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Colloids and Surfaces A: Physicochemical and Engineering Aspects

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Coagulation of silica microspheres with hydrolyzed Al(III)—Significance of Al_{13} and Al_{13} aggregates

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ARTICLE INFO

Article history:

Received 19 February 2008
Received in revised form 1 July 2008
Accepted 19 July 2008
Available online 30 July 2008

Keywords:

Al_{13}
 $[Al_{13}]_n$ aggregates
Species transformation
Coagulation

ABSTRACT

Coagulation of silica microspheres by Al coagulants with high basicities was investigated at the constant pH 6.5. Aluminum coagulants were consisted of Al_{13} and $[Al_{13}]_n$ aggregates, with OH/Al ratios of 2.46, 2.6 and 2.8, respectively. The species distribution and transformation of the coagulants upon aging were studied by using ferron assay and ^{27}Al NMR. In addition, size distribution and morphology of coagulants were also examined by PCS and SEM. The results showed that the tridecamer Al_{13} and outer sphere aggregated $[Al_{13}]_n$ were the dominant species for coagulants aged weekly, while sol–gels or precipitates were formed upon further aging. Accordingly, charge neutralization, electro-patch coagulation and bridge aggregation were proceeding for particle aggregation at lower aluminum concentration. Besides other three mechanisms, sweep flocculation was also involved at higher dosages. Hence, chemical interaction between particles and coagulants evolved from adsorption to surface precipitation for aluminum polycations by virtue of species transformation.

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1. Introduction

Hydrolyzing metal salts such as alum are widely used as coagulants in the water treatment for years. Recently, inorganic polymer flocculants (IPFs), e.g. polyaluminum chlorides (PACl), are already commercially available around the world. Chemical aspects of coagulation have been studied extensively and interpreted in terms of coordination requirements of the metal ions [1], and surface precipitation coupled with charge neutralization [2,3]. With nuclear magnetic resonance (NMR) and small angle X-ray scattering (SAXS), aluminum polycation $Al_{13}(O)_4(OH)_{24}^{7+}$ is thought to be the most effective species of PACl owing to its high positive charge and Keggin structure [4–10]. Although a model has tried to interpret the coagulation mechanism of PACl quantitatively [11], additional improvements are needed to understand the coagulation process comprehensively through the coagulant speciation.

Many studies have shown that the formation and decomposition of Al_{13} depend critically on the pH, mineral ions and organic matter [12–18]. It is generally accepted that the Al_{13} remains stable at the optimal pH (~5) and relative low concentration ($<10^{-3}$ M) in the absence of organic substances and minerals. The aggrega-

tion and precipitation of Al_{13} complex occurs when pH >6 [18]. Below pH 6, the positive charge of 7+ maintains and aggregation is avoided [16]. Investigations suggested that the local range order of Al_{13} would not be significantly modified upon dilution and pH shock [10], while structural changes were observed in presence of humic material at different pH values [8]. However, a few studies have reported that a major rearrangement of Al_{13} must take place when hydrolysis advanced to OH/Al ratio of 3.0 [19–21]. The tridecamer was suggested to transform from the gel with open fractal structure to the bayerite hydroxide upon base hydrolysis and aging [19,20]. Exact definition of such transformation is still desired for the full application of the aluminum salt. As PACl exhibits coagulation efficiency over a wider temperature and pH range [4,6–8], it is important to unveil the coagulation mechanisms induced by its active species, i.e. Al_{13} . For this reason, hydrolysis aluminum species need to be separated and investigated during coagulation.

The aim of this paper is to describe the nature of the transformed aluminum polycations, i.e. the Al_{13} and Al_{13} aggregates with high basicities (OH/Al = 2.6, 2.8), and their interactions with silica microspheres during coagulation. Particle aggregation induced by various species were investigated as a function of aluminum concentration at pH 6.5. Consequently, coagulation mechanisms are discussed by virtue of species distribution combined with jar test results in this study. Better understanding is extended on the effects of species transformation accordingly.

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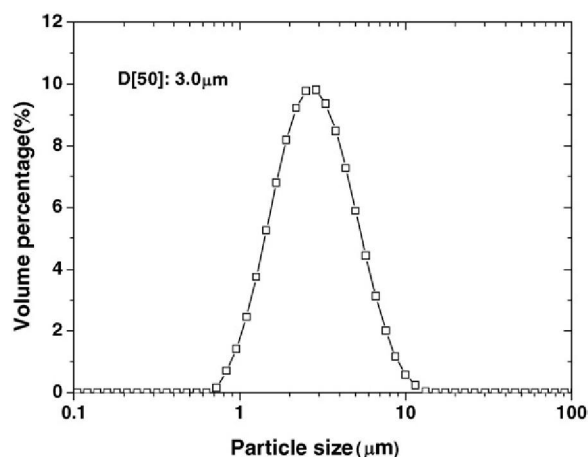


Fig. 1. Size distribution of silica microspheres measured by Mastersize 2000.

2. Materials and methods

2.1. Silica microspheres and coagulants

All the chemicals were analytical grade and experiments were conducted at room temperature ($22 \pm 3^\circ\text{C}$).

