

Effect of thermal treatment on the formation and transformation of Keggin Al_{13} and Al_{30} species in hydrolytic polymeric aluminum solutions

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Abstract

The effect of thermal treatment on the formation and transformation of Al_{13} and Al_{30} species in highly concentrated hydrolytic polymeric Al solutions (HPA) ($0.2\text{--}1.0\text{ mol L}^{-1}$) were studied quantitatively using high-field ^{27}Al nuclear magnetic resonance (NMR) and time-developed Al-Ferron complex colorimetry. The results indicate that the metastable Al_{13} species in HPA tends to polymerize and transform into Al_{30} and other high polymers upon thermal treatment. The polymerization and transformation are speed up by heating at high temperature. Al_{13} content in HPA decreases upon thermal treatment, and Al_{30} content increases. Al_{13} does not convert to Al_{30} quantitatively due to its aggregation and acidic dissociation reactions. Al_{13} species is a dominant nanosized Al species in freshly prepared HPA solutions, and its content reaches above 80.0% in HPA with $\text{Al}_T = 0.2\text{ mol L}^{-1}$ and optimal hydrolysis ratios (B) (*ca.* 2.3–2.4). But the content of Al_{30} becomes higher than that of Al_{13} when the HPA solution is heated at 95°C for more than 12 h. Al_{30} becomes the dominant nanosized Al species in HPA, and its content reaches 76.8% in sample with $\text{Al}_T = 0.2\text{ mol L}^{-1}$ and $B = 2.4$. Although Al_{30} is more stable than Al_{13} , it is also a metastable species during the process of Al hydrolysis, polymerization and precipitation. The decomposition and polymerization of Al_{30} are also speed up by increase the heating temperature. The optimal preparation temperature of Al_{30} is *ca.* 95°C . Al species in HPA solutions transform into more stable and inert species through inter-species polymerization and intra-species structure rearrangement upon thermal treatment. So Al_b contents decrease, and Al_c contents increase. Al_{30} cannot react with Ferron within 120 min, and it is classified as Al_c species in Al-Ferron analysis. The effect of thermal treatment on Al speciation in HPA solutions with different total Al concentration and B value were also investigated.

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1. Introduction

The aqueous chemistry of hydrolytic polymeric aluminum (HPA) solutions has been extensively investigated during the last 40 years [1–5]. Hydroxides and oxo-hydroxides of Al polycation species are widely used as flocculants in water treatment [6,7], as pillaring agents in clay minerals and inorganic oxides chemistry [8,9], as precursor materials in ceramics and catalytic materials [10], as antiperspirants in pharmaceutical and cosmetic [11], and as model compound in geochemistry [12,13]. In addition, Al hydrolysis also plays important roles in environmental science [14] and bio-toxicology [15]. A series of hydrolysis species form

depending on various factors, such as Al concentration, degree of basification, reaction temperature and time, bases adopted, rate and style for base addition and coexisting anions [16,17]. Many analytical instruments and experimental methods, such as potential titration, ^{27}Al nuclear magnetic resonance (NMR), X-ray powder diffraction (XRD), small angle X-ray diffraction and scattering, infrared and Raman spectroscopy, laser light scattering, electron microscopy, atomic force microscopy, Al-Ferron colorimetry and other wet chemical methods, have been employed in the study of Al speciation and the structural characterization of Al species. In spite of a great deal of literatures, the chemistry composition in hydrolyzed Al solutions is not completely determined yet due to the complexity of the solutions [1–5]. Only eleven Al species have been crystallized and identified in HPA solutions up to now. These species include: five monomers Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$ (aq) and $\text{Al}(\text{OH})_4^-$; dimers $[\text{Al}_2(\text{OH})_2]^{4+}$; trimers $[\text{Al}_3(\text{OH})_4]^{5+}$;

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two Keggin polymers $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ ($\epsilon\text{-Al}_{13}$) and $[\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{24}]^{18+}$ ($\delta\text{-Al}_{30}$); and two flat polymers $[\text{Al}_{13}(\text{OH})_{24}(\text{H}_2\text{O})_{24}]^{15+}$ and $[\text{Al}_8(\text{OH})_{14}(\text{H}_2\text{O})_{18}]^{10+}$ [1–5,18,19].

