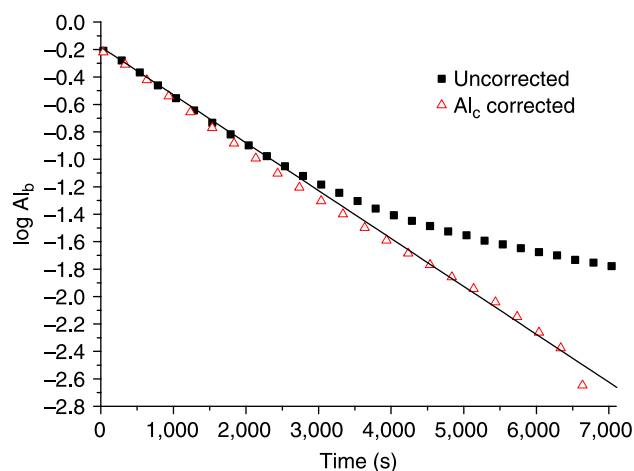


Figure 1 | The pseudo-first-order kinetics plot for Al_{13} -ferron reaction. Al_c corrected, the concentration of un-reacted Al_{13} calculated by minus of Al_c ; uncorrected, the raw data. Solid line represents the linear fitting result of uncorrected.

early as $t < 3,000$ s (Figure 1). On the contrary, as the Al_c component was detracted from the un-reacted Al_{13} (defined as Al_c corrected herein), the plot exhibited a perfect linearity over the entire reaction. Obviously, the presence of curvature resulted from the inert Al species with different composition included in the un-reacted Al_p (Jardine & Zelazny 1986; Bertsch 1989a). Since various species inevitably exist in the natural samples, which renders the selection of linear reaction period more arduous, then the linear analysis is seldom used.

Constancy of k values

Thus we used nonlinear least square analysis to fit two simultaneous reactions of pseudo first-order, i.e., the absorbance-time functions of Equation (4), and disparate kinetic constants (k values) for various Al species reactions with ferron were obtained. Ten partially neutralized Al solutions, as well as three typical solutions were investigated. The results were listed in Table 2. The coefficients of determination (r^2) were > 0.998 for all samples. The k values from Table 2 were well-regulated.

For nominal Al_{13} solution, two rate constants with the same value of 0.00087 s^{-1} were obtained. Compared with other kinetics (see below), the value rank the “moderate” reaction between aluminium polycation and ferron. Calculated from this value, the 99.9% completion of the moderate reaction is ca. 2 hrs which is usually used to determine the

Table 2 | Rate constants of samples derived from nonlinear least square analysis

Sample	k value* ($\times 10^{-3} \text{ s}^{-1}$)		Distribution of species†				Half time‡ (min)		R ²
	k ₁	k ₂	RP	MD/Al ₁₃	SL	IN	t _{1/2} ¹	t _{1/2} ²	
Mononuclear Al solutions									
1 mM AC	13.36	0.15	Yes	ND/ND	Yes	?	0.9	77.0	0.9957
0.05 M AC	8.71	0.22	Yes	ND/ND	Yes	?	1.3	52.5	0.9986
1 mM AS	10.47	0.05	Yes	ND/ND	?	Yes	1.1	231.0	0.9977
0.1 M AS	9.25	0.2	Yes	ND/ND	Yes	?	1.2	57.8	0.9952
Al ₁₃ solution									
Al ₁₃	0.87	0.87		Yes/Yes	?	?	13.3	13.3	0.9996
Larger polynuclear Al solutions									
Gel	14.54	0.13	Yes	ND/ND	Yes	?	0.8	88.9	0.9992
Al _{th22}	0.37	0.02		ND/ND	Yes	Yes	31.2	577.6	0.9994
Partially neutralized Al solutions									
b = 0	13.91	0.11	Yes	ND/ND	Yes	?	0.8	105	0.9958
b = 0.5	13.86	0.75	Yes	Yes/Yes	?	?	0.8	15.4	0.9979
b = 0.8	18.89	0.82	Yes	Yes/Yes	?	?	0.6	14.1	0.9993
b = 1	17.00	0.61	Yes	Yes/Yes	?	?	0.7	18.9	0.9999
b = 1.2	15.78	0.74	Yes	Yes/Yes	?	?	0.7	15.6	0.9999
b = 1.5	1.01	0.11		Yes/Yes	Yes		11.4	105	0.9998
b = 1.8	1.04	0.09		Yes/Yes	Yes		11.1	128	0.9999
b = 2	0.94	0.11		Yes/Yes	Yes		12.3	105	0.9999
b = 2.2	0.99	0.12		Yes/Yes	Yes		11.7	96.2	0.9997
b = 2.5	0.82	0.14		Yes/Yes	Yes		14.1	82.5	0.9998

*k value derived by fitting from Equation (4) letting $k_1 > k_2$.

