Effect of aging condition on species transformation in polymeric Al salt coagulants

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Effect of aging time and aging temperature on the transformation process of Al species in hydroxyl Al solutions were analyzed by Ferron assay and \textsuperscript{27}Al NMR spectroscopy with the help of analysis results of pH, turbidity and morphology of samples. Owing to the high chemical energy provided by elevated temperature, aging temperature exerted greater effect on the transformation of polymers than aging time. Elevation of aging temperature enhanced the transformation rate of various Al species in solution. Polymerization or hydrolysis of monomers in solution was not detected under various aging conditions. Polymeric Al species with non-Keggin structure (e.g., hexameric ring structure) less stable than Keggin-Al\textsubscript{13}. The decomposition of Al\textsubscript{13} only occurred at higher aging temperature. The coexistence of oligomers affected the transformation of Al\textsubscript{13}. Morphology and species composition of colloidal Al species transformed from Al\textsubscript{13} were different from those from polymeric Al species with non-Keggin structure. Changes in pH, turbidity and morphology of samples agreed well with the distribution of Al species obtained by Ferron assay and \textsuperscript{27}Al NMR spectroscopy.

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1. Introduction

Hydroxyl Al polymeric coagulants have been widely used in water plants throughout the world. Various species in hydroxyl Al solution often exhibit different performance in coagulation process. An in-depth investigation on the nature of different hydroxyl Al species in Al salt coagulants enhances the basic understanding of coagulation mechanism and the development of inorganic polymer flocculants as well [1,2].

The distribution and transformation of Al species existing in Al salt coagulants often vary with the synthesis condition and aging condition. Therefore, much attention has been paid to the optimization of synthesis condition to improve the content of high performance species in coagulants in the past few decades [3–6]. Few studies have focused on Al species transformation under various aging conditions. Moreover, most of these studies only put emphasis on the effect of aging time on the transformation process of polymeric Al species [7–9]. Since synthesis temperature has been proved to have great effect on the content of high performance species in Al salt coagulants, aging temperature might also affect the further decomposition or polymerization of these species in solution during the aging period [10–13]. Thus it is necessary to analyze the changes of Al species in Al salt coagulants under various conditions to obtain the optimal storage and application conditions for liquid coagulants.

Among all the species in hydroxyl Al solution, Al\textsubscript{13} with Keggin structure is often taken as the high performance species because of its high charge and large molecular [3,4,6,14]. Thus, many researchers have put emphasis on the transformation process of Al\textsubscript{13} in hydroxyl Al solution under various aging conditions [12–15]. In fact, besides Al\textsubscript{13}, some other polymeric Al species have also been proved to exist in solution by chemical calculation methods and instrumental characterization [16,17]. In our previous studies, Al\textsubscript{13} and some other polymeric Al species have been proved to coexist in hydroxyl Al solutions, especially the solutions with lower basicity [18]. Additionally, more categories of Al species have also been identified with electrospray ionization mass spectrometry (ESI-MS) by many researchers [19,20]. These species are often considered to be composed of hexameric ring structure and also play an important role in coagulation process. However, little attention has been given to the study of transformation process of these polymers under various aging conditions. Additionally, whether these co-existing species affect the transformation of Al\textsubscript{13} in solution is still lack of thorough study.

Various chemical and instrumental methods have been applied to characterize species in polymeric Al solution. However, the
transformation of Al species under various aging conditions was often discussed from the aspect of Al content obtained with $^{27}$Al NMR spectroscopy. Since every speciation method has its own deficit, the combination application of several methods might be a better pattern to characterize Al species at present [18]. Thus, solution pH and turbidity were often simultaneously discussed to help the understanding of Al speciation results obtained by some other methods [7,9,11]. Structures of precipitate were also analyzed with X-ray diffraction analysis to probe the transformation process of Al species from monomer or polymer to Al(OH)$_3$ [21]. Additionally, morphology of hydroxyl Al sample has also been used to analyze Al species in solution. However, only morphology of some precipitates separated from hydroxyl Al solution were studied by SEM [9,21]. The difference in morphology of hydroxyl Al solutions aged at various conditions has not yet been investigated. In recent years, atomic force microscopy (AFM) has been increasingly applied to study morphology of materials. This method has little effect on the transformation of Al species and might represent the original status of Al species in solution. The analysis results of AFM might also help the explanation of Al species obtained with some other methods [22]. Thus, the combination application of several methods might provide more information for Al species in solution.