The micro-sized silica spheres were used as model particles to prepare the working suspension because of their strong negative charge and simple morphology as our previous study reported [22]. Furthermore, a narrow size distribution of silica suspension was also indicated by static light scattering techniques (Malvern, Mastersizer 2000, UK) as Fig. 1 shows. The mean diameter of silica particle was $3.0\ \mu\text{m}$.

The Al_{13} was prepared by $\text{SO}_4^{2-}/\text{Ba}^{2+}$ displacement method from the stock PACI solution as shown in [23]. The concentration and OH/Al ratio (B values) of PACI solution were fixed to $0.1\ \text{mol/L}$ and 2.3 , respectively. A batch of Al_{13} was stocked to prepare Al_{13} aggregates with a slow base titration method. According to the target B values (2.6 and 2.8), certain amount of NaOH ($0.1\ \text{M}$) was titrated slowly ($0.1\ \text{ml/min}$) to Al_{13} solution under rapid stirring. The final aluminum concentration of all the prepared coagulants was fixed to $0.05\ \text{mol/L}$.

2.2. Size distribution and morphology of coagulants

The photon correlation spectroscopy (PCS) or dynamic light scattering was used to characterize the size of coagulant, by BI-200SM (Brookhaven, USA) instrument equipped with a BI-9000AT digital correlator. The instrument was operated at a $532\ \text{nm}$ wavelength with vertical polarization. Before measurement, all the samples were filtered twice using $0.45\ \mu\text{m}$ membrane (Millipore, USA). The instrument alignment and size determination were carried out as Wang et al. described [24].

Scanning electron microscopy (SEM) was used to examine the morphology of aggregated coagulants by a HITACHI S-570. The samples were prepared on the copper tab of aluminum pin stub. A drop of coagulant solution was placed on and air-dried at room temperature. In addition, the prepared substrate was sputter coated with gold in case of charging. The working distance and acceleration voltage are $8.0\ \text{mm}$ and $5.0\ \text{keV}$, respectively.

2.3. Speciation and zeta-potential analysis

All the coagulants were examined with ferron assay and solution ^{27}Al NMR spectroscopy at different ages. Species distribution

was characterized with ferron assay divided as Al_a , Al_b and Al_c [25]. The Al_{13} was analyzed by a $500\ \text{MHz}$ ^{27}Al NMR spectroscopy (Brookhaven, USA). The sequences, recording method, and Al_{13} content calculation were described earlier [22], and will not be repeated.

The electrical property of coagulant was investigated by Zeta-sizer 2000 (Malvern, UK). It should be noted that difficulties still exist to directly measure the zeta-potential of coagulants, though sol-gels formed for aluminum solutions with high basicities. In this regard, the same method as measuring the zeta-potential of coated silica particle was followed [22], and $100\ \text{mg/L}$ of silica suspension was used as the carrier and excess coagulants of $2 \times 10^{-4}\ \text{mol Al/L}$ were added to ensure completely coverage of particles.

2.4. Jar test

Coagulation test was performed by a JTY laboratory stirrer (Daiyuan Company, Beijing). The working suspension was prepared by adding silica microspheres into deionized water with $0.001\ \text{M}$ NaHCO_3 and $0.01\ \text{M}$ NaNO_3 , providing the alkalinity and ionic strength buffer, respectively. Jar test was taken in a $500\ \text{ml}$ suspension and followed the procedure as: $2\ \text{min}$ rapid mixing ($200\ \text{rpm}$), $10\ \text{min}$ slow mixing ($40\ \text{rpm}$) and $15\ \text{min}$ sedimentation. The zeta-potential was measured after rapid mixing, and the residual turbidity was measured separately with HACH 2100N turbid meter after sedimentation. Suspension's pH was adjusted with HCl ($0.05\ \text{M}$) or NaOH ($0.05\ \text{M}$) before coagulant injection, and was not readjusted as pH drop resulting from hydrolysis can be neglected. The floc size distribution was measured in situ by small angle light scattering (Mastersizer 2000, Malvern, UK). The instrument determined the scattered intensity at measuring angles ranging from 0° to 46° with a He-Ne laser light of $632.8\ \text{nm}$. An integration time of $40\ \text{s}$ per curve was chosen to compromise measuring speed and data quality. The size information of aggregated particles was monitored during coagulation using standard $1\ \text{L}$ glass beaker, and performed the same procedure as jar test.

3. Results

3.1. Coagulant size distribution and morphology

Size determination of coagulant remains to be uncertain due to the polydispersity fluctuations, hydrodynamic interactions and sample contamination, though some pioneer work had been reported [24]. However, the speciation transformation of coagulant can also be reflected through the size information. For the IPFs such as PACI, colloidal aluminum species formed with increasing basicity and could be detected by PCS. Fig. 2 shows the size distribution of coagulants analyzed by NNLS after 1 week aging. Two sectional distributions can be seen clearly for three coagulants, indicating size aggregation and structure rearrangement of Al_{13} with further alkalification. With increasing B values, particle size increases from about 10 to several decade nm and the large size section becomes broader. It is well known that the size of Keggin Al_{13} is $\sim 2\ \text{nm}$ and its freshly formed aggregates can be hundreds nm [10]. As can be seen from Fig. 2a, the small section is of size about $2\ \text{nm}$ and the large one is of size between 10 and $20\ \text{nm}$, the analyzed results agrees well with the previous reports. However, owing to the requirement of instrument measurement, the hundreds nm aggregates may be filtrated and could not detected by PCS.