The Keggin $\epsilon\text{-Al}_{13}$ polycation received the most extensive attention in previous investigations on HPA solutions due to its ubiquity and high charges. Some “ Al_{13} -like” aggregations were found in some of previous ^{27}Al NMR studies on HPA solutions [20–22]. The nature of these species was not fully depicted until the identification of the Keggin Al_{30} polycation by Allouche et al. [23], and Rowsell and Nazar [24] using *in situ* ^{27}Al NMR and single crystal X-ray diffraction in 2000. The highly charged Al_{30} is consisted of two $\delta\text{-Al}_{13}$ Keggin units connected by a crown made of four hexa-coordinated aluminum atoms (AlO_6), and it is prepared by thermal treatment of the HPA solution containing $\epsilon\text{-Al}_{13}$ precursor.

Previous studies indicate that total Al concentration (Al_T), monomer concentration, temperature and aging have important effect on the conversion of Al_{13} to Al_{30} species. The conversion was accelerated by the increase in Al monomer concentration in HPA solutions [25]. Fluorination of Al_{13} also can enhance the formation of Al_{30} [26]. Although there are a few reports on Al_{30} species, and a great deal of progress has been achieved, most of these investigations were carried out in diluted solutions and were aimed to structural characterization. Shafran et al. [27,28] have studied the Al speciation in medium concentration at high temperature using improved ^{27}Al NMR quantification method. To date, much less was concerned on the formation and transformation of Al_{30} species in highly concentrated HPA solutions ($0.2\text{--}2.0\text{ mol L}^{-1}$). Our research results indicate that the conversion of Al_{13} to Al_{30} was accelerated by the increase in Al_T [29]. The effect of temperature on Al speciation in HPA solutions had been intensively studied before the identification of Al_{30} [30–33]. But how Al_{13} transforms into Al hydroxide upon thermal treatment is still not fully understood because this process include many complex steps, and the intermediate products are difficult to determine quantitatively. The identification Al_{30} sheds new light on the further investigation of the transformation mechanism of Al_{13} into unidentified high polymers and Al hydroxide.

In the field of water treatment, Al_{13} has long been thought to be the optimal coagulation/flocculation species in polyaluminum coagulants. The high content of Al_{13} is the goal of the production of polyaluminum coagulants [34]. However, the commercial polyaluminum coagulant contains only small amount of Al_{13} due to the aggregation of Al_{13} in highly concentrated HPA solutions [35]. But our research indicates that Al_{30} is another high active species in HPA solutions that responsible for coagulation/flocculation besides Al_{13} . Compared with Al_{13} species, Al_{30} achieves better turbidity removal within a broader dosage range and a wider pH range due to its high charge neutralization capacity and good flocs formation capacity [36]. Furthermore, the formation conditions of Al_{30} species are consistent with the preparing process of commercial polyaluminum coagulants. High temperature and long-term thermal treatment is inevitably needed during the preparation of polyaluminum coagulants. And high Al concen-

tration is absolutely necessary on consideration of application cost.

In the present research, the effect of thermal treatment on the formation and transformation of Al_{13} and Al_{30} species in highly concentrated HPA solutions were quantitatively studied using high field ^{27}Al NMR and Al-Ferron method. Scan electron micrograph was used to study the characteristics of sulfate precipitates of the HPA solutions. The research will help to elucidate the transformation mechanism of Al speciation in highly concentrated HPA solutions. At the same time, the research will provide theoretic guide for the development of coagulants with high content of Al_{13} or Al_{30} .

2. Materials and methods

The reagents used in current research are all of analytical grade. All solutions were prepared by deionized water, and glassware were washed with 5% hydrochloric acid and carefully rinsed with deionized water.

2.1. Sample preparation

The HPA samples with total Al concentration of 0.2 mol L^{-1} were prepared by the following methods: 80 ml AlCl_3 aqueous solution with Al concentration of 1.0 mol L^{-1} was added into a 500-ml glass reactor equipped with a Teflon anchor stirrer and a reflux condenser. And the solution was heated to a predetermined temperature (*i.e.* 80°C and 100°C) using a thermostatic apparatus, then 320 ml NaOH aqueous solution with a calculated concentration (0.6 mol L^{-1} and 0.45 mol L^{-1} for $B=2.4$ and 1.8, respectively) was pumped into the reactor through peristaltic pump at a speed of 4 ml min^{-1} under rapid stirring until the hydrolysis ratio ($B=[\text{OH}^-]/[\text{Al}^{3+}]$) reached a prearranged value. After the addition of NaOH solution finished, the reactants were continuously stirred and heated at a predetermined temperature, and samples were taken at different times. The samples with $\text{Al}_T=0.5\text{ mol L}^{-1}$ and 1.0 mol L^{-1} were prepared referring to the methods described above. All samples were rested at room temperature for five days before analysis and characterization.