†RP, MD, SL and IN refer to polynuclear species with rapid, moderate, slow and inert kinetics, respectively. Yes refer to the affirmative presence of corresponding species determined by two fitted k values and ? refer to the possible presence of corresponding species which should be determined from calculation, ND, not detected, by whether k values (MD) or ²⁷Al NMR (Al₁₃).

‡t_{1/2}¹ and t_{1/2}² refer to the half time calculated from k₁ and k₂, respectively.

Al_b fraction in traditional ferron assay (Wang et al. 2004). Hence, the corresponding fraction derived either from this analysis ($f_1 + f_2$, %) or from traditional ferron assay (Al_b, %) is equivalent to the Al₁₃ fraction (Al_{13%}) determined by ²⁷Al NMR. Clearly, the polycation with moderate reaction kinetics ($k \sim 0.00087 \text{ s}^{-1}$ or $t_{1/2} \sim 13 \text{ min}$) should be ascribed to Al₁₃ polycation.

However, this moderate kinetics was not found in other two typical solutions, implying the absence of Al₁₃ in those samples. The results were consistent with those obtained by ²⁷Al NMR (Table 1). For nominal mononuclear Al solutions, there were two distinct rate constants in term of k₁ and k₂ ($k_1 \gg k_2$) with $k_1 > 0.01 \text{ s}^{-1}$ and $k_2 < 0.0002 \text{ s}^{-1}$, k₁ is two magnitude order bigger than k₂ for the nominal mononuclear Al solution, while the k value obtained from

Al₁₃ solution is in the middle position. Thus at least three kinetics resembling three types of species could be classified, i.e., the rapid, the moderate and the slow kinetics with the half time ($t_{1/2}$) value of <1 minute, ~13 minutes and >40 minutes, respectively. Since the slow kinetics in term of half time involves dramatically as k approaches 0.0001 s^{-1} ($t_{1/2} = 115 \text{ minutes}$), the species with slow kinetics could further be grouped into two types: i) the “slow species”, with $t_{1/2}$ values no more than 115 min, and ii) the “inert species”, with $t_{1/2}$ values above 115 min.

The fractions corresponding with the slow kinetics were mostly classified as Al_c in traditional ferron assay, however, little amount of these fractions, varying with their kinetics, might contribute to Al_b. In Al₁₃ solution, there were no other k values than moderate kinetics; the Al_c fraction

derived from traditional ferron assay could not be assigned to the species with exact kinetics. But it was easily conducted in larger polynuclear Al solutions, where Al_c fraction is the dominant species (Table 1). There were rapid species ($t_{1/2} < 1$ minute) and slow species ($t_{1/2} \sim 89$ minutes) in the gel solution, whereas there were slow species ($t_{1/2} \sim 40$ minutes) and inert species ($t_{1/2} \sim 580$ minutes) in Al_{ph22} . It was safely to conclude that Al_c fraction in both solutions mainly consist of inert species and slow species. No Al_{13} can be detected in both solutions whether by this method or by ^{27}Al NMR. Therefore, additional to the instantaneous reaction of mononuclear Al, at least four other sorts of polynuclear species could be grouped based on the differentiate kinetics with ferron: rapid, moderate, slow, and inert species, corresponding with the k values of $>0.01 s^{-1}$ ($t_{1/2} < 1$ minute), $\sim 0.00087 s^{-1}$ ($t_{1/2} \sim 13$ minutes), $0.0001-0.0004 s^{-1}$ (40 minutes $< t_{1/2} < 115$ minutes), and $< 0.0001 s^{-1}$ ($t_{1/2} > 115$ minutes), respectively. Notably, the moderate species can be ascribed to tridecamer with confidence as aforesaid. Based on the kinetics, Al_{13} could be single out from combined Al_b fraction.

