

Effects of Ca on the distribution, structure and morphology of aluminum species in polyaluminum chloride

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Abstract The flocculation efficiency of polyaluminum chloride (PAC) is closely related to the distribution and structure of its Al species, and Al_{13} is the optimal species in PAC for flocculation. A series of PAC containing Ca was prepared by adding Ca before and after the basifying reaction. The effects of Ca on the Al species were studied by ^{27}Al nuclear magnetic resonance (NMR) and atomic force microscope (AFM) techniques. The experimental results show that the introduction of Ca increases the content of Al_m and Al_{13} in PAC and decreases their chemical shifts in NMR spectra due to the electric repulsion between the positive Ca species and Al species and the formation of Al-O-Ca complexes. With the rise of Ca/Al molar ratio, the Al species in PAC tend to scatter. It is observed that the formerly branch-aggregated clusters are tending to form granule-aggregated ones whose diameter gets smaller and smaller, and the floccule aggregates are formed at a higher Ca/Al molar ratio. The introduction of Ca to PAC, which increases the Al_{13} content, is certainly to enhance the flocculation efficiency of PAC in water treatment.

Keywords: Al_{13} species, distribution of Al species, structure and morphology, polyaluminum chloride containing Ca.

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In current water treatment field, polyaluminum chloride (PAC) is the most widely used inorganic polymeric flocculant in the coagulation process. The flocculation property of PAC is closely related to the characteristics and content of its Al species. PAC is actually a kinetically stable mid-product from the process of hydrolyzation, polymerization, and precipitation of Al^{3+} . It is believed that only a few species can be transformed between each other in PAC, such as monomer (Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$), dimer ($\text{Al}_2(\text{OH})_2^{4+}$), Al_{13} polymer ($\text{AlO}_4\text{-Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$, abbreviated to Al_{13}), and other higher polymers^[1]. The nano-sized Al_{13} species, whose particle size is only 2.5 nm in diameter, is the optimal spe-

cies of PAC for flocculation due to its high charge-neutralization ability. Thus the content of Al_{13} can reflect the flocculation efficiency of PAC^[1]. Much more attention has been given to Al_{13} species currently, and the research on it covers not only the field of water treatment, but also other scopes, such as aquatic chemistry, soil chemistry, geochemistry, and material sciences^[2-5].

The positive and negative ions in PAC have an influence on the properties and content of Al species, and in the end, on the flocculation efficiency of PAC. More researches concentrated on the effects of negative ions, such as SO_4^{2-} , SiO_3^{2-} , and PO_4^{3-} , are carried out^[6-9], but the effects of positive ones have not got much attention. Calcium aluminate is always used as a basification agent in the process of synthesis or manufacture of PAC, which results in the existence of a certain amount of Ca in the product. It is significant to make clear about the effects of Ca on the Al species for the study on the fundamental theory of PAC and the Al_{13} function in PAC and water treatment. Unfortunately, the research in this respect has not been reported so far.

The Al monomer (Al_m) and Al_{13} aggregate can be identified and quantified by ^{27}Al nuclear magnetic resonance (NMR)^[10,11]. The resolution sensitivity of atomic force microscope (AFM) can be precise to nanometer, and moreover, this technique is not influenced by the sample conductivity^[12]. The effects of Ca on the Al species in PAC are studied by ^{27}Al NMR and AFM in this paper.

1 Experimental

(i) Instruments and materials. Peristaltic pump (BT01-100), electromotive stirrer (JJ-1), thermostatic water-bath (model 501), NMR spectrometer (VARIAN^{UNITY} INOVA, 500 MHz), AFM (Nanoscope IIIa Multimode, DI Instrument Co.). $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, NaOH. All the above reagents are of analytical-reagent-grade.

(ii) Synthesis of PAC containing Ca. Adding Ca before basification: To a three-necked flask (250 mL), 25 mL of $2.5 \text{ mol} \cdot \text{L}^{-1}$ AlCl_3 solutions were added firstly, and then some solid $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was added to acquire the desired Ca/Al molar ratio. After adding 50 mL of deionized water, 125 mL of $1 \text{ mol} \cdot \text{L}^{-1}$ NaOH solutions were pumped by peristaltic pump for 5 h under rapid agitating. The reaction was conducted at 20°C all along. After the 125 mL of NaOH solutions were added, the solution in the flask was diluted to 250 mL and then aged for 96 h at 20°C .

