k-Value-based ferron assay and its application

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ABSTRACT

Al_{13} is notable for its promising application in many fields. It has been believed that Al_{13} could be assayed in term of Al_b derived from traditional ferron assay. But the inherent relation between Al_{13} and Al_b is not clear. Here, the new k-value-based ferron assay using nonlinear least squares analysis is suggested to resolve the ambiguity. The experimental results reveal that the moderate kinetics (k value) around $0.001\ s^{-1}$ can be ascribed to Al_{13}. In the short-term aging of freshly neutralized aluminum solutions with OH/Al molar ratio of 2.2, the rapid progress of Al_{13}-like transformation into Al_{13} can be traced by this method, whereas it may be masked by traditional ferron assay because the metastable intermediates also contribute absorbance to Al_b fraction. Al_b can only be regarded as Al_{13} when Al_{13} forms completely and becomes the stable specie in the matured solution.

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1. Introduction

When aluminum salt solution is neutralized quite slowly with base, clear solution can be easily obtained with OH/Al molar ratio (b value) bigger than 2.5. The presence of OH–Al polymers in such partially neutralized Al solutions has been already recognized. Among those polymers, the tridecamer $(Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+},$ $Al_{13})$, a novel polymeric specie consisting of a central tetrahedral AlO_4 surrounded by 12 Al octahedral AlO_6, is receiving much attention for its special physico-chemical properties and applicable potentials in water and wastewater treatment, pharmaceutical and catalyst fields [1].

Many studies [2–5] have indicated that the formation and transformation of Al_{13} might be affected by basicity, concentration, temperature and the rate of neutralization. Most of the aforesaid studies regarding the formation of Al_{13} dealt with those "matured" solutions which were aged for several days. The following aluminum hydrolysis in partially neutralized solution during long term aging has been studied elsewhere [4,5]. When the neutralization is rapid enough, the clear solution would become turbid due to the transformation of aluminum hydroxide from polymeric species including Al_{13} during prolonged aging [4]. Tsai and Hsu [5] also concluded that the OH–Al polymers would slowly change during prolonged aging even though the solution is neutralized to a low degree with OH/Al molar ratio of 1.0. In laboratory-hydrolyzed OH–Al solutions, Al_{13} will slowly convert into $Al_{30}[(AlO_4)_2A$-$l_{28}(OH)_{56}(H_2O)_{26}]^{18+}(Al_{30})$ at room temperature [2], but the conversion occur in much longer duration of several years. The origin and formation of Al_{13} should be more sensitive during short-term aging than prolonged aging, but to date the effect of short-term aging on Al_{13} formation and transformation in partially neutralized aluminum solutions are not well understood yet.

Al_{13} can be well identified by ^{27}Al NMR spectroscopy. Other various empirical techniques can be used to estimate the distribution of Al species in such partially neutralized Al solutions [6]. The most common method may be the ferron assay [7] which based on the different kinetics of Al–ferron reaction. Different dissolution rates arise from differences in the nature and size of the species. However, the reliable rate constants of species are difficult to achieve for the absence of standard analysis [8,9]. Then the classification by traditional ferron assay is operationally categorized into three fractions: (i) the mononuclear Al, defined as Al_a, derived from the first 30 s or 1 min absorbance; (ii) the reactive polynuclear Al, defined as Al_b, derived from the following increase of absorbance within 2 h; and (iii) the inert or colloidal Al, defined as Al_c, the difference between the total Al content (Al_T) and $Al_a + Al_b$ [10]. Obviously, the traditional ferron assay is much dependent on the cutoff time selected and the speciation resulting from this method is labile [8,11,12]. However, many studies [12–14] have concluded that Al_b might be equitable to Al_{13}, which can be confirmed by ^{27}Al NMR [14–17]. The inherent correlation between them remains vague since the kinetic models and analyses employed to describe the kinetic aluminum species reaction with ferron are various, and the derived rate constants are not regulated. It is expected that the rate constant which correlates well with the structure could be

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diagnostic for speciation. Al_{13} was suggested an unlikely product of natural biogeochemical processes, but this assumption needs reevaluation in light of the detection of Al_{13} in acid soils by direct NMR analysis [18]. Moreover, aluminum is a major plant growth-limiting factor in many acid soils; many efforts have been focused on assessment of the relative toxicities of Al species. Considering the increasing interests on Al phytotoxicity and PACl application [19,20], a convenient method for precise speciation based on the rate constant rather than ^{27}Al NMR is basically required.