In this regard, the SEM was employed to study the morphology transformation and also the size growth of Al_{13} aggregates.

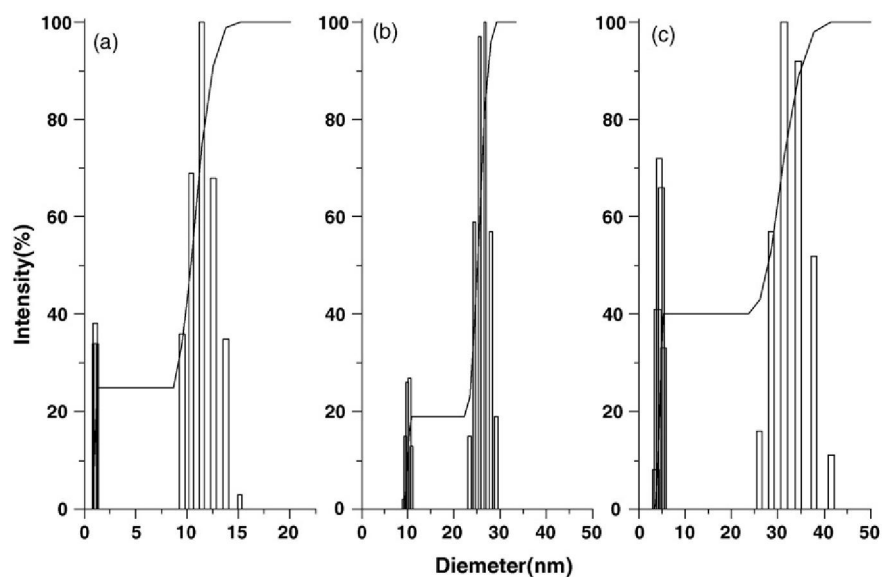


Fig. 2. Size distribution of weekly-aged coagulants measured by PCS.

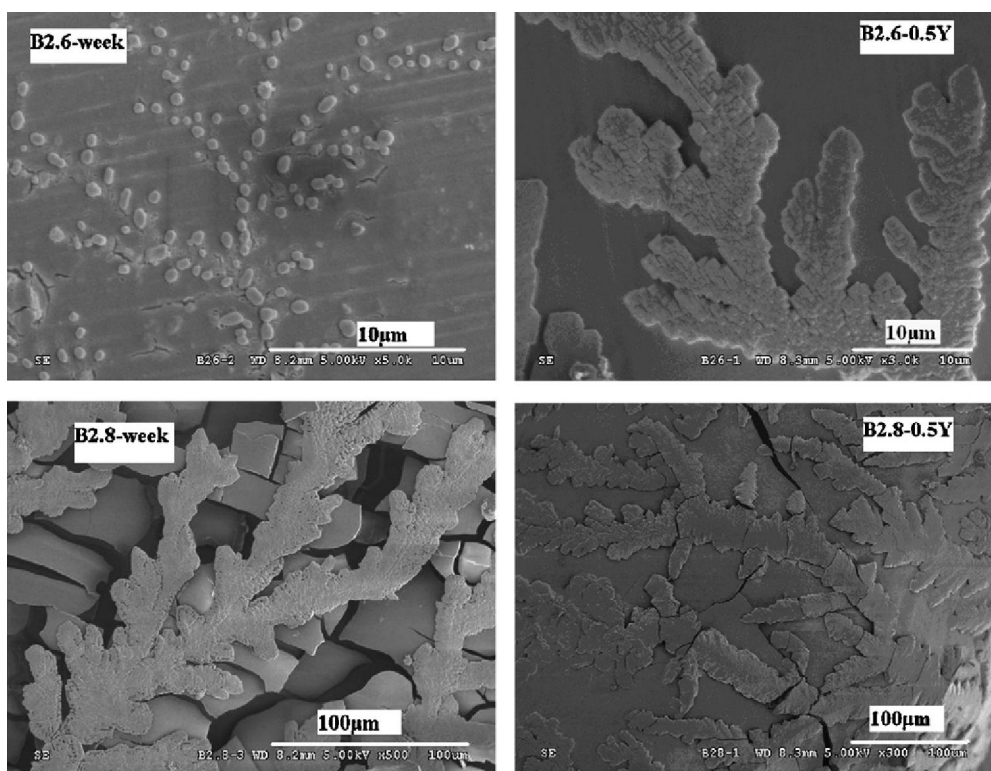


Fig. 3. SEM images of the Al_{13} aggregates at different ages.