The samples used for study on the effect of heating temperature were synthesized as described above except the following differences: after the addition of NaOH solution finished, the reactants were continuously stirred and heated at 80°C for 20 min, then the resultant was spilt into five portions, which were subsequently stirred and heated for 12 h at 25°C , 50°C , 80°C , 95°C and 100°C , respectively.

2.2. Liquid ^{27}Al NMR spectroscopy

^{27}Al NMR is the most powerful and exclusive way to describe Al speciation directly, which can measure the content of Al species quantitatively [37]. In the present research, ^{27}Al NMR spectra were generated at 70°C on a Fast Fourier Transformation spectrometer (JNM-ECA600, JOEL), which was operated at a field strength of 14.09 T, single pulse method, resonating frequency 156.39 MHz, X-pulse of $6.4\text{ }\mu\text{s}$, X-acq-duration 0.20 s, repetition time 0.50 s, relaxation delay

0.30 s, scans 2048, X-sweep 78.25 KHz. Samples were placed into a 5 mm NMR tube, and a coaxial capillary filled with the same volume of $\text{NaAl}(\text{OH})_4$ aqueous solution and D_2O was inserted into the center of the sample tube. The coaxial capillary was used as the internal standard of Al content and the deuterium lock. The same operating conditions, NMR tube and capillary internal standard were adopted in the preparation of calibration curve and measurement of samples.

There are six signals in the typical ^{27}Al NMR spectra. The resonance signals at $\delta = 0$ ppm, 4 ppm and 80 ppm are assigned to Al monomer (Al_m), Al dimmers & trimers, and $\text{NaAl}(\text{OH})_4$, respectively [37]. The resonance peaks at $\delta = 62.5$ – 63.0 ppm and 70 ppm (broad peak) are attributed to central tetrahedral Al in Al_{13} and Al_{30} , respectively. The broad peak at $\delta = 10$ – 12 ppm is corresponded to octahedral Al of Keggin external shells in Al_{13} and Al_{30} [23]. The octahedral Al is located in an asymmetric coordinated environment, and the extremely fast spin relaxation shortens the relaxation time and broadens the linewidth [37]. Due to the overlapping of the peaks at $\delta = 4$ ppm and 10–12 ppm, areas of these peaks cannot be accurately integrated. In addition, there exist other polymeric Al species in hydrolytic polyaluminum solution which cannot be identified using current high-field ^{27}Al NMR, and these undetected Al and Al at $\delta = 4$ ppm are named as Al_u in the current research.

The peak areas in the ^{27}Al NMR spectra were integrated on condition that the peak area of 80 ppm was set as 1.0. To quantitatively analyse the concentration of various species in sample solutions, five standard AlCl_3 aqueous solutions with known Al^{3+} concentration were used as a primary standard. The concentration of various species with different chemical shift could be calculated through the calibration curve equation. The concentration for 62.5 ppm and 70 ppm signal were multiplied by 13 and 15, respectively, to obtain the concentration of Al_{13} and Al_{30} , respectively. The concentration of Al_u was calculated by Al_T minus Al_m , Al_{13} and Al_{30} .

2.3. Time-developed Al-Ferron complex colorimetry

The kinetically based Al-Ferron method is an indirect colorimetric analysis [38], which is widely applied to study on Al speciation in HPA solutions. The Ferron reagent was prepared referring to the methods described by Parker and Bertsch [38]. The operation procedures are as follows: 10 ml Ferron reagent was added into a 50 ml colorimetric cylinder, and it was diluted to the scale with deionized water. A measured amount of sample was injected into it using a micro-injector. The sample and reagent were mixed vigorously and were pipetted into a 10 mm path-length quartz cuvette. Then it was placed into a UV-vis spectrophotometer (DR/4000U, HACH) to test its absorbance at a wavelength of 370 nm at a frequency of one reading per minute. All these operations finished within 1 min. The Al concentration in colorimetric solution maintained $4 \times 10^{-5} \text{ mol L}^{-1}$.