For partially neutralized Al solutions, k values exhibit a routine evolution with the b values (Table 2). The rapid k does not disappear until $b < 1.2$. Companied by the disappearance of rapid k , inert k and slow k would present as $b \geq 1.5$. Moderate k began to present as $b > 0$ implying the presence of tridecamer after neutralization. The absorbance data were plotted against the reaction time (Figure 2). Metamorphic curves in Figure 2 can be interpreted by the evolution of k values. As $b < 1.2$, the curves consisted of two parts, the first stage of rapid increase of absorbance and the following steady increase of absorbance to shaping a plateau. The former was due to the presence of the rapid species ($t_{1/2} < 1$ minute), which will react with ferron completely within ca. 500 seconds. The latter was due to the presence of moderate species, inert or slow species. It should be noted that only one of above kinetics besides the rapid can be derived from in one fitting of the curve. For example, the other kinetics was slow kinetics and moderate kinetics for $b = 0$ and $1.2 > b > 0$, respectively. For $b = 0$, there was little slow species and its contribution on the increase of absorbance could be neglected, thus the plateau appeared quickly right after the completion of rapid species within 500 minutes. For $b > 0$, given a relatively large

fraction of both the rapid species and moderate species, the curve exhibits an obvious transition between the first rapid increase and plateau. This will mislead to a relatively large Al_b fraction by traditional ferron assay because it would contain some residual rapid species after 60s reaction duration. To explain the transition, there are other technology to divide the Al_b into two labile components of Al_{b1} and Al_{b2} , but the two intersected components can not be ascribed clearly. This problem can be solved by the kinetic constant easily using the modified analyses in this work. The amount of this rapid species decreased sharply with b values. Finally the first stage of rapid increase of absorbance could not be observed with the disappearance of the rapid species. For $b = 2.2$, moderate species (Al_{13}) with $t_{1/2} \approx 12$ minutes predominant the PACl solution (ca. 85% of Al_T). Calculated from this value, the 99.9% completion of the moderate reaction is ca. 2 hrs, which renders the curve exhibit a smooth increase of absorbance in the whole experimental duration. Only under this condition, Al_b fraction mainly be composed of Al_{13} and hence, it can be regarded as Al_{13} . For $b = 2.5$, absorbance increases slowly and the plot could never gets a stable plateau in 2 hrs for large quantity of slow species (ca. 60% of Al_T) with $t_{1/2} \approx 83$ minutes is contained in the solution.

Unlike the traditional ferron method, where Al_a and Al_b fractions are operationally defined by arbitrary cutoff of time, the modified ferron method based on k value could get preciser determination of Al species, especially for Al_{13} . The comparison of speciation results for partially neutralized Al solutions derived from both methods, as well as ^{27}Al NMR method, are shown in Figure 3. In modified ferron assay, the species with moderate reaction kinetics and the species deemed to react with ferron instantly are denoted as F_r and F_m , respectively. All the analyses yield virtually identical estimates of $[Al_{13}]/[Al_b]/[F_r]$ with b value in a range 1.0 to 2.2 (Figure 3a), because the samples mainly consist of Al_{13} . For $b = 2.5$, $[Al_b]$ is obviously bigger than $[F_r]$ or $[Al_{13}]$, which results from large quantities of Al_c included in Al_b , but $[F_r]$ is still very closed to $[Al_{13}]$, indicating the superiority of modified ferron assay. For $b = 0$, where no base is added into aluminium solution, no Al_{13} signal could be detected through ^{27}Al NMR spectroscopy, but simultaneous hydrolysis would be observed for the presence of k values assigned to either rapid or inert reaction through modified