Table 1

The Al species distribution of coagulants at different ages

$B(OH/Al)$	Al_T (mol/L)	Ferron assay (%)						^{27}Al NMR(%)		pH ^a	pH ^b
		Al_a^a	Al_b^a	Al_c^a	Al_a^b	Al_b^b	Al_c^b	Al_{13}^a	Al_{13}^b		
2.46	0.05	5.0	95.0	0	3.2	90.3	6.5	99.0	99.0	5.23	4.97
2.6	0.05	1.9	81.1	17	2.3	52.1	45.6	81.0	47.7	5.60	4.95
2.8	0.05	0.7	78.1	21.2	0.2	15.2	84.6	37.1	0	5.87	5.82

^a Coagulants aged for a week.

^b Coagulants aged for 6 months.

In Fig. 3, the distinct structures of coagulants are presented at different transformation stages, and correspond well with former studies [10,19]. The independently formed particles stick together for weekly aged B2.6, and a more compact structure appears upon aging and alkalification. Furthermore, the sizes of aggregates increase to hundreds micrometers in Fig. 3 for B2.8 and B2.6 (6-month aged). Although species transformation occurring during air-drying process may lead to size enlargement for all the coagulants, the relatively large scales can be clearly observed by SEM. A precise determination of Al species in the aggregates were carried out by ferron assay and NMR, showing the existence of Keggin Al_{13} in the weekly aged aggregates (next part). With further aging (6-month), larger polymer species may be formed and are not possible to be precisely detected with our data. However, it can be hypothesized that the Al_{13} aggregates were formed by individual Al_{13} unit via out-sphere bridging, and these structures maintain the identical tetrahedral environment under certain condition [17]. Consequently, $[\text{Al}_{13}]_n$ is referred as such fractal species, and their corresponding coagulation behaviors are compared with Al_{13} later on.

3.2. Speciation of coagulants at different ages

Although large amount of studies have addressed on the chemical speciation of hydrolyzed aluminum, disagreements still exist on the species transformation [7,17,26]. With aging time, the species distributions change greatly for Al_{13} aggregates (B2.6, B2.8) and remain stable for pure Al_{13} (B2.46), as Table 1 and Fig. 4 indicate. Comparing the species analysis, it can be seen that the Al_b almost equals to Al_{13} for B2.46 and 2.6, while Al_{13} decrease greatly for B2.8 when Al_b proportion was high. Apparently, larger polymeric species, even sol-gels, had formed and led to the unclear solution of B2.8. It can be suggested herein that structure rearrangement occurred during further alkalification for Al_{13} to form larger polymers like $[\text{Al}_{13}]_n$. When contacting with ferron colorimetric solution, this kind of $[\text{Al}_{13}]_n$ can be decomposed upon dilution and pH shock and hence exhibited higher activity within 2 h. On the other side, these $[\text{Al}_{13}]_n$ aggregates may transfer to be the colloidal Al species or precipitates upon aging. These colloidal Al species cannot be disassembled and are inert to the ferron solution, which is demonstrated in Table 1 as Al_b percentages decrease greatly (6-month-aged B2.6 and B2.8). It was not clear whether this kind of Al_{13} aggregates could be assigned to Al_{30} or not, since no aluminum monomer was presented in the pure Al_{13} solution (Fig. 4a) and the aging temperature was set at room temperature [27]. Furthermore, the formed precipitates may differ from the aluminum hydroxide with gibbsite structure, which will be shown by the following coagulation test, although clear definition is needed in the future study.

3.3. Zeta-potential of coagulants

The measured zeta-potentials of silica particles coated with weekly-aged coagulants are presented in Fig. 5, and values of the original particles are also indicated [22]. It can be seen that positive zeta values maintain stable in the pH range of 4–7 for coated silica particles. Compared with pure Al_{13} , the zeta values of Al_{13} aggregates are higher in the acidic range, which can be possibly caused by the release of Al_{13} unit under pH shock. Therefore, the suggested structure of $[\text{Al}_{13}]_n$ can be indirectly proved, while direct information is required and under further investigation in our group. The zeta-potential of half-year aged Al_{13} aggregates were not measured in this study, since the electrical properties of coagulants are controlled by the proportions of polycations. Although the Al_b percentage decreased greatly for the half-year aged B2.8 (Table 1), the jar test results also indicated high zeta-potential when alu-