Based on the difference of the dissociation and complex reaction kinetic rate between Ferron and hydrolyzed Al species, Al species in HPA solutions can be divided into three types [39]: monomeric species (Al_a) (reacting with Ferron from 0 min to 1 min), planar oligomeric and medium polymeric species

(Al_b) (reacting with Ferron from 1 min to 120 min), and three-dimensional species or sol-gels (Al_c) (reacting with Ferron after 120 min and non-reacting with Ferron). The pseudo first-order rate constant (k) of Al-Ferron complex reaction from 1 min to 60 min was estimated according to the methods described by Luan [40]. Al_T was measured by inductively coupled plasma-atomic emission spectroscopy (Vista-MPX ICP-AES, VAR-IAN). B value was measured by chemical analysis according to the Chinese standard GB 15892-1995.

2.4. Scan electron microscopy

The sulfate precipitates of Al polynuclear species were prepared by adding a calculated amount of $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ aqueous solution to a measured amount of HPA solutions under stirring. The molar ratio of $\text{SO}_4^{2-}/\text{Al}^{3+}$ was 0.33. After 10 min stirring, the solution was rest 3 days at room temperature. The white precipitates were collected by filtration using a $0.45 \mu\text{m}$ Millipore filter membrane. The precipitates were air-dried for 24 h at room temperature before taking scan electron micrographs (SEM) on a Hitachi S-3000 N scanning electron microscope.

3. Results and discussion

3.1. Effects of thermal treatment on the conversion of Al_{13} into Al_{30}

Fig. 1 shows the ^{27}Al NMR spectra of the HPA solutions, which were prepared at 80°C , then were heated at 95°C for different duration. The contents of Al species in these solutions measured by ^{27}Al NMR quantitative analysis are listed in Table 1.

As can be seen from Table 1, the content of Al_m changes very little upon thermal treatment. Al_{13} content decreases rapidly firstly, and the decrease slows down when the solutions were heated for more than 12 h. In contrast, the content of Al_{30} increases rapidly firstly, and the increase also slows down when heated for more than 12 h. The sum of Al_{13} and Al_{30} decreases. Thus, the content of Al_u increases stably. Thermal treatment on HPA solutions promotes the decay of Al_{13} and the formation of Al_{30} . Although Al_{13} species does not convert into Al_{30} species quantitatively, a close relationship between the decrease of Al_{13} content and the increase of Al_{30} content can be clearly seen from the data listed in Table 1. The transformation of Al_{13} into Al_{30} and Al_u is favored not only by thermal treatment, but also by increase in Al_T . The detailed Al species distribution and changing tendency in HPA solutions are dependent on Al_T and B value. This will be described in detail in the following sections.

For the samples with $\text{Al}_\text{T} = 0.2 \text{ mol L}^{-1}$ and $B = 2.4$, the content of Al_{13} decreases from 81.45% to 16.51% when the heating time increases from 40 min to 12 h. However, upon heating, the content of Al_{30} increases firstly, and reaches a maximum of 76.76%, then decreases slowly when the solution was heated further. Al_{30} becomes the dominant nanosized polynuclear Al species after heating for 12 h. The same changing tendency can