In this study a modified ferron assay based on the regulated kinetic value, i.e., k-value-based ferron assay, is established firstly. The conundrum between Al_b and Al_{13} should be clarified by the k-value-based ferron assay. Then the method is applied in the study of aluminum hydrolysis in fresh partially neutralized aluminum solution with b = 2.2. There is lack of agreement on the mechanisms of Al_{13} formation and transformation in aqueous solution. Whether the precursor of fourfold coordination, i.e., $Al(OH)_4^-$ is necessary or not is the key issue [21,22], through the application of this method, insightful information on Al_{13} formation and transformation during the short-term aging is to be discovered. Significantly, the k-value-based ferron assay is potential to be used to monitor the occurrence of Al_{13} in natural system where Al_{13} is difficult to be measured by ^{27}Al NMR mainly due to the low concentration of total Al.

2. Materials and methods

2.1. 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. Aluminum samples were derived from 0.5 M $AlCl_3 \cdot 6H_2O$ stock solution. The pH of the stock solution was below 3.0 and thus pre-acidified was not adopted. Total Al content (Al_T) of the stock solution was determined by comparison with standards prepared from pure Al wire using ICP–AES.

Ten partially neutralized Al solutions and one nominal Al_{13} solution were used for establishment of k-value-based ferron assay. It should be noted that partially neutralized $AlCl_3$ solution is actually the polyaluminum chloride (PACl) solution which is more popularly called in water and wastewater treatment. And hence, partially neutralized $AlCl_3$ solution is nominated PACl herein for abbreviation. PACls were obtained by the slow (0.1 ml min^{-1}) injection of standardized NaOH (0.25 M) using a peristaltic pump under rapid stirring on $AlCl_3$ solutions. The amount of NaOH varied with the target basicity ([OH]/[Al] molar ratio, b value). The chosen b value of 10 PACls ranged from 0 to 2.5. All PACls were made to their final volume of 200 ml and concentration of 0.1 M in Al. All samples were stored at room temperature for a week before analyses, i.e., matured PACl solutions. Nominal Al_{13} solution (0.20 M) was prepared by dissolving the solid phase of Al_{13}, which was purified through sulfate precipitation and nitrate metathesis [23].

Two freshly partially neutralized aluminum samples with OH/Al molar ratio of 2.2 were used for application of k-value-based ferron assay. They were prepared by different neutralization method which has been described in some detail previously [21]. Briefly, one is "slow neutralization", carried out by a peristaltic pump at a rate of 0.5 ml min^{-1}, and the other is "instant neutralization", conducted by pouring pre-calculated base solution into aluminum chloride solution instantly and stirring vigorously. The speciation using k-value-based ferron assay was initiated right after neutralization and was conducted throughout short-term aging within 3 days.

2.2. ^{27}Al NMR analyses

The ^{27}Al NMR method was used to 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 are: temperature 293 K; number of scan 128; pulse width 0.8 μs. 0.2 M $NaAlO_2$ solution diluted with D_2O was used as inner standard of deuterium lock and Al quantification. The probe diameter is 5 mm, and either 8000 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, $Al(H_2O)_6^{3+}$, is assigned a chemical shift of 0 ppm, as established in the literature [24]. The resonance at 62.5 ± 0.5 ppm downfield corresponds to the tetrahedrally coordinated Al in the center of the Al_{13} polycation [13,14]. 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 [8,13].

2.3. Ferron analyses

The speciation by traditional ferron method has been described in detail previously [23], where three fractions (Al_a, Al_b, Al_c) were operationally defined. Briefly, three stock solutions described previously [25] were prepared, filtered, and combined to yield the mixed, working ferron colorimetric solution 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- to 7-day-old batch was always available for use. Volumes of sample and working solution were selected such that the ferron/Al_T molar ratio kept a value >10.