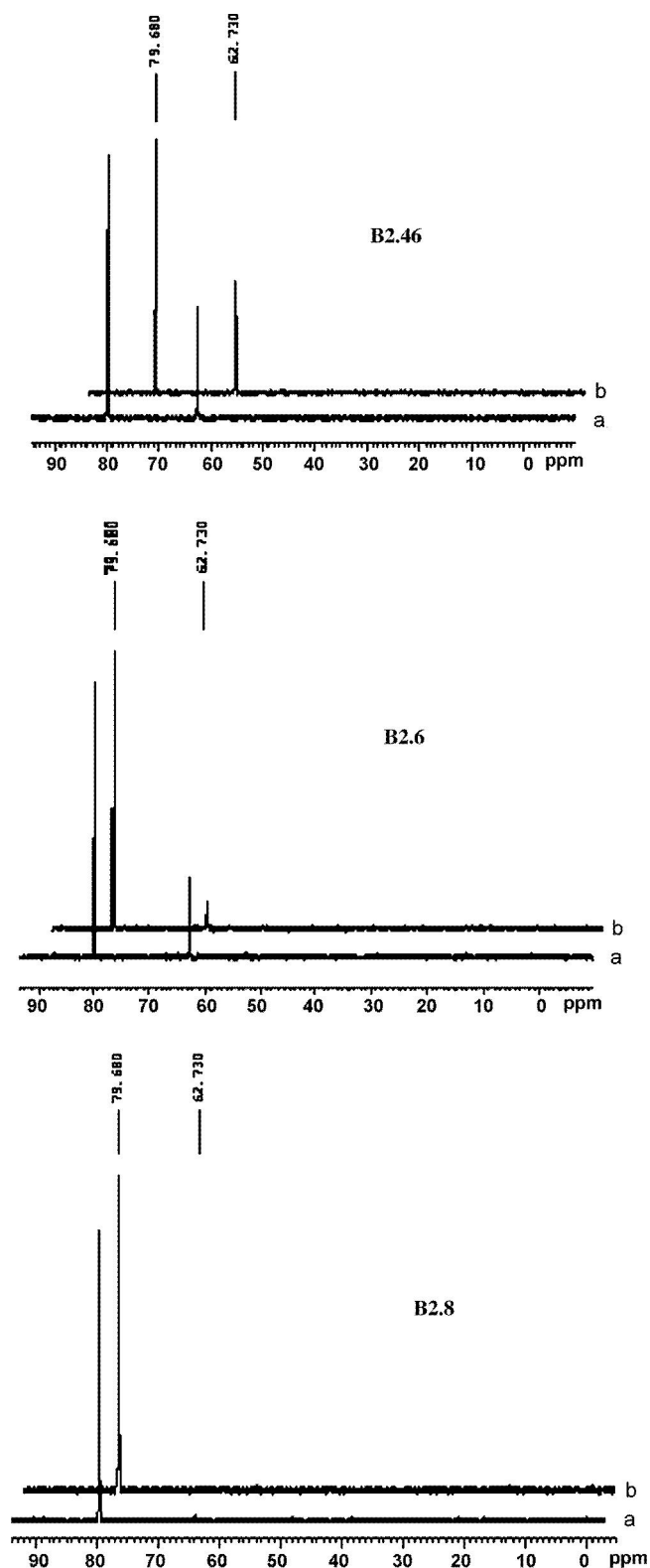


Fig. 4. ^{27}Al NMR spectra of the coagulants. (a) Coagulants aged for a week; (b) coagulants aged for 6 months.

minum concentration reached 10^{-4} mol/L (Fig. 6b). This could be attributed by the some released Al_{13} and some undetected larger polymers by NMR [27], yet precise determination has not been reported.

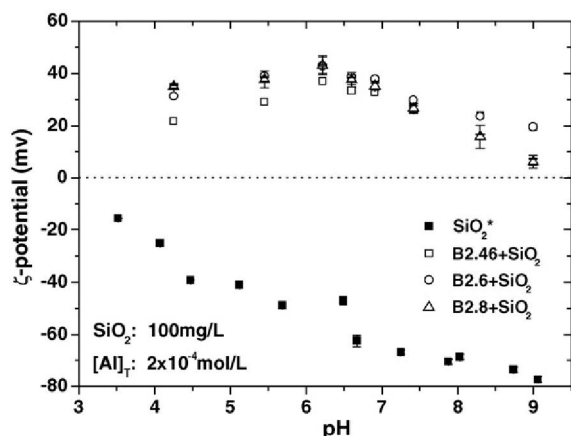


Fig. 5. Zeta-potential curves of silica microspheres with or without coating of coagulants as a function of pH. Silica concentration: 100 mg/L; total aluminum concentration $[Al]_T$: 2×10^{-4} mol/L; (*) measure by Wu et al. [22].

3.4. Coagulation results

3.4.1. Particle removal and zeta-potential

All the jar tests were performed at constant pH value (6.5) under room temperature. As pure Al_{13} (B2.46) remained stable in almost a year (data is not shown), only 6-month-aged Al_{13} was selected to compare the coagulation performances between the Al_{13} aggregates. The zeta-potential and residual turbidities are presented in Fig. 6 as a function of coagulant dosage. It can be seen that the suspension injected with pure Al_{13} reaches the C.C.C (critical coagulation concentration) at the lower dosage around 1×10^{-6} mol/L, when particles are still negatively charged. Moreover, re-stabilization occurs right after charge reversal, which is similar to the former report about high Al_{13} -content PACI [22]. For B2.6 and B2.8 of different ages, the distinct coagulation behaviors exhibit clearly in the Fig. 6a and b. With increasing dosages, suspension destabilization and re-stabilization occur for the weekly-aged coagulants, whereas re-stabilization zone disappears for the 6-