Adding Ca after basification: 25 mL of $2.5 \text{ mol} \cdot \text{L}^{-1}$ AlCl_3 solutions and 50 mL of deionized water were added to a flask, then pumping NaOH solution, diluting, and aging was conducted in the same way as adding Ca before basification. After aging for 72 h, an amount of solid $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was added to acquire the desired Ca/Al

molar ratio. Shaking the flask to melt the solid CaCl_2 , and then the aging continued for 24 h.

The Al concentration, basicity (B) and pH of the PAC prepared by the above methods are $0.25 \text{ mol} \cdot \text{L}^{-1}$ (about 1.2%, if expressed as $\text{Al}_2\text{O}_3\%$), 2.0 and 4.5, respectively. After the aging was finished, the samples taken from the products were analyzed by ^{27}Al NMR and AFM.

(iii) Determination by ^{27}Al NMR and quantitative analysis of Al species. The operation was performed on ^{27}Al NMR spectrometer. A capillary centered in a sample tube (diameter 5 mm) was filled with $0.2 \text{ mol} \cdot \text{L}^{-1}$ $\text{NaAl}(\text{OH})_4$ and the same volume of D_2O as an inner reference and the reagent to lock field, respectively. All the samples were undiluted and analyzed directly. Before the Al species was quantified, a standard curve must be plotted first by the peak area and Al concentration of a series of acidified Al standard solution. Then the percentage of Al_m , Al_{13} and the unidentified Al species (Al_u) can be obtained by applying the NMR spectra to the standard curve.

(vi) Determination by AFM. About 5 μL of sample solution was taken and dropped on the fresh surface of mica flake. After standing in a desiccator for 10h, the sample on the mica flake was imaged by AFM in atmosphere at room temperature. The imaging was conducted by touch mode and all the images were patterned under constant force. The low-frequency noise in the direction of slow scanning was removed by "Flatten auto". A commercial Si_3N_4 probe was used in the experiment. The micro-cantilever is 120 μm long and the force constant is 0.6 N/m.

2 Results and discussion

(i) Effect of Ca on distribution of Al species. The ^{27}Al NMR spectra of PAC containing different amount of Ca added before or after the basification were analyzed. The chemical shifts (δ) of the peaks and the content of Al_m , Al_{13} and Al_u quantified from their peak area are shown in Table 1. It can be found from Table 1 that both Al_m and Al_{13} content increase after CaCl_2 is added, and the Al_{13} content is even much higher if CaCl_2 is added before the basification. CaCl_2 exists in the system in the forms of Ca^{2+} and $\text{Ca}(\text{OH})^+_{13}$, which may be intercalated in the Al species. Owing to the repulsion between the positive charges on Ca or Al species, the Al species gets scattering and its tendency to polymerization decreases, which results in the increase of the Al_m and Al_{13} content. This repulsion can prevent the formation of Al_{13} as well as its further polymerization, but the latter is even obvious. In the case of adding CaCl_2 after the basification most of Al_{13} have already formed before the introduction of CaCl_2 , thus the former effect of the repulsion is relatively weak, which results in an even higher Al_{13} content.

The δ and linewidth in NMR spectra change with the changes of the structure and environment of the com-

pound. Both δ and linewidth of Al_m decrease with the increase of total Al concentration (Al_T), and increase with the rise of B , ionic strength and viscosity. However, the δ and linewidth of Al_{13} are not influenced by Al_T and B because of the strong shielding of the central fourfold coordinated Al^[14]. In this experiment, all the samples have the same Al_T , B and pH values, and only the ionic strength increases with the increase of Ca/Al molar ratio. The δ of Al_m or Al_{13} does not increase but decreases when the Ca/Al molar ratio of a sample rises, which implies that the structure and chemical environment of Al_m or Al_{13} are changed, because the shielding of the sixfold or fourfold coordinated Al in Al_m or Al_{13} gets weak due to the complex of Ca^{2+} with the oxygen atom of Al species^[13] to form the structure of Al-O-Ca. It is also found from Table 1 that adding Ca before or after the basification has no effect on the change of δ .