Ferron assay was carried out at room temperature maintaining at 25 ± 3 °C throughout. 5.50 ml of the working solution were transferred into a 25 ml graduated glass tube and diluted to certain volume with distilled water, and then pre-calculated amount of sample was added to get the graduation. After mixing, the mixture was subsampled in a 1 cm glass cuvette and measured using the DU650 Beckman UV–visible spectrophotometer immediately. Absorbance was monitored in 2 h. Traditionally, three fractions is operationally defined: the absorbance recorded at the first 1 min and the increase of absorbance from 1 min to 2 h result from Al_a and Al_b, respectively, and then Al_c is obtained by Al_T minus Al_a and Al_b [25].

We use nonlinear least square analysis and two simultaneous reactions conforming pseudo-first-order to fit the absorbance-time function. The detail deduction can be found elsewhere [26]. Briefly, the assumption that the mononuclear Al and ferron react instantaneously [10] is accepted in this study and the mononuclear Al contribute all its absorbance at $t = 0$, i.e., A_0. The subsequent increases of absorbance comprise of absorbance resulting from parallel reactions between ferron and polynuclear species. Since the reactions between polynuclear Al species and ferron conform to pseudo-first-order, their kinetic can be expressed in terms of exponential functions. And hence, the whole model can be expressed in the following equation:

$$A_t = A_0 + \sum_x (A_x - c)(1 - \exp(-k_x t)) \tag{1}$$

where A_t and A_0 are the absorbance measured at any time and zero time, respectively. Clearly, A_0 is the absorbance resulting from the instant reaction between mononuclear Al and ferron. The latter sum in terms of exponential function refers to the reaction between ferron and polynuclear Al species, $A_x(x = 1, 2)$ is the absorbance that would be measured at infinite time if only the certain kind of

polynuclear Al species is present, and c is introduced herein for that the intercept would occur in the absorbance linear function with concentration, it 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 suitable 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 aluminum species in a practical analyses. After the coefficients (A_0, A_1, A_2, k_1, k_2) are determined by fitting, 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) polynuclear Al and f_2 for the relatively slow dissolving polynuclear Al can be calculated.

3. Results and discussion

3.1. k-Value-based ferron assay

Disparate kinetic constants (k values) for various Al species reactions with ferron were obtained. The k values fitted by Eq. (1) (Table 1) are well-regulated. The coefficients of determination ($r^2 > 0.998$) are very high for all samples. In matured PACl solutions, three types of distinct rate constants fitted from Eq. (1) can be observed clearly in Fig. 1. The k values decrease by one order of magnitude, i.e., the rapid kinetics around 0.01 s^{-1}, the moderate kinetics around 0.001 s^{-1} and the slow kinetics around 0.0001 s^{-1}. Thus at least three categories of polymeric Al–OH complexes corresponding to their kinetics, i.e., the rapid species (RP), moderate species (MD) and slow species (SL) can be classified, respectively (Table 1). As shown from Fig. 1, rapid species does not disappear until $b < 1.2$. Moderate species begins to present as $b = 0.5$. As $b \geqslant 1.5$, the rapid species is replaced by the slow species. It is confused that the slow species can be found as $b = 0$. The self-hydrolysis might be responsible for this phenomenon. The evolution of aluminum species with b values consists well with the hydrolysis of aluminum and the aforesaid three species (the kinetics rank descend in sequence) can be reasonably assigned to the oligomers, Al$_{13}$ and other large polymers or colloidal aluminum species, respectively. In nominal Al$_{13}$ solution, two fitted kinetics are identical with value of 0.00087 s^{-1} implying the presence of the "unique" species of Al$_{13}$.