In this study, two sets of hydroxyl Al solutions with various OH/Al molar ratios ($B$ values) were prepared to study the effect of aging time and aging temperature on the transformation of various Al species in Al salt coagulants. Changes in solution pH, turbidity and morphology have also been simultaneously discussed to help the understanding and identification of hydroxyl Al transformation process obtained with Ferron assay and $^{27}$Al NMR spectroscopy. Special attention would be paid to the transformation process of polymers with hexameric ring structure during the aging period.

2. Materials and methods

2.1. Preparation of hydroxyl Al solutions

All reagents used in this study were analytical grade chemicals. Deionized water was used to make all solutions. Under rapid stirring, a calculated volume of 0.5 M AlCl$_3$ solution was neutralized slowly with 0.5 M NaOH with a titrometer (665 Dosimat, Metrohm, Switzerland) at 25 ± 0.1 °C. The volumes of NaOH added varied with the target $B$ values (OH/Al molar ratios). $B$ values of 0, 0.5, 1.0, 1.5, 2.0 and 2.5 were chosen in this study. The resulting solutions (usually called polyaluminum chloride, PAC) obtained were denoted as PAC05, PAC10, PAC15, PAC20 and PAC25 respectively [23]. The final concentration of total Al (Al$_T$) in every sample was adjusted to about 0.1 M, and their exact concentrations were identified by ICP–OES (PerkinElmer Co. USA).

Two sets of hydroxyl Al solutions were prepared separately with the method mentioned above. One set was preserved for aging under three different temperatures of 4 °C, 25 °C, and 60 °C for 180 days respectively. The other set were preserved at 4 °C for different periods of time (0 day, 60 days, 150 days and 480 days). To help the explanation of the distribution and transformation of Al species in every sample, turbidity was measured using Hach 2100N Turbidimeter and solution pH was measured by pHS-3C (Shanghai, China).

2.2. $^{27}$Al NMR spectroscopy

500 MHz $^{27}$Al NMR (Brookhaven Co., U.S.A.) was used in this study. The instrumental settings and experimental conditions were: NS = 128, P1 = 20 μs, PL1 = −3 dB. Solvent: D$_2$O, and T = 298 K. The inner standard was 0.05 M Al(OD)$_4$ solution and its chemical shift is 80 ppm. The signals near 0, 3–4 and 62.5 ppm represent mononuclear Al (Al$_{1m}$), trimeric Al (Al$_3$) and the tetrahedral Al(O)$_4$ core (and 1/13 content) of Al$_{13}$ ([AlO$_2$Al$_{12}$(OH)$_{24}$(H$_2$O)$_{12}$])$^{7+}$ respectively. The concentration of each species was determined by the ratio of the integrated intensity of its corresponding peak to that of Al(OD)$_4$− at 80 ppm. The Al$_{13}$ content was calculated by multiplying the Al(OD)$_4$ concentration by 13. The amount of the undetectable species (Al$_{1m}$) was obtained by subtracting the sum of the detected Al species from the total Al (Al$_T$) concentration.

2.3. Ferron assay

The detailed procedures for the preparation of Ferron colorimetric solution can be found in Wang et al. [24]. For the speciation of each sample, 5.5 ml Ferron colorimetric solutions were firstly transferred into a graduated glass tube and diluted to 25 ml. Then, 20 μl test Al solutions were added to the tube and the reaction time was recorded simultaneously. After homogeneous mixing, the reacting sample was quickly added to a 1 cm quartz cell. The timed absorbance measurements, using a UV–vis 8500 spectrophotometer (Tianmei Co., China), were carried out at 366 nm after 30 s and recorded for further 7200 s. It was operationally divided that the first 30 s absorbance as Al$_{1m}$ (mononuclear Al), and 30 s to 7200 s as Al$_b$ (reactive hydroxyl Al polymers), then Al$_c$ (colloidal or precipitated Al species) was obtained by total Al (Al$_T$) minus Al$_b$ and Al$_c$.