month-aged B2.8. Obviously, different coagulation mechanisms are involved, resulting from the species transformation in situ and pre-formed alkalification. For the B2.6 and B2.8 aged for a week (Fig. 6a), part of the larger polymer or colloidal $[Al_{13}]_n$ (higher Al_b) may decompose into Al_{13} units upon injection, and result in higher zeta-potential and re-stabilization at higher dosages. The charge variation of silica suspension is consistent with the electrical properties of Al_{13} and Al_{13} aggregates presented in Fig. 5. Furthermore, as mentioned earlier, the particle size Al_{13} aggregates are larger than pure Al_{13} , which decade nm particles appear. With that respect, Al_{13} aggregates can interact and bridge more particles than Al_{13} unit does. Therefore, a rather gentle increasing slope of residual turbidity is observed for B2.6, although the corresponding zeta-potential is higher than B2.46. Moreover, the stabilization zone is much wider for B2.8 at that condition. Accordingly, strong charge neutralization and electro-patch coagulation are performed between negative silica microspheres and positive polycations (Al_{13} and $[Al_{13}]_n$), combining with a weak bridge aggregation. For the 6-month aged Al_{13} aggregates, significantly lower turbidities are observed at the higher dosages ($[Al] > 10^{-5}$ mol/L), while similar trends of coagulation behavior can be observed for B2.46 and B2.6, yet re-stabilization zone disappears for B2.8 (Fig. 6b). It can be understood that other mechanisms dominate the coagulation process besides charge neutralization for these 6-month-aged coagulants, as part of the $[Al_{13}]_n$ transformed into sol-gels or precipitates upon aging (lower Al_b). No matter original or destabilized particles can be both linked together or wrapped by this kind of sol-gels or precipitates, and led to relative lower turbidities after charge reversal (zeta > 10 mV).

3.4.2. Floc size distribution

Based on the coagulation behaviors shown in Fig. 6, it is evident that the optimum coagulation concentration occurs at higher dosage for B2.8 than that for B2.46 and B2.6, i.e. 10^{-5} mol/L and 10^{-6} mol/L, respectively. Figs. 7 and 8 show the comparison between the size distributions for them. For both weekly-aged B2.6 and B2.8, large flocs of $\sim 500 \mu m$ are formed as well as pure Al_{13} (B2.46) does at lower dosage (10^{-6} mol/L). Moreover, the pro-

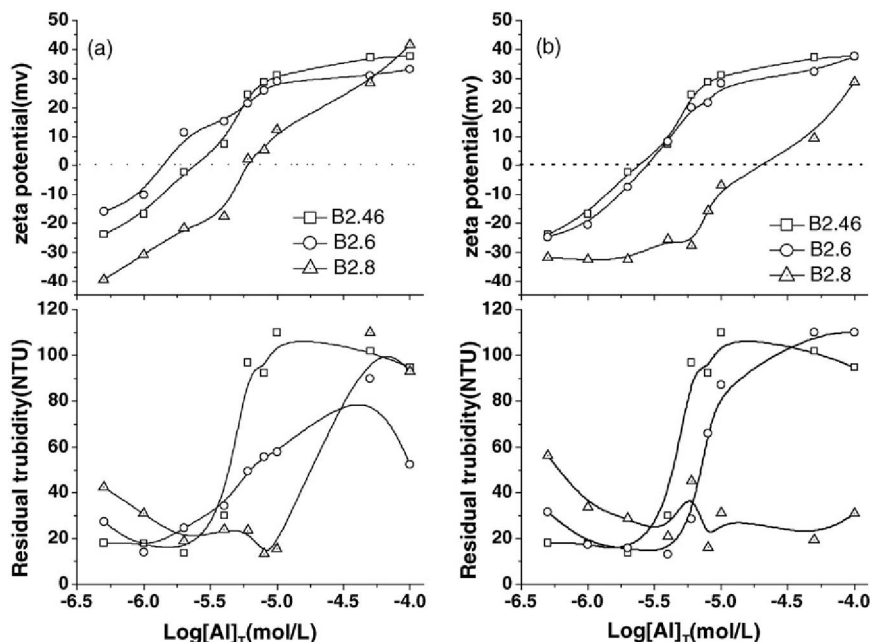


Fig. 6. Coagulation results as a function of aluminum concentration using different coagulants. (a) Weekly-aged coagulants; (b) 6 months aged coagulants; (silica suspension concentration: 0.5 g/L; ξ : -45 ± 5 mV; pH 6.5).