Therefore, the so called "k-value-based ferron assay" can be established by the k values and the fitted parameters of A_x corre-

Fig. 1. Plot of fitting k values derived from k-value-based ferron assay. Samples are the same as Table 1. For Al$_{13}$ sample, k_1 and k_2 are overlapped.

sponding to k_x in Eq. (1). In this method, the polymeric species can be identified by its k value and its fraction can be calculated from A_x. The monomer fraction is calculated from the A_0 by fitting Eq. (1) since the monomer is deemed to react with ferron instantly. In some cases, the slow kinetics might not be analyzed and the corresponding species might present as the remainder via mass equilibrium, the species with slow kinetics could further be grouped into two categories, i.e., the "slow species" (SL) and the "inert species" (IN), which are mostly classified as Al$_c$ in traditional ferron assay.

In the k-value-based ferron assay, the aluminum fraction of the species with moderate kinetics is denoted as F_t. Fraction of Al$_{13}$ determined by ^{27}Al NMR and fraction of Al$_b$ determined by traditional ferron assay are denoted as [Al$_{13}$] and [Al$_b$], respectively. Comparison of analysis results by three methods is shown in Fig. 2. Clearly, F_t is virtually equal to [Al$_{13}$] in all cases, indicating that the species with moderate reaction kinetics can be ascribed to Al$_{13}$ polycation. As the solution is predominated by Al$_{13}$, e.g. in

Table 1
Rate constants and speciation derived from k-value-based ferron assay. PACl samples with various b values were matured after one week, nominal Al$_{13}$ solution was dominated by Al$_{13}$ (93%).

Sample	k value[a] ($\times 10^{-3}$ s^{-1})		Species identified[b]					R^2
	k_1	k_2	RP	MD	SL	Al$_{13}$	Al$_b$	
$b = 0$	13.91	0.11	Yes	ud	Yes	ud	Yes	0.9958
$b = 0.5$	13.86	0.75	Yes	Yes	?	Yes	Yes	0.9979
$b = 0.8$	18.89	0.82	Yes	Yes	?	Yes	Yes	0.9993
$b = 1$	17	0.61	Yes	Yes	?	Yes	Yes	0.9999
$b = 1.2$	15.78	0.74	Yes	Yes	?	Yes	Yes	0.9999
$b = 1.5$	1.01	0.11		Yes	Yes	Yes	Yes	0.9998
$b = 1.8$	1.04	0.09		Yes	Yes	Yes	Yes	0.9999
$b = 2$	0.94	0.11		Yes	Yes	Yes	Yes	0.9999
$b = 2.2$	0.99	0.12		Yes	Yes	Yes	Yes	0.9997
$b = 2.5$	0.82	0.14		Yes	Yes	Yes	Yes	0.9998
Al$_{13}$	0.87	0.87		Yes	?	Yes	Yes	0.9996

[a] k Value derived by fitting from Eq. (1), letting $k_1 > k_2$.
[b] RP, MD and SL refer to polynuclear species with rapid, moderate and slow kinetics, respectively. "Yes", the affirmative presence of corresponding species determined by two fitted k values; "?", the possible presence of corresponding species which should be determined from calculation, "ud", not detected whether by k values (MD) or by ^{27}Al NMR (Al$_{13}$).
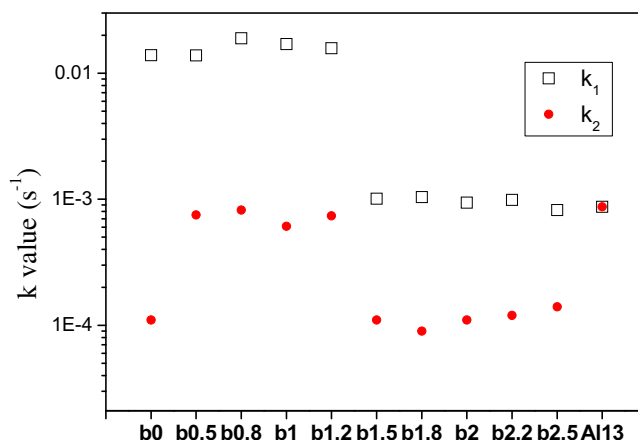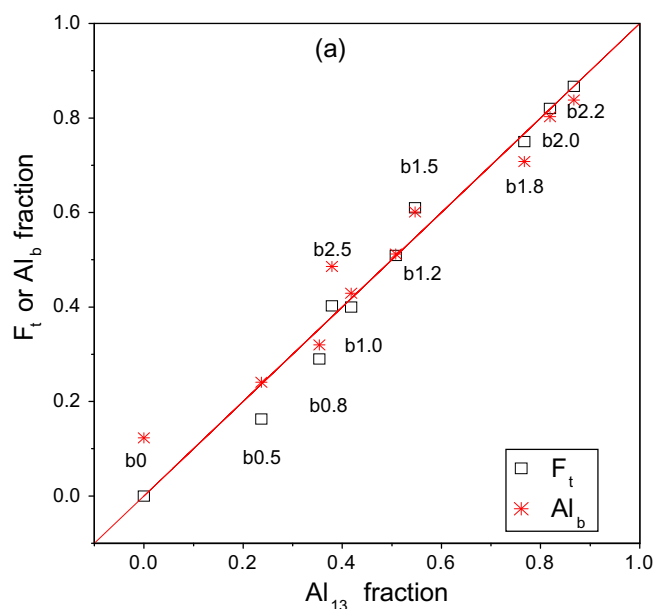