2.4. Atomic force microscopy (AFM)

Nanoscope IIIa Multimode Scanning Probe Microscopy Instrument (Digital Instruments, Santa Barbara, CA) used in this study was equipped with an E-scanner. The images were acquired by using the retrace signal in the tapping mode. The silicon cantilevers were employed with 125 μm in length and 300 kHz in frequency (Nanprobe, Model RTESP14). The scanning speed and the loop gain factors varied during the imaging process. Line scan rates were set typically at 1.0 Hz. With Nanoscope Image analysis software, section analysis of images was conducted to measure the size of particles and their aggregates.

3. Results and discussion

3.1. Effect of aging temperature on transformation of Al species

One set of hydroxyl Al solutions with different OH/Al ratios ($B$ values) were aged at various temperatures for 180 days. Al species in these samples before and after aging were characterized with Ferron assay (Fig. 1) and $^{27}$Al NMR spectroscopy (Fig. 2). There exists a good consistency between the changes of Al species (i.e., Al$_{1m}$, Al$_b$ and Al$_c$) in Ferron assay and the changes of species (i.e., Al$_{1m}$, Al$_{13}$ and Al$_{1m}$) obtained with $^{27}$Al NMR spectroscopy. The content of Al$_c$ in Ferron assay decreased obviously with the increase of Al$_b$ and Al$_c$ until the $B$ value of samples arrived at about 2.0. For the samples with bigger $B$ value, the changes in the content of Al$_c$ were in agreement with those of Al$_b$, but in conflict with those of Al$_c$. Similar distribution of various Al species (i.e., Al$_{1m}$, Al$_{13}$ and Al$_{1m}$) in the samples can also be observed with $^{27}$Al NMR spectroscopy. With the increase of $B$ value, the dominant species in Al samples changed from monomer, Al$_b$ or Al$_{13}$ and finally to colloidal Al species. From the difference in Al speciation results between Ferron assay and $^{27}$Al NMR spectroscopy, it can be inferred that some other polymers, besides Al$_{13}$, also exist in hydroxyl Al solutions. These polymers are often classified as Al$_b$ or Al$_c$ in Ferron assay, but can not be detected with $^{27}$Al NMR spectroscopy [18,21,24]. With the addition of strong base into Al solution, these polymers changed from oligomers to high polymers and also finally transformed into Al(OH)$_3$ in these samples. Thus, at least five categories of Al species (i.e., monomer,
oligomer, $A_{13}$, high polymer and colloidal Al species) existed in polymeric Al solutions.

Transformation process of Al species in solutions obviously varied with $B$ values when aging at different temperatures (Figs. 1 and 2). For the samples with $B \leq 2.0$, the content of $A_{13}$ in Ferron assay slightly decreased with the increase of aging temperature, but the changes in the content of $A_{lm}$ in $^{27}$Al NMR spectroscopy exhibited an opposite distribution. The main reason might be well explained by the speciation difference between $A_{ls}$ in Ferron assay and $A_{lm}$ in $^{27}$Al NMR spectroscopy. Many previous studies have proved that part of oligomers react with Ferron reagent at a relative fast rate and are often classified as monomers (i.e., $A_{ls}$) in Ferron assay [8,24]. Unlike the $A_{13}$ species of Keggin structure, these oligomers often do not have Keggin structure and are undetectable with $^{27}$Al NMR spectroscopy. As the hydroxyl Al speciation results proposed by Singhal and Seichter, these species might be composed of six member ring structure [5,16]. It can also be inferred from above experimental results that these species might be formed without strict synthesis condition and thus could decompose easily into monomers or polymers with lower polymerization degree. Since no obvious differences in the content of $A_{ls}$ or $A_{13}$ have been detected between the original samples and the samples aged at 4 °C for 180 days, no transformation of $A_{ls}$ or $A_{13}$ happened during the aging period. Thus, the decomposition of oligomers in samples have resulted in the increase of $A_{lm}$ and the decrease of $A_{ls}$.