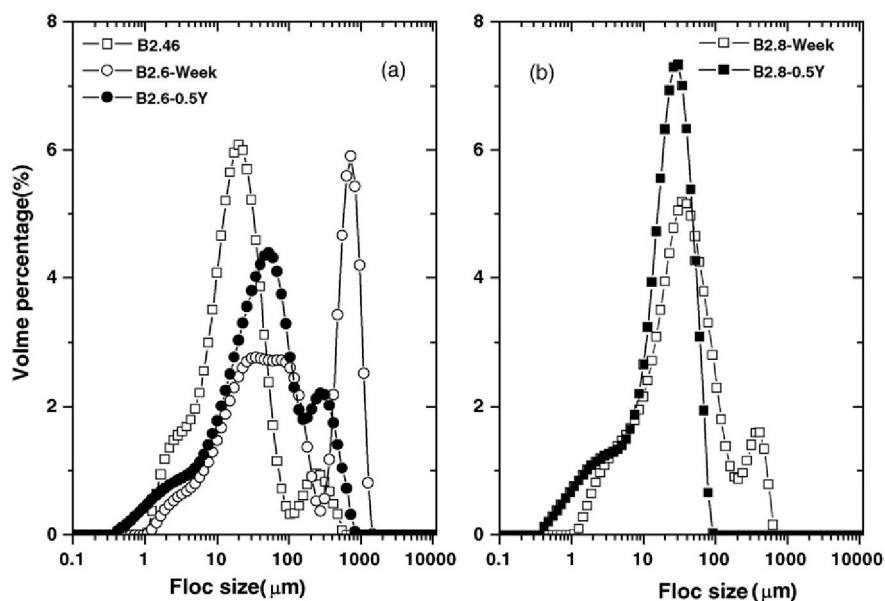


Fig. 7. Volume based size distribution of flocs at the end of slow mixing for all the coagulants. At the optimum concentration for B2.46 and B2.6. ($[Al]_T = 10^{-6}$ mol/L).

portions of larger size floc for aggregates are greater than that of pure Al_{13} , owing to their larger size and branched structure (Figs. 2 and 3). However, without enough positive polycations to destabilize negative silica particles, particle aggregation induced by B2.8 is retarded, resulting in a lower turbidity removal at dosage of 10^{-6} mol/L (Fig. 6). On the other side, floc size decreases and primary silica particles dominate for the B2.46 at dosage of 10^{-5} mol/L, contrary to the great proportions of larger flocs for Al_{13} aggregates, especially the B2.8 (Fig. 8). Obviously, this can be attributed to their different speciation associated with charge properties, size distribution, etc. For B2.46, high content Al_{13} (99%) induced strong repulsion between coated particles (zeta = 31.2 mV) and prevented particle aggregation subsequently. For B2.6 and B2.8, portions of larger polymers like $[Al_{13}]_n$ (part of Al_b and Al_c) catalyzed particle aggregation in terms of bridge aggregation or sweep flocculation forming larger flocs. With sol–gel or precipitates formed for 6-month-aged B2.8 (no Al_{13} and higher Al_c), voluminous flocs

($D_{50} > 1000 \mu m$) turn to be the predominant and lower turbidity maintains at higher dosages as Fig. 6b shows.

4. Discussions

The performance of inorganic polymer flocculants (IPFs), such as PACI, has shown to be efficient in water treatment [6,7,28]. On addition to water, such inorganic coagulant may undergo hydrolysis reactions and alter the original speciation, yet the species formation has not been well understood due to the difficult determination in the condition of water treatment. However, Keggin- Al_{13} is generally thought to be stable, though the aggregation of Al_{13} occurs in natural and artificial environment. For the aluminum solutions with high basicities of 2.46, 2.6 and 2.8, Keggin- Al_{13} and Al_{13} aggregates are the predominant species for weekly-aged coagulants. Consequently, Al_{13} and $[Al_{13}]_n$ are assumed to be the active species, and their coagulation behaviors are distinct correspondingly. Com-

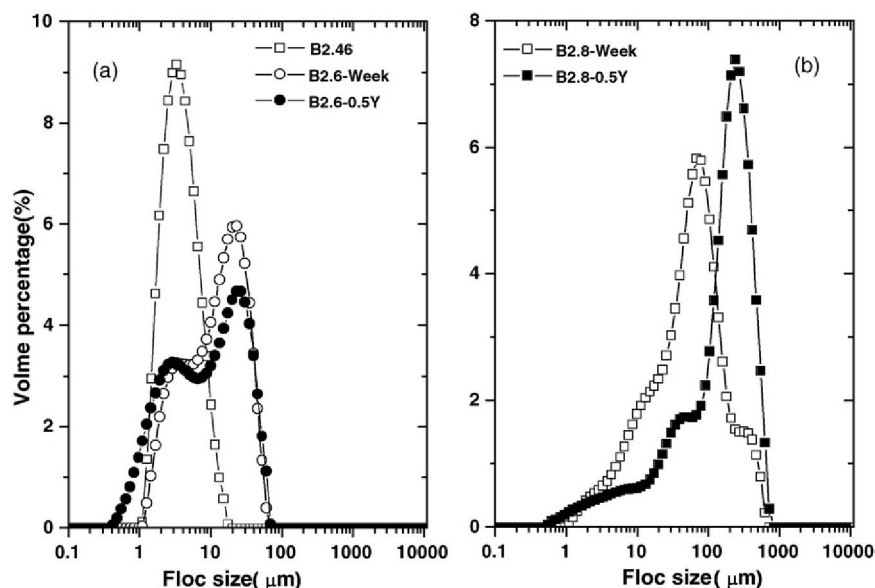


Fig. 8. Volume based size distribution of flocs at the end of slow mixing for all the coagulants. At the optimum concentration for B2.8 ($[Al]_T = 10^{-5}$ mol/L).