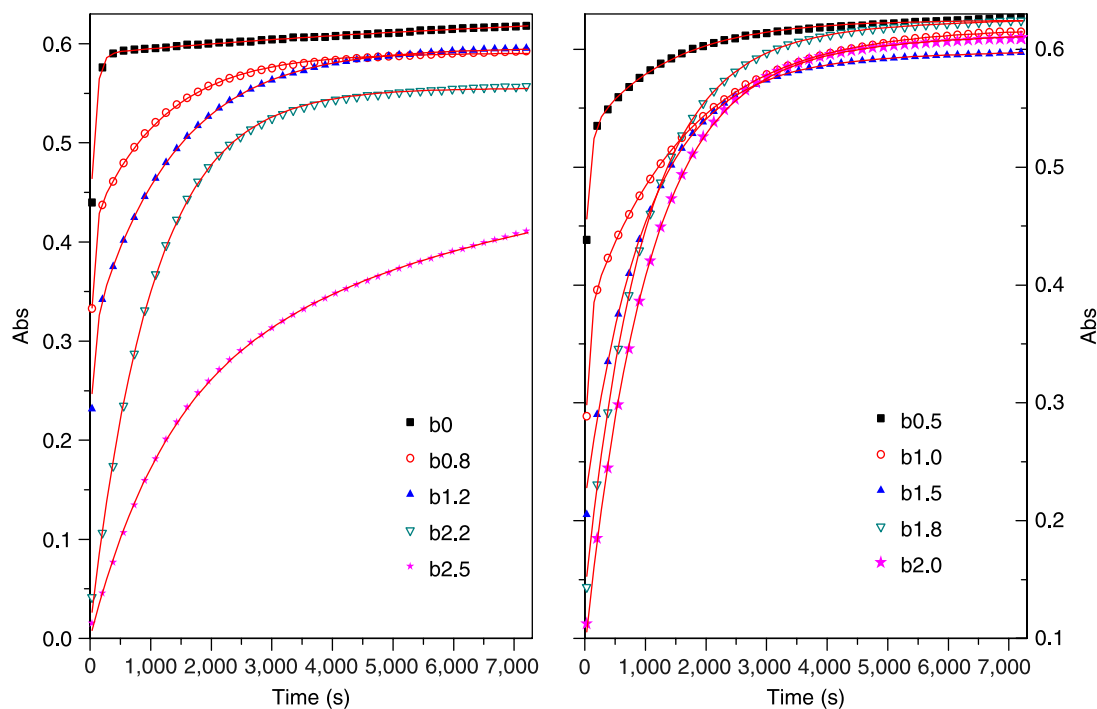


Figure 2 | Raw absorbance function vs. time plot for partially neutralized solutions. Solutions were partially neutralized with aqueous NaOH, solid lines are fitting results.

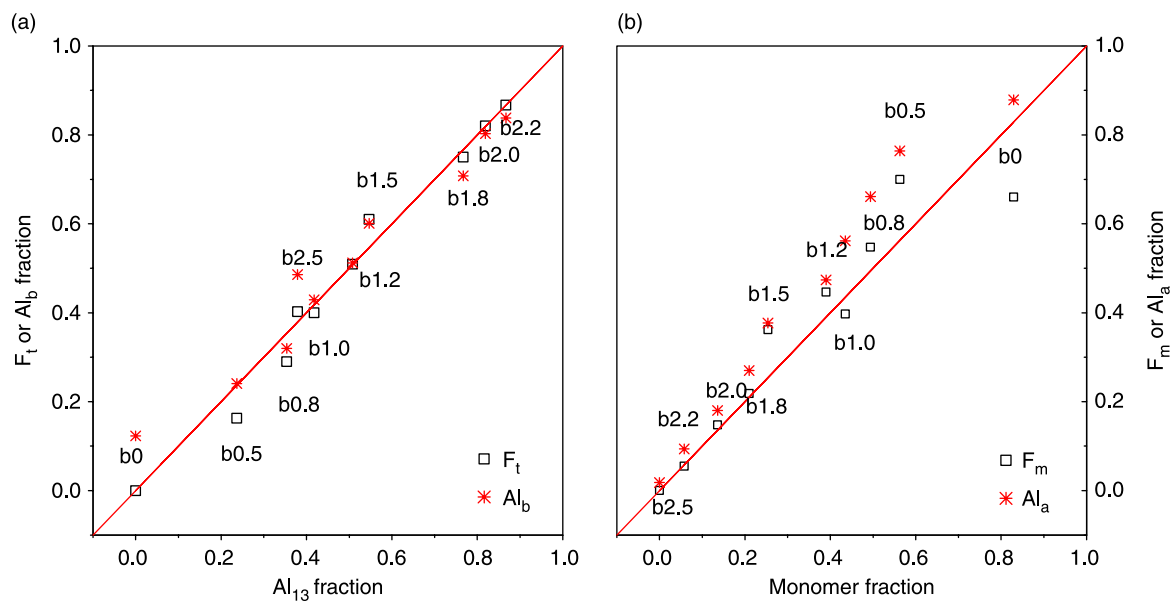


Figure 3 | Comparison of speciation results by three methods. (a) fraction of moderate reactive Al: Al_b , F_t and Al_{13} , assayed by traditional, modified ferron method, and ^{27}Al NMR, respectively; (b) fraction of monomeric Al: Al_a , F_m , and monomer, assayed by traditional, modified ferron method and ^{27}Al NMR, respectively. Solutions were partially neutralized with aqueous NaOH, and the number adjacent to each symbol indicates the b value.

ferron assay. No value assigned to the moderate can be found, therefore, $[F_i] = 0$, which is well consistent with the result of ^{27}Al NMR. Meanwhile, $[\text{Al}_b]$ is much higher than $[\text{Al}_{13}]$. The Al_a fraction estimated by the traditional ferron assay is also found greater than the monomer concentration derived by the other two methods (Figure 3b). It is understandable for that the absorbance in any cutoff time is an admixture of various species other than the one to be analysed.