In the samples with $B > 2.0$, small amount of monomers or oligomers can be detected. The obvious increases in the content of $A_{ls}$ and $A_{13}$ were mainly ascribed to the decomposition of $A_{ls}$ or $A_{13}$. Since little of $A_{13}$ have been detected in the samples with $B$ values over 2.0 (Fig. 2), some other polymers in $A_{ls}$ should have transformed into colloidal species and accounted for the increases of the $A_{ls}$ and $A_{13}$ content in Figs. 1 and 2.

Aging temperature greatly affected the transformation of $A_{13}$ in solution. Although very small amount of $A_{13}$ decomposed at 4 °C in the aging period of 180 days, obvious decreases in the content of $A_{13}$ in samples aged at higher temperature could be observed (Fig. 3). When the aging temperature was elevated to about 60 °C, even no $A_{13}$ could be detected with $^{27}$Al NMR spectroscopy. Perhaps the increase of aging temperature could provide chemical energy for some ligands in solution to bombard the $A_{13}$ molecular and resulted in the decomposition of Keggin structure of $A_{13}$ [25–28]. Since no obvious increases of monomers were observed in
the samples aged at higher temperatures for 180 days, the decrease of Al$_{13}$ content should have led to the formation of high polymers or colloidal species (Al$_c$ or Al$_{un}$) in samples.

It can also be drawn from Figs. 1 and 2 that the elevation of aging temperature enhanced the transformation rate of species in solution. No significant changes in the speciation results can be found between the original samples and the samples aged at 4°C for 180 days, but higher aging temperature (i.e., 25°C and 60°C) resulted in significant decrease in the content of various Al species in these samples after aged for the same period of time.

3.2. Effect of aging time on Al species transformation

In order to investigate the effect of aging time on the changes of Al species in solution, another set of polymeric Al samples were aged at 4°C for different days (0 day, 60 days, 150 days and 480 days) and Al species in the aged samples were analyzed with Ferron assay.

Compared with the speciation results of the samples mentioned above, no significant difference in the distribution of Al species were observed between the samples aged at 4°C for different days (Fig. 3). As far as B values were concerned, aging time exerted greater effect on the transformation of Al species in samples with lower B values. These samples often have higher content of oligomers. Unlike oligomers mentioned in previous sections, most of oligomers observed in this set of samples might have higher polymerization degree, which can be inferred from the difference in the contents of Al$_b$ and Al$_{13}$ in these samples. These species should also be composed of hexameric ring structure and have been classified as Al$_b$ in Ferron assay [8,18]. As indicated in Fig. 2, another main species (i.e., Al$_{13}$) detected in Al$_b$ were often difficult to decompose at the aging temperature of 4°C within 180 days. The decreases of Al$_b$ and the increases of Al$_{13}$ in Fig. 3 should also be ascribed to the decomposition of oligomers in solution. Since aging time can not provide enough chemical energy to promote Al$_{13}$ decomposition, aging time exerted greater effect on the transformation of oligomers than Al$_{13}$. The polymerization or decomposition reactions only occurred between polymers with hexameric ring structure during the aging process with low aging temperature.

It can be seen from Fig. 3 that the transformation pattern of Al species in the former aging period was distinct from those in the later aging period. In the first 60 aging days, oligomers in samples might have further polymerized into high polymers or colloidal Al species, and thus led to the decrease of the Al$_b$ and Al$_{13}$ content and the increases of Al$_c$ content in Fig. 3. In the longer aging period (150–480 days), the decomposition of high polymers became the dominant transformation pattern of Al species. High polymeric Al species in the Al$_c$ fraction decomposed into low polymers. Meanwhile, part of low polymers (e.g., oligomers) also decomposed into monomers. As for the samples with lower B values, the decomposition of oligomers resulted in the further decrease of Al$_b$ content and the increase of Al$_c$ content. However, the increase of Al$_b$ in samples with higher B values might be ascribed to the decomposition of high polymers in the Al$_c$ fraction.