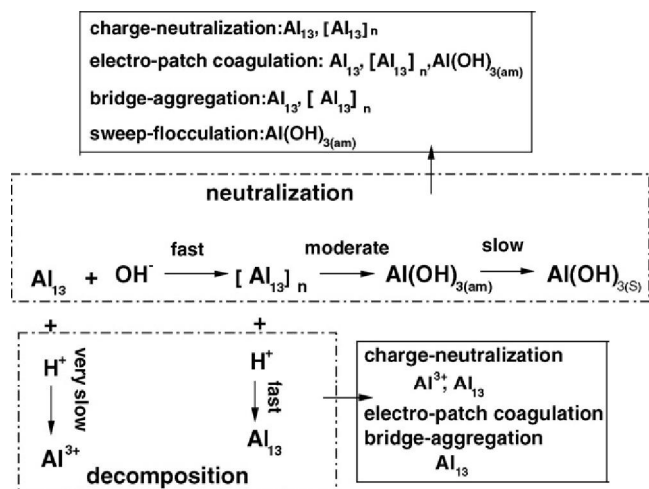


Fig. 9. Schematic representation of species transformation of aluminum polycations and the performed corresponding main coagulation mechanisms.

pared with Al_{13} aggregates, highly positive Al_{13}^{7+} adsorbed on the negative particles rapidly and covered the surfaces as scattered patches. The particle destabilization and aggregation were carried out simultaneously through charge neutralization and electro-patch coagulation. Moreover, $[\text{Al}_{13}]_n$ can be formed in situ after the addition of Al_{13} and bridge aggregation may also involved at higher dosage. However, for Al_{13} aggregates, more particles were destabilized and agglomerated with bigger units and longer chain structure of $[\text{Al}_{13}]_n$ (Figs. 2 and 3), including preformed and in situ formed. Upon aging, part of $[\text{Al}_{13}]_n$ may transform into amorphous hydroxides, as shown by Ferron assay (higher Al_c for 6-month-aged B2.8, Table 1). In addition, the particle size measurement by dynamic light scattering indicated strong intensity for monthly-aged B2.8 and hundred nm colloidal Al species were observed. Therefore, bridge aggregation and sweep flocculation dominated the particle and cluster interactions along the coagulation course. It should be noted that charge neutralization is the pre-requisite for efficient particle removal. As Fig. 6b shows, relatively higher residual turbidity is observed for B2.8 at lower dosages ($[\text{Al}]_T < 10^{-5}$ mol/L) despite larger size flocs formed then (Fig. 7), owing to the negative zeta-potential values ($\xi \sim -30$ mV). Without sufficient destabilization, the residual less aggregated particles would be lower down the coagulation efficiency consequently.

Previous studies indicated that pre-hydrolyzed coagulants are often more effective than traditional coagulants due to their substantial component of tridecamer Al_{13} [6,14,28]. Because of their various specie distributions, coagulants with different ages and basicities interact with particles through various pathways. With high content Al_{13} , B2.46 exhibited strong adsorption ability and formed relatively small and compact flocs (Figs. 7 and 8). For the Al coagulants with high basicities, particle–coagulants interactions evolved from adsorption to co-precipitation, corresponding to the coagulation mechanisms as charge neutralization, electro-patch coagulation and sweep flocculation. Although precipitate was involved during the process for these coagulants, its nature and performance was distinct from that of the traditional alum which had already been demonstrated by Van Benschoten and Edzwald [29]. This kind of precipitate or sol–gel remains active and can be disassembled or decomposed upon stirring and proton-promotion. In fact, it is the $[\text{Al}_{13}]_n$ that plays a major role in the coagulation process, and its transformation pathways based on the experimental conditions will determine the coagulation behavior ultimately. Fig. 9 shows the possible transformation pathways of

Al_{13} accompanied with corresponding coagulation mechanisms. For each coagulant containing various portions of Al_{13} , $[\text{Al}_{13}]_n$ and $\text{Al}(\text{OH})_{3(\text{am})}$ (based on Table 1), different coagulation mechanisms predominate the particle interactions thereby and result in distinct coagulation behaviors (Fig. 6).

5. Conclusions

Aluminum solutions with high basicities experienced species transformation upon aging, and the final phases formed depend on the exact conditions of hydrolysis (e.g. solution pH). Characterization of such aluminum solutions showed that tridecamer Al_{13} and aggregated $[\text{Al}_{13}]_n$ were the dominant species, and distinct structures were observed corresponding with the formed species. The species transformation was demonstrated with coagulation behaviors of different aluminum polycations, and different coagulation mechanisms were assigned accordingly. Although these experimental results do not exactly define the species transformation, enough evidence is provided for speculation. With increasing use of PACl, further work is needed to investigate the nature of the formed aluminum polycations such as Al_{13} during coagulation. Consequently, better understanding can be obtained on the improved performance of these coagulants.

Acknowledgement

The authors would like to thank the National Natural Science Foundation of China (NSFC) in support of this project (No. 20537020, No. 50678167 and No. 20677073).

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