Fig. 2. Comparison of results by three methods, i.e., traditional ferron assay (Al$_b$), k-value-based ferron assay (F_t) and ^{27}Al NMR (Al$_{13}$). Samples were partially neutralized with various b values and aged a week (matured PACls); the number adjacent to each symbol indicates the b value.

nominal Al_{13} solution or PACls with b ranging from 1.0 to 2.2, all the analyses yielded virtually identical estimates of $[Al_{13}]$. The dominant species with typical kinetic values around 0.001 s^{-1} is responsible for the phenomenon. Calculated from the k values, the reaction time around 2 h is required to complete the reaction for Al_{13}–ferron system, which is just the cutoff time selected to determine the Al_b fraction in traditional ferron assay [23]. Only when the sample mainly consists of Al_{13}, $F_t = [Al_b]$. The case is different as $b = 0$, where $[Al_b] = 16\%$, but no moderate k value presents, leading to $F_t = 0$, which is well consistent with the result of ^{27}Al NMR in that $[Al_{13}] = 0$. Generally, the fraction assayed by traditional ferron method is higher than that assayed by k evaluating method. It is understandable for that the absorbance in any cutoff time is an admixture of various species other than the one to be analyzed.

3.2. Application in short-term aging in slow neutralization

The absorbance function with colorimetric time for the freshly neutralized aluminum solution with $b = 2.2$ derived from slow neutralization is plotted in Fig. 3. The shape of curves at different aging phase exhibit no evident differences except that the initiate absorbance (at $t = 60$ s, A_{60}) decreases with aging, i.e., $A_{60} = 0.0946$, 0.0756, 0.0735, 0.0618 for aging of 0 h, 6 h, 12 h and 65 h, respectively. A_{60} is used to infer Al_a in traditional ferron assay, which means Al_a transform into Al_b with aging herein. Fig. 4 shows the results derived from k-value-based ferron assay. The rapid k value (k_1) decreases sharply within 10 h. Thereafter, it drops into the range of 0.001–0.0015 s^{-1} (Fig. 4a), just the characteristic k value of Al_{13}, implying the presence of Al_{13}. As aforesaid, the fraction of this species corresponding to this value is denoted as F_t. As shown from Fig. 4b, the F_t is virtually close to Al_{13} fraction derived from ^{27}Al NMR analyses in the whole aging duration, which proves the success of the modified ferron assay. Al_b fraction obtained by traditional ferron assay is always larger than Al_{13} or F_t, especially at initial stage where Al_b accounts for 68% of total Al, whereas Al_{13} accounts for 44% and F_t accounts for 40% of the total Al. Al_b increases with aging rapidly and Al_b reaction gets equilibrium in hours, with