Table 1 Effects of Ca-adding method and Ca/Al molar ratio on the content and chemical shift (δ) of Al species in PAC

Ca-adding method	Ca/Al molar ratio	Content of Al species (%)			δ of Al species		
		Al_m	Al_{13}	Al_u	inner reference	Al_{13}	Al_m
No Ca	0	7.76	52.32	39.91	80.12	62.887	0.058
Adding Ca before the basification	0.2	10.11	60.37	29.51	80.12	62.866	0.048
	0.4	10.42	62.26	27.32	80.12	62.845	0.037
	0.6	10.52	59.80	29.67	80.12	62.834	0.037
Adding Ca after the basification	0.2	10.47	67.48	22.05	80.12	62.865	0.047
	0.4	10.24	65.37	24.39	80.12	62.844	0.037
	0.6	10.03	63.41	26.56	80.12	62.834	0.037

(ii) Effect of Ca on structure and morphology of Al species. The AFM images of PAC containing different amount of Ca added before the basification are shown in Fig. 1. It can be seen that PAC without CaCl_2 is made up of some aggregated small-particles, which displays the specific fractal structure and it is mainly the aggregated Al_{13} ^[10]. From the simulated three-dimensional image corresponding to (a) in Fig. 1, the structure and morphology of the Al species can be observed intuitively (Fig. 2). It is also found from Fig. 1 that the Al species tend to scatter and the density of the aggregates decreases with the increasing of Ca/Al molar ratio. The branch aggregates disappear gradually and are converted into granule ones whose diameter gets smaller and smaller. The granule aggregates are very small and stick to each other to form floccule aggregates at higher Ca/Al molar ratio, because the Al-O-Ca complexes surround the Al species and divide the branch aggregates into granule ones (Fig. 3). The higher the Ca/Al molar ratio is, the smaller the granule will be. The divided Al species pile simply without the former fractal structure and the tendency to branch any longer. While the granules are too small to define, their density gets low further, and the Al species take on floc-

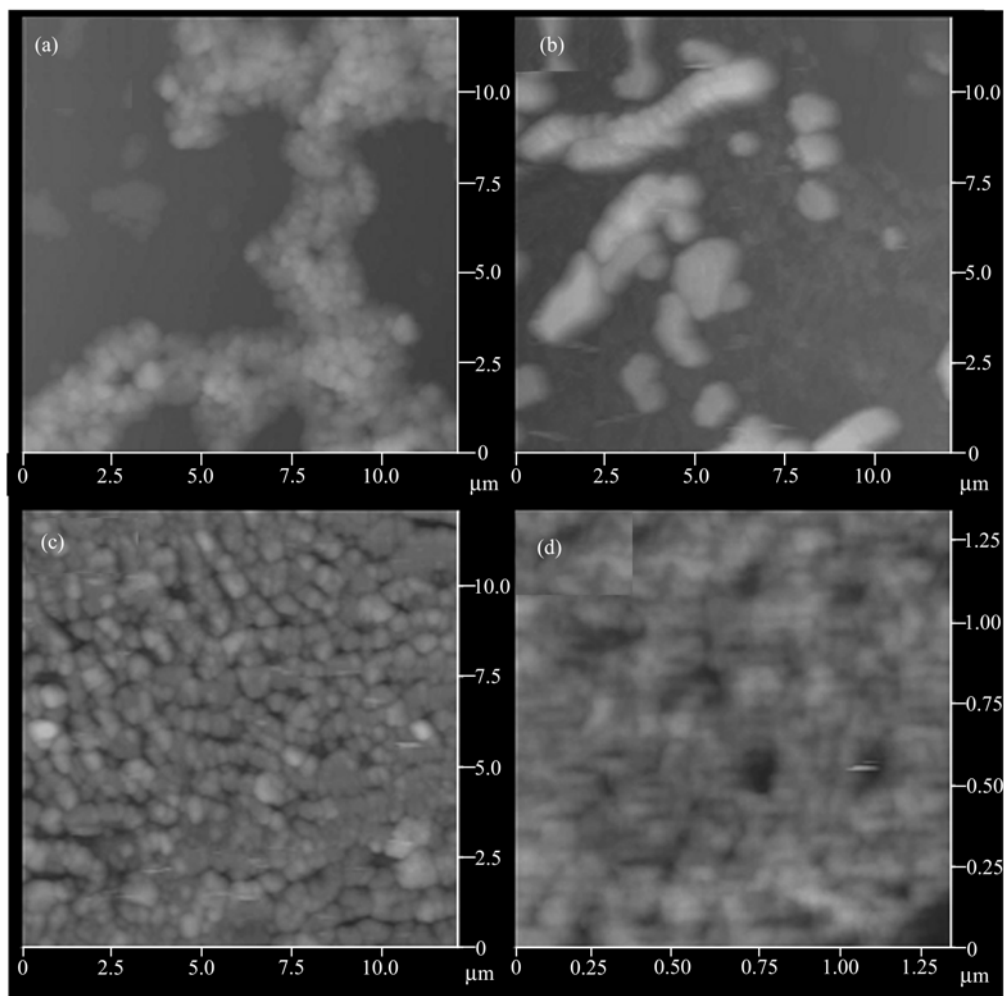


Fig. 1. AFM images of PAC with different Ca/Al molar ratios. (a) Ca/Al=0; (b) Ca/Al=0.2; (c) Ca/Al=0.4; (d) Ca/Al=0.6.