Aluminium speciation

As so far, the aluminium species could be categorized into five sorts, i.e., four sorts of polynuclear species identified by their kinetics constants, and the mononuclear aluminium species with valence in the range $(+3) \sim (-1)$. Monomer is assumed to react instantaneously with ferron and hence, its kinetics is infinite. But monomer can be quantified by prolongation from Equation (4) at 0 s reading. The k values of the other four polynuclear species are in good consistency, implying a minimum of polymeric species in the partially neutralized Al solution. It would seem plausible that the rapid fraction can be ascribed to a small oligomeric Al species (the dimer or a combination of this and the trimer) that breaks down rapidly. This fraction is mostly included in the arbitrary 30–90 s reading in the traditional ferron assay, being erroneously assigned to the Al_a . Identification of moderate species as Al_{13} can be confirmed since it seems very unlikely that another polynuclear species could exhibit such constancy with the result derived by ^{27}Al NMR method. Two slow kinetics can not be unequivocally assigned due to the uncertainty of their compositions, but it will open a window to know about the Al_{30} or other larger polycations. Although recently discovered Al_{30} can be well identified by ^{27}Al NMR (Allouche & Taulelle 2003; Shafran *et al.* 2004), whether its identification can be achieved by ferron assay need to further investigation on solution dominated by Al_{30} later on. Generally, the observed consistent k values can be diagnostic for speciation of Al, and the modified ferron assay can be used to quantify Al_{13} at concentrations below practical detection limits of ^{27}Al NMR (Parker & Bertsch 1992), which would give the advantage for Al_{13} identification in coagulation where Al_{13} would in situ form (Zhao *et al.* 2008).

CONCLUSIONS

The model that two simultaneous Al-OH polymeric complex reactions conforming to pseudo first-order kinetics and one monomer reaction conforming to zero-order kinetics could fit the reaction between Al solution and ferron perfectly. Four disparate kinetic constants (k values) derived from the model could be used to classify Al polynuclear species. Generally, the fraction assayed by traditional ferron method is higher than that assayed by k evaluating method. Al_{13} ascribed to the moderate reaction kinetics can be precisely singled out from combined Al_b fraction, which is confirmed by ^{27}Al NMR. The latter also can be used for speciation in dilute Al(III) solution. It is of great significance for the identification of Al_{13} in coagulation with Al-based coagulants.

ACKNOWLEDGEMENTS

This work was supported by the NSF of China under 50578155, innovative research group fund (No. 50621804), and the China national 863 projects 2006AA06Z312.

REFERENCES

- Allouche, L. & Taulelle, F. 2003 Conversion of Al_{13} Keggin ϵ into Al_{30} : a reaction controlled by aluminium monomers. *Inorg. Chem. Commun.* **6**(9), 1167–1170.
- Batchelor, B., McEwen, J. B. & Perry, R. 1986 Kinetics of aluminium hydrolysis: measurement and characterization of reaction products. *Environ. Sci. Technol.* **20**(9), 891–894.
- Bersillon, J. L., Hsu, P. H. & Fiessinger, F. 1980 Characterization of hydroxy-aluminium solutions. *Soil Sci. Soc. Am. J.* **44**, 630–634.
- Bertsch, P. M. 1989a *The Environmental Chemistry of Aluminium*. CRC Press, Boca Raton, FL.
- Bertsch, P. M. (ed.) 1989b *Soils, Aquatic Processes, and Lake Acidification*, (Vol. 4). Springer-Verlag, New York, pp. 63–105.
- Bertsch, P. M., Layton, W. J. & Barnhisel, R. I. 1986 Speciation of hydroxyaluminium solutions by wet chemical and aluminium-27 NMR methods. *Soil Sci. Soc. Am. J.* **50**, 1449–1454.
- Bi, S. P., Wang, C. Y., Cao, Q. & Zhang, C. 2004 Studies on the mechanism of hydrolysis and polymerization of aluminium salts in aqueous solution: correlations between the “Core-links” model and “Cage-like” Keggin- Al_{13} model. *Coord. Chem. Rev.* **248**, 441–455.