a plateau value of 77% (Fig. 4b), but Al_{13} is continuously growing within decades of hours. Obviously, the formation of Al_{13} in the short-term aging is easily masked by the Al_b analysis. Notably, the k_1 value of 0.0032 s^{-1} obtained from the sample quickly after neutralization is a little bigger than the characteristic k value of Al_{13}, but much smaller than that of oligomer. However, this spe-
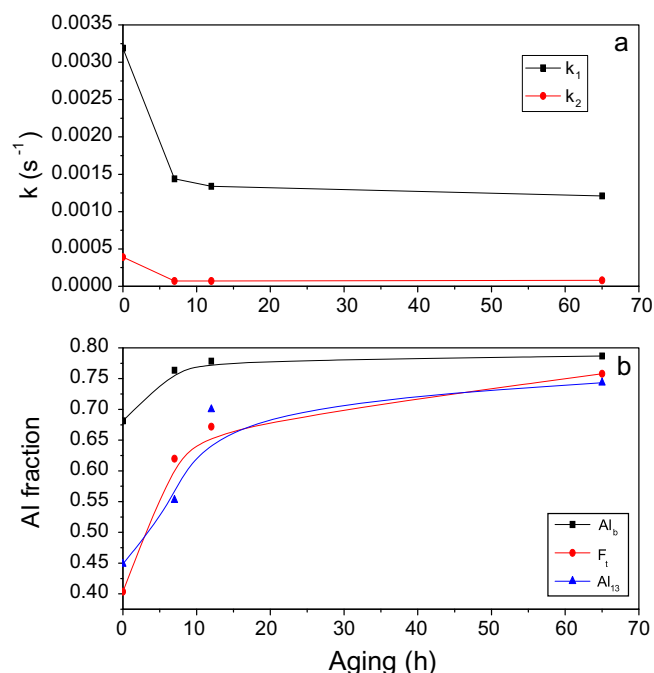
Fig. 4. Nonlinear regressions of data from timed colorimetric experiments on the same sample as Fig. 3. (a) k values vs. aging, (b) Al fraction vs. aging.

cies can be detected by ^{27}Al NMR spectroscopy, implying that the species has the similar structure of Al_{13}, i.e., Al_{13}-like, its structure could be inferred consisting of a central four-coordinated AlO_4 tetrahedron and uncompleted four surrounding trioctahedral OH–Al units. Bertsch [1] has assumed that Al_{13}-like structure might be contained in the precipitation formed in rapidly neutralized aluminum solutions and would be dissolved upon heating. The central four-coordinated AlO_4 tetrahedron results to a peak at 62.5 ppm in the ^{27}Al NMR spectroscopy, but the surrounding trioctahedral OH–Al units might not complete to form Al_{13} and could not be detected by the NMR analysis. The content of Al_{13} is obtained from the 13 times of the integrated intensity of the central AlO_4 units at 62.5 ppm by Al NMR method [8]. Treating Al_{13}-like as Al_{13} to achieve the quantitative estimate may lead to an erroneous result on the observation that Al_{13} fraction is a little higher than F_t fraction in the initial stage.

3.3. Application in short-term aging in instantaneous neutralization

Unlike the slow neutralization, the plots of sample prepared by instantaneous neutralization are more erratic in the short-term aging (Fig. 5). Only after 8 h of aging, the plot exhibits the typical shape of slow neutralization. The curve for aging of 22 days behaves the same as matured PACl derived from slow neutralization. The more insight information can be obtained by the nonlinear regression method. The rapid reaction rate, k_1 is much higher at initial aging than the later aging stage (Fig. 6). At initial aging the value of 0.0087 s^{-1} should be assigned to the oligomer; at later aging the value around 0.0015 s^{-1} should be assigned to Al_{13}. Therefore, we can conclude that Al_{13} is absent and it is replaced by the oligomer after neutralization, the conclusion is also confirmed by the NMR method since no Al_{13} was detected by the NMR analysis [21]. The oligomer and precipitates disappear with time, accompanied with the continuous formation of Al_{13} within 8 h of aging.