Perhaps, chemical energy in the original solution encouraged the polymerization reaction of polymers in the former aging period. With the energy in solution was exhausted and no external energy (e.g., elevating the aging temperature) was added into samples, part of the metastable polymers in solution began decomposition reactions. Since the Al$_{13}$ species has Keggin structure, its formation or decomposition often need high energy. Therefore, the decomposition reactions in long period of aging time should only occur to polymers with hexameric ring structure which may be formed with relative low chemical energy [27,28]. This can also be easily inferred from the changes in Al speciation results of various Al species in the two sets of samples. The main chemical reaction for Al species aged at high temperature is polymerization. However, Al species aged at low temperature often underwent polymerization first and then decomposition later.

Transformation rate of Al species varied with aging time. Significant changes in the content of various Al species can be observed in the initial aging period but the content of various Al species changed more slowly in the longer period of aging time (e.g., 60–480 days) (Fig. 3). The phenomena might agree well with the conclusion deduced form the difference in transformation pattern of Al species between the former and the later aging period.
On the whole, polymerization reactions of monomers in solution have not been deduced from the above experimental results. Aging conditions (i.e., aging temperature and aging time) only affected the transformation of metastable polymers (e.g., oligomer, Al$_{13}$ and high polymer) in solution. The decomposition or polymerization of these metastable polymeric species resulted in the changes in the content of monomers or colloidal Al species. These species are all composed of hexameric ring structure and can easily transform into each other during the aging period.

### 3.3. Changes in pH values of polymeric Al solutions

Transformation of hydroxyl Al species often affects solution pH and turbidity. On the contrary, the changes of solution pH and turbidity can reflect the polymerization or decomposition process of Al species in solution [7,11]. Thus the changes in solution pH and turbidity were also analyzed simultaneously to help the explanation of Al species transformation under various aging conditions.

Table 1 shows solution pH values of the original samples and the samples aged at various temperatures (4°C, 25°C and 60°C) for 180 days. It can be seen from the table that aging time and aging temperature both have significant effect on the changes of solution pH. For the samples with $B \leq 2.0$, significant increases in pH values were observed after aged at 4°C for 180 days. Based on the Al species transformation pattern proposed in the former sections, the main chemical reaction happened in the aging process was the decomposition of oligomers, though part of oligomers also simultaneously polymerized into high polymers or colloidal species. The decomposition reaction mainly accounted for the increases of solution pH values, which was in accordance with Tai and Hsu [9]. Similar experimental results can also be observed from the changes in solution pH of the samples aged at 25°C for 180 days (Table 1). However, higher increases in solution pH were mainly ascribed to the decomposition of Al$_6$ or Al$_{13}$ in the samples.

In fact, further elevation of aging temperature to 60°C could not bring larger increases in solution pH values. Although pH values of samples aged at 60°C for 180 days were higher than those of the original samples, they were still lower than that of samples aged at 4°C and 25°C. The reason can be explained as follows: higher aging temperature provided enough chemical energy for the polymerization and decomposition of Al$_6$ or Al$_{13}$ in the samples. Compared with the polymerization process, the decomposition process of Al$_6$ or Al$_{13}$ exerted greater effect on changes of solution pH values.

It can be seen from above analysis results that the changes in solution pH values were attributable to the relative dominance of the above two processes (i.e., polymerization and decomposition). As for the samples with $B > 2.0$, almost no Al$_6$ and Al$_{13}$ were observed (Figs. 1 and 2). Al species in the samples were mainly composed of high polymers or colloidal species (Al$_6$ and Al$_{13}$). The decreases of solution pH were evidently due to the further polymerization of high polymers into colloidal Al species or gibbsite. The elevation of aging temperature promoted the further polymerization of these species and thus resulted in the obvious decrease of pH values.