- Bottero, J. Y., Axelos, M., Tchoubar, D., Cases, J. M., Fripiat, J. J. & Fiessinger, F. 1987 Mechanism of formation of aluminium trihydroxide from keggin Al13 polymers. *J. Colloid Interface Sci.* **117**(1), 47–57.
- Bottero, J. Y., Cases, J. M., Fiessinger, F. & Poirier, J. E. 1980 Studies of hydrolyzed aluminium chloride solutions. 1. Nature of aluminium species and composition of aqueous solutions. *J. Phys. Chem. A* **84**, 2933–2939.
- Clarke, N., Danielsson, L.-G. & Sparen, A. 1996 Analytical methodology for the determination of aluminium fractions in natural fresh waters. *Pure App. Chem.* **68**(8), 1579–1638.
- Duffy, S. J. & vanLoon, G. W. 1994 Characterization of amorphous aluminium hydroxide by the ferron method. *Environ. Sci. Technol.* **28**(11), 1950–1956.
- Hu, C., Liu, H., Qu, J., Wang, D. & Ru, J. 2006 Coagulation behavior of aluminium salts in eutrophic water: significance of Al13 species and pH control. *Environ. Sci. Technol.* **40**(1), 325–331.
- Jardine, P. M. & Zelazny, L. W. 1986 Mononuclear and polynuclear aluminium speciation through differential kinetic reactions with ferron. *Soil Sci. Soc. Am. J.* **50**, 895–900.
- Jardine, P. M. & Zelazny, L. W. 1987 Influence of inorganic anions on the speciation of mononuclear and polynuclear aluminium by ferron. *Soil Sci. Soc. Am. J.* **51**, 889–892.
- Jiménez, B., Martínez, M. & Vaca, M. 2007 Alum recovery and wastewater sludge stabilization with sulfuric acid. *Water Sci. Technol.* **56**(8), 133–141.
- Li, F., Yuasa, A. & Ando, Y. 2008 Characterization of micro-flocs of NOM coagulated by PACl, alum and polysilicate-iron in terms of molecular weight and floc size. *Water Sci. Technol.* **57**(1), 83–90.
- Parker, D. R. & Bertsch, P. M. 1992 Identification and quantification of the Al13 tridecameric polycation using ferron. *Environ. Sci. Technol.* **26**(5), 908–914.
- Shafran, K., Deschaume, O. & Perry, C. C. 2004 High-temperature speciation studies of Al-ion hydrolysis. *Adv. Eng. Mat.* **6**(10), 836–839.
- Shi, B., Li, G., Wang, D. & Tang, H. 2007 Separation of Al13 from polyaluminium chloride by sulfate precipitation and nitrate metathesis. *Sep. Purif. Technol.* **54**(1), 88–95.
- Smith, R. W. & Hem, J. D. (eds) 1972 *Effect of Aging on Aluminium Hydroxide Complexes in Dilute Aqueous Solutions*. D.U.S.Gov.Print.Office, Washington, DC, pp. 1–1827.
- Tang, H. X., Wang, D. S. & Ge, X. P. 2004 Environmental nanopollutants(ENP) and micro-interfacial processes. *Water Sci. Technol.* **50**(12), 103–109.
- Wang, D. S., Tang, H. X. & Gregory, J. 2002 Relative importance of charge-neutralization and precipitation during coagulation with IPF-PACl: effect of sulfate. *Environ. Sci. Technol.* **36**(8), 1815–1820.
- Wang, D. S., Sun, W., Xu, Y., Tang, H. & Gregory, J. 2004 Speciation stability of inorganic polymer flocculant-PACl. *Colloids Surf. A* **243**(1–3), 1–10.
- Ye, C., Wang, D., Shi, B., Yu, J., Qu, J., Edwards, M. & Tang, H. 2007 Alkalinity effect of coagulation with polyaluminium chlorides: role of electrostatic patch. *Colloids Surf. A* **294**(1–3), 163–173.
- Zhao, H., Hu, C., Liu, H., Zhao, X. & Qu, J. 2008 Role of aluminium speciation in the removal of disinfection byproduct precursors by a coagulation process. *Environ. Sci. Technol.* **42**(15), 5752–5758.