The natures and solubility of Al precipitation products played vital roles in the subsequent formation of Al_{13}. During the neutralization, localized high alkalinity at the point of NaOH mixing
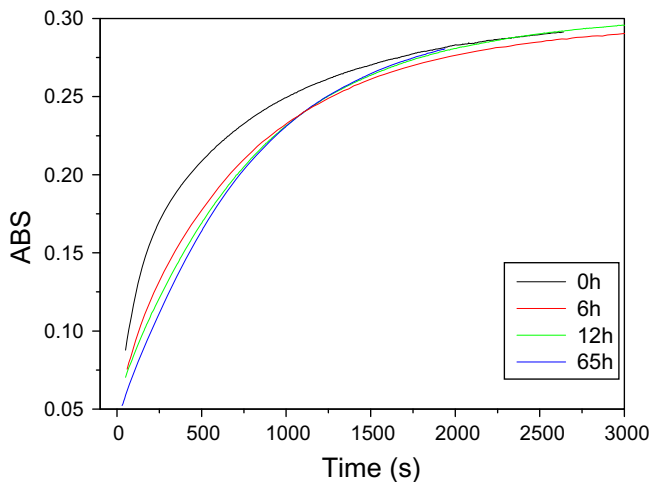

Fig. 3. Timed colorimetric analysis of PACl (0.025 M Al) with $B = 2.2$ allowed to react for various aging period quickly after the end of slow neutralization at rate of 0.5 ml min^{-1}.
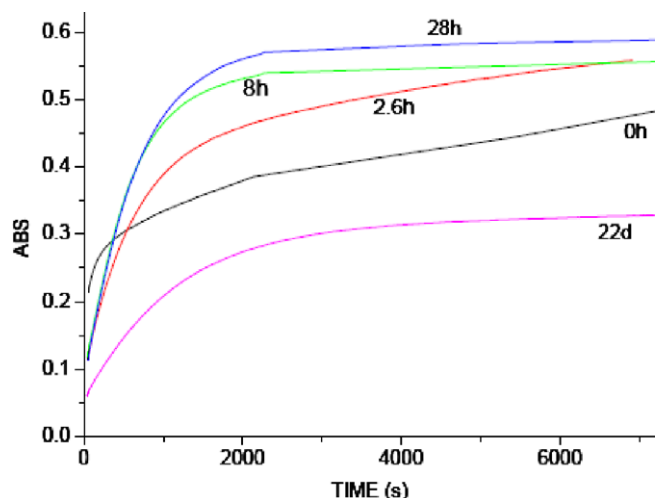
Fig. 5. Timed colorimetric analysis of PACl solution (0.1 M Al) with $B = 2.2$ allowed to react for various aging period quickly after the end of instantaneous neutralization with NaOH.
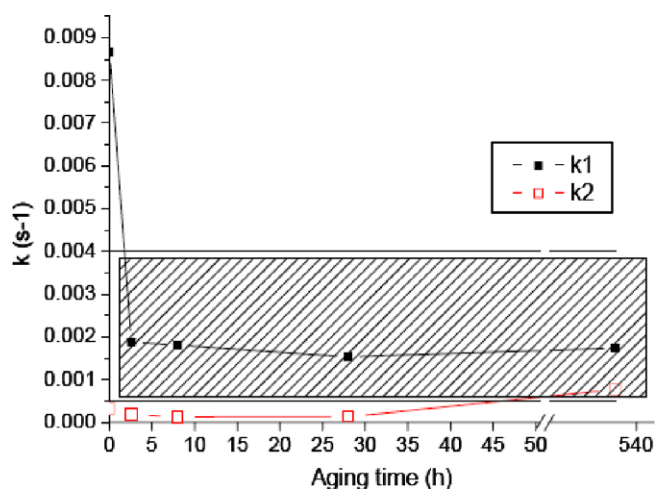

Fig. 6. Nonlinear regressions of data from timed colorimetric experiments on the same sample as Fig. 5.