### 3.4. Changes in turbidity of polymeric Al solutions

Turbidity of polymeric Al samples aged at different temperatures for 180 days were showed in Table 2. With the increase of aging temperature and aging time, turbidity of samples decreased obviously. This phenomenon might be well explained by the transformation process of various species and the difference in molecular size between them. As for the samples with $B \leq 2.0$, the decomposition of oligomers and Al$_{13}$ into monomers or lower polymers resulted in the decrease of molecular size of hydroxyl Al complex and thus lowered solution turbidity. This may further indentify the conclusion deduced in previous sections that the dominant reaction happened in samples aged at various temperatures was the decomposition of polymers (e.g., oligomers and Al$_{13}$). Similar experimental results can also be observed from the samples aged at 25°C for 180 days. Elevation of aging temperatures from 4°C to 25°C only resulted in slight increases of turbidity of samples.

As for the samples aged at 60°C for 180 days, turbidity was higher than that of the original samples and samples aged at 4°C and 25°C for 180 days. Perhaps, the elevation of aging temperature has promoted the transformation rate of Al species from oligomers and Al$_{13}$ to colloidal Al species or gibbsite. A very small amount of intermediate species formed during the transformation process. Additionally, colloidal species or gibbsite formed in the initial aging period may often act as nuclei to promote more polymers to precipitate on it [6,12]. Thus the diameter of these precipitates grew at a relatively fast rate. High content of colloidal Al species with bigger diameter accounted for the obvious increases of turbidity of samples aged at 60°C for 180 days.

On the whole, the transformation of Al species deduced from changes in solution pH or turbidity agreed well with the speciation results in Ferron assay and $^{27}$Al NMR spectroscopy. The response correlation between the changes in solution pH or turbidity with hydroxyl Al speciation might provide an indirect but efficient approach to study the transformation process of various Al species in solution. The combination application of these analysis methods could provide detailed information on the speciation results of various Al species.

### 3.5. Morphology of polymeric Al solutions

As indicated in previous sections, aging temperature often has greater effect on Al species transformation than aging time. Thus microscopic morphology of Al species in the samples aged at various temperatures (4°C, 25°C, and 60°C) for 180 days were analyzed by atomic force microscopy (AFM). With the increase of $B$ value, the microscopic morphology of samples changed gradually (results not shown). On the whole, morphology of samples in AFM changed accordingly with the variation of Al species in samples. Since morphology of samples with $B = 2.5$ were mainly observed as some amorphous precipitates, little information on Al species transformation process could be inferred from the AFM images. Thus, more emphasis has been laid on the difference between AFM images of samples with $B \leq 2.0$. Two typical groups of AFM images of samples with lower $B$ values (e.g., $B = 1.0$) and higher $B$ values (e.g., $B = 2.0$) were showed in Figs. 1 and 2.
values (e.g., $B = 2.0$) were selected to analyze the effect of aging conditions on the changes in morphology of hydroxyl Al samples.

Figs. 4 and 5 shows the AFM images of the above two groups of samples. It can be seen from the two figures that obvious differences existed between the microscopic morphology of Al species aged at different temperatures for 180 days. With the increase of aging temperature, morphology of Al species in samples with $B = 1.0$ transferred from sphere-like particle, cube crystalline, to clubbed and perforated sheet assemblies (Fig. 4). However, small difference in AFM images have been observed between samples with $B = 2.0$. Morphology of Al species in these samples changed from sphere-like particles, little sphere-like particles, to filiform-like and cypress leaf-like aggregates (Fig. 5). The changes in morphology among each group of samples should mainly be ascribed to the difference in the species composition in solution. As for the samples with $B = 2.0$, the dominant species was Al$_{13}$ and its content was over 85% in the original solution (Fig. 2). Perhaps, the relative single component resulted in the uniform distribution of particles in the morphology of Fig. 5a. Based on speciation results of chemical calculation and instrument characterization, many researchers have brought forward that the morphology of Al$_{13}$ was sphere with the diameter of 2–3 nm [29]. Thus the morphology of Al$_{13}$ observed in Fig. 5a agreed well with those in former studies. With the increase of aging temperature from 4°C to 25°C, part of Al$_{13}$ have been decomposed and polymerized into higher polymers or colloidal species, and thus resulted in the formation of filiform-like aggregates in Fig. 5b and c. After aged at 60°C for 180 days, no Al$_{13}$ can be detected in the sample and also no sphere-like aggregates can be observed. Since colloidal species has become the dominant species in the sample, the filiform-like aggregates also transformed into the cypress leaf-like aggregates.