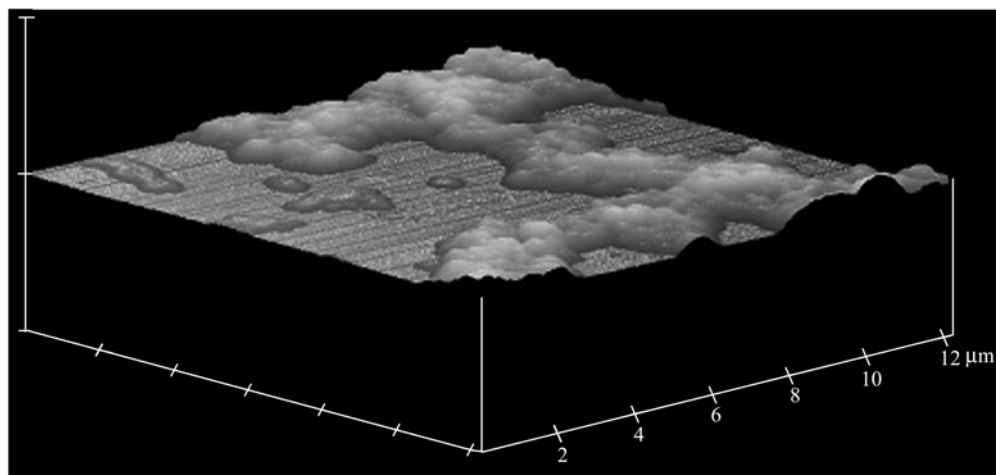


Fig. 2. Three-dimensional AFM image of PAC (Ca/Al = 0).

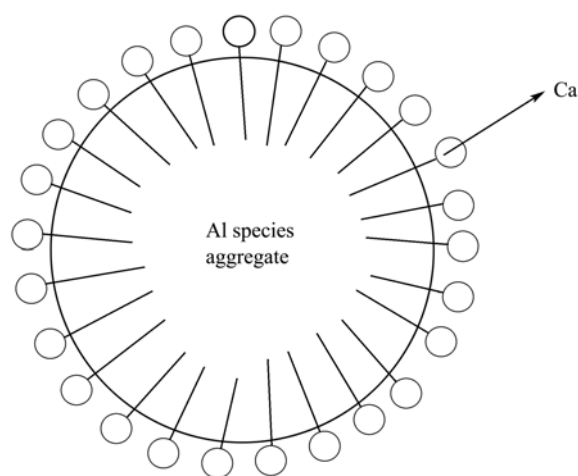


Fig. 3. Schematic diagram of granule aggregate formed from Ca and Al species.

cule in the AFM image (Fig. 1 (d)).

The Al_{13} species can be aggregated in solution^[10,15], which results that Al_{13} transforms into the species with a high molecular weight and its charge-neutralization ability decreases. The introduction of Ca to PAC can produce Al-O-Ca complex that surrounds and divides the Al_{13} aggregates to prevent Al_{13} further polymerizing and increase its content in PAC, which can enhance the charge-neutralization ability of PAC and improve its flocculation efficiency in water treatment^[16]. The above results by AFM are consistent with those by ^{27}Al NMR, and prove intuitively that there are very important effects of Ca on the Al species in PAC.

3 Conclusion

The introduction of Ca to PAC increases the content of Al_m and Al_{13} in the product and decreases their δ in NMR spectra due to the electric repulsion and the Al-O-Ca complexes from Ca species and Al species. With the rise of Ca/Al molar ratio, the branched Al species tend to scatter to convert into granule aggregates whose diameters get smaller and smaller to form floccule aggregates at higher Ca/Al molar ratio. The change of Al aggregates is a result that the Al-O-Ca complexes surround and divide the branched aggregates. The introduction of Ca to PAC increases the Al_{13} content and is certainly to enhance the flocculation efficiency of PAC in water treatment.

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