is unavoidable. The localized high alkalinity has a tendency to pull Al^{3+} and OH^- ions together, giving rise to the formation of "clusters". Most clusters, however, are unstable and rapidly dissociate into monomers and oligomers upon rapid stirring. The formation and rearrangement of Al_{13} would then take place in this process because a critical degree of super saturation had been reached [21,27]. The intermediate precipitate could transform into Al_{13} through a rearrangement of complex composed of 13 Al nucleuses [21,28]. Generally, the rearrangement of the precursor of Al_{13} is the limited reaction in Al_{13} formation and it could be monitored in slow neutralization. But if the rate of neutralization is big enough, the "cluster" then agglomerate to form amorphous precipitates, the dissociation of the amorphous precipitates will delay the subsequent rearrangement if the neutralization rate is too high, thus the oligomer could be detected in the instantaneous neutralization. Furthermore, if the conditions are inappropriate, e.g. high basicity, fast rate of neutralization and gentle mixing, large amounts of the cluster is difficult to dissociate into oligomer, and they might reach the critical size and structure of nuclei for $Al(OH)_3$ crystallization. Thus the Al_{13} yields are reduced.

3.4. Comparison between Al_b and Al_{13}

Traditionally, Al_b is obtained by the cutoff time from 1 to 120 min, and it is practically used to represent the Al_{13}. However, Al_b fraction differed from Al_{13} significantly at the initial stage of aging (Fig. 4b). Al_b is rather an operational definition than a chemical definition; accordingly, it should be regarded as admixture of polymeric species. Using k-value-based ferron assay, the constituent species in Al_b and the weights of these species can be identified. For example, as for slow neutralization, Al_b at initial stage consists of Al_{13}-like and the less reactive polymer with k_2 value, accounting for 40% and 31% of total Al, respectively. Calculated from the k values, i.e., $k_1 = 0.00319$ and $k_2 = 0.00039$ s^{-1} herein, the former has completed reaction with ferron while the latter has reacted 93% with ferron within 2 h, the weight of each polymer then is ascertained 100% and 93%, respectively. And the mixture of these two polymers account for 68% of total Al concentration, just the same as Al_b content. As for instantaneous neutralization, Al_b at initial stage consists of oligomer with k_1 value of 0.0087 s^{-1} and the polymer with k_2 value of 0.00032 s^{-1}, accounting for 17% and 38% of total Al, respectively. The former reacts completely within 1 h and 40% in 1 min, the latter reacts with ferron 90% in 2 h, therefore 60% of the oligomer and 90% of the latter make Al_b account for 44% of total Al concentration. Obviously, no Al_{13} is included in Al_b in this case. Although the trend that Al_{13} continuously forms during the aging is evident, it is difficult to be observed by Al_b evaluation.

Al_{13} concentration increases with time during the short-term aging. After aging for at least 3 days, the OH–Al solution with $b = 2.2$ is predominated by Al_{13}. Other less reactive polymers decreases with time in both quantity and k value, which makes less contribution on the Al_b fraction analysis. Al_{13} is the predominant component in the mixture of Al_b and hence, Al_b can be regarded as Al_{13}. As aforesaid, it is tenable in nominal Al_{13} solution and "matured" PACls with b ranging from 1.0 to 2.2, all the analyses yielded virtually identical estimates of Al_{13} (Fig. 2). It is meaningful to understand the different behaviors of coagulation with aluminum-based coagulants, such as PACl and alum.

4. Summary

Using nonlinear least square analysis, three regular k values can be achieved and correlate well with the structure of polymeric Al–OH complexes in partially neutralized aluminum solution. Moreover, the moderate reaction kinetics around 0.001 s^{-1} being ascribed to Al_{13} polycation can be confirmed by ^{27}Al NMR spectrum.

The modified ferron assay based on k value is capable of analyzing the rapid transformation in fresh partially neutralized aluminum solution. Using k-value-based ferron assay, Al_{13} is found continuously growing in quantities during the short-term aging. Al_{13} is transformed from the Al_{13}-like formed in slow neutralization. Neutralization rate would influence the formation of Al_{13} greatly. When the rate of neutralization is high enough, Al_{13} formation would be delayed by the formation of amorphous precipitate, which would then dissociate into oligomers, Al_{13}-like and Al_{13} by sequence.

The operational cutoff of Al_b masks the insightful information of Al_{13} formation during the short-term aging. Al_b can only be regarded as Al_{13} if the PACl solution with optimum b value has aged for at least 3 days insuring that Al_{13} forms completely and becomes the predominant species in the solution.

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