For the morphology of samples with $B = 1.0$, greater difference in AFM images existed between the samples aged under various conditions (Fig. 4). Although Al$_{13}$ was also detected as one of the main species in these samples, the dominant Al species was mainly composed of monomers and oligomers. Some sphere-like aggregates observed in Fig. 4a also proved the existence of Al$_{13}$ (accounting for about 40%) in solution. The other aggregates observed between sphere-like aggregates might be ascribed to monomers and oligomers in solution. From the difference in morphology of the original sample (Fig. 4a) and the sample aged at 4°C for 180 days (Fig. 4b), it can be inferred that aging time also has great effect on morphology of Al species. Since no obvious changes in the content of Al$_{13}$ or Al$_{8}$ have been detected with $^{27}$Al NMR spectroscopy (Figs. 1 and 2) after aged at 4°C for 180 days, the most possible explanation for the formation of the cubic aggregates in Fig. 4b might be that the decomposition products of oligomers have co-precipitated with Al$_{13}$ to form this type of aggregates. However, the co-precipitation process has little effect on the Keggin structure of Al$_{13}$. With the increase of aging temperature, more oligomers and Al$_{13}$ decomposed and then aggregated with the remaining Al$_{13}$ to form clubbed aggregates. Perhaps, the sphere-like Al$_{13}$ provided precipitation nuclei for the decomposition products of oligomers have co-precipitated with Al$_{13}$ to form this type of aggregates. However, the morphology of Al species existed between Figs. 4d and 5d. This phenomenon might indicate that colloidal Al species in the two samples have different structure and species composition. Since the dominant species in original sample with $B = 2.0$ was Al$_{13}$, cypress leaf-like aggregates in AFM should be mainly composed of decomposition products of Al$_{13}$. These products might still have high polymerization degree but have no Keggin structure, which can be inferred form the difference in species composition with that of the sample in Fig. 4d. The perforated sheet assemblies in Fig. 4d might be mainly composed of...
gibbsite crystals which were mainly transformed from oligomers [5,12,17]. From the comparison of species composition between the original samples with $B = 2.0$ and $B = 1.0$, it can be seen that the existence of oligomers greatly affected morphology of the aged samples. Oligomers in the sample with $B = 1.0$ might transform easily into gibbsite with hexameric ring structure and thus resulted in the formation of amorphous aggregates. Although the decomposition products of Al$_{13}$ might also be observed as cypress leaf-like aggregates in the sample with $B = 1.0$, the coexistence of oligomers should destroyed the structure during the aged period in the same solution and resulted in the formation of perforated sheet assemblies in Fig. 4d. Certainly, it is also possible that the decomposition products of Al$_{13}$ have also transformed into gibbsite crystal with the existence of oligomers.

4. Conclusions

Aging temperature exerted greater effect on the Al species transformation than aging time. Elevation of aging temperature promoted transformation rate of various Al species in solution. Polymerization of monomers in solution was not detected under various aging conditions. Polymers with hexameric ring structure are less stable than Al$_{13}$ of Keggin structure. The analysis results of the changes in solution pH, turbidity and morphology can help the explanation of Al speciation results obtained with Ferron assay and $^{27}$Al NMR spectroscopy.

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