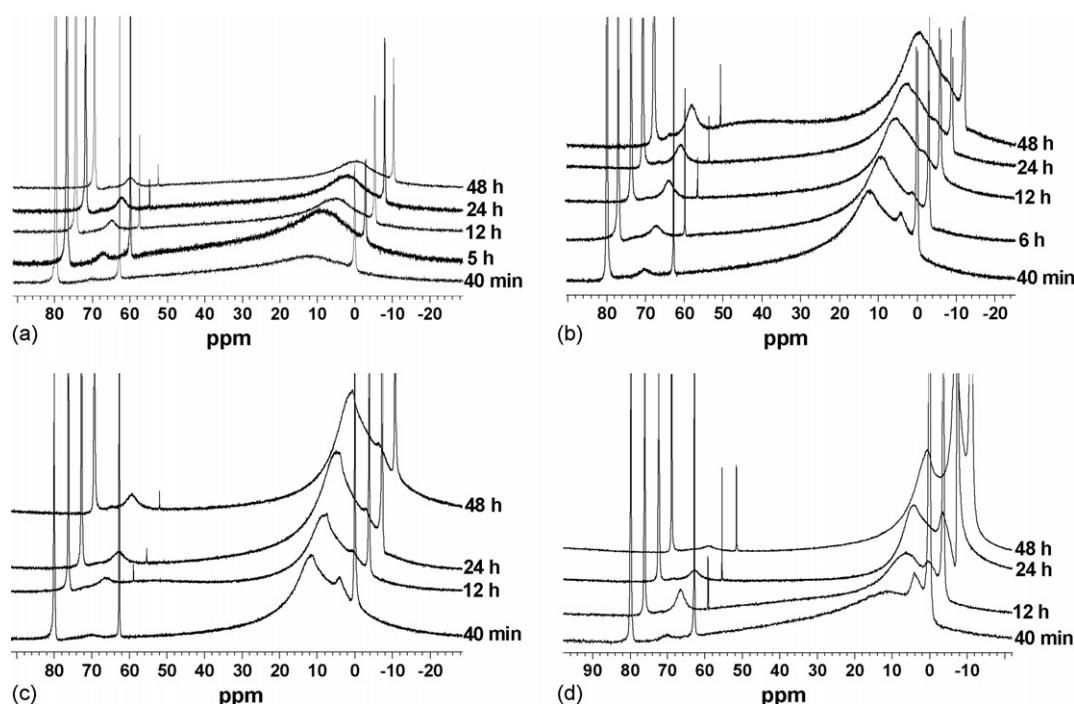


Fig. 1. ^{27}Al NMR spectra of HPA solutions which were heated at $95\text{ }^{\circ}\text{C}$ for different durations after being synthesized at $80\text{ }^{\circ}\text{C}$. (a) $\text{Al}_\text{T} = 0.2\text{ mol L}^{-1}$, $B = 2.4$; (b) $\text{Al}_\text{T} = 0.5\text{ mol L}^{-1}$, $B = 2.4$; (c) $\text{Al}_\text{T} = 1.0\text{ mol L}^{-1}$, $B = 2.3$; (d) $\text{Al}_\text{T} = 0.2\text{ mol L}^{-1}$, $B = 1.8$.

be seen for the sum of Al_{13} and Al_{30} . Because the tetrahedral coordinated Al (AlO_4) which forms at locally high pH and interfacial disequilibrium during the process of synthesis does not form in the acidic solutions during thermal treatment [41], the AlO_4 in Al_{30} can only be originated from the conversion of Al_{13} and a small quantity of residual AlO_4 in Al sol–gels which are soluble in solutions. The AlO_4 encapsulated in sol–gels could

not be detected by liquid ^{27}Al NMR as it locates in asymmetry chemical environment. These AlO_4 can exist in acidic solutions for a long time due to the shield of the outer Al sol–gels. Heating treatment enhances the acidic peptization and dissolution of the sol–gels [42], which may accounts for the increase of the sum of AlO_4 in Al_{13} and Al_{30} during thermal treatment for some samples.

Table 1

Al species distribution measured by ^{27}Al NMR in HPA solutions which were synthesized at $80\text{ }^{\circ}\text{C}$ and then heated at $95\text{ }^{\circ}\text{C}$ for different duration

Heating times	Al_T (M)	B	Species distribution									
			Al_m		Al_{13}		Al_{30}		Al_u		$\text{Al}_{13} + \text{Al}_{30}$	
			MCA (M)	RTA (%)	MCA (M)	RTA (%)	MCA (M)	RTA (%)	MCA (M)	RTA (%)	MCA (M)	RTA (%)
40 min	0.20	2.40	0.0095	4.73	0.1629	81.45	un	un	0.0276	13.82	0.1629	81.45
5 h	0.20	2.40	0.0081	4.07	0.1019	50.93	0.0628	31.42	0.0272	13.58	0.1647	82.35
12 h	0.20	2.40	0.0073	3.66	0.0330	16.51	0.1535	76.76	0.0061	3.07	0.1865	93.27
24 h	0.20	2.40	0.0107	5.34	0.0129	6.45	0.1461	73.07	0.0303	15.14	0.1590	79.52
48 h	0.20	2.40	0.0100	5.01	0.0021	1.07	0.1435	71.76	0.0443	22.16	0.1457	72.83
40 min	0.50	2.40	0.0260	5.20	0.2420	48.39	0.0470	9.40	0.1851	37.01	0.2890	57.79
6 h	0.50	2.40	0.0272	5.44	0.0991	19.81	0.1061	21.22	0.2677	53.53	0.2052	41.03
12 h	0.50	2.40	0.0297	5.93	0.0243	4.85	0.1654	33.07	0.2808	56.15	0.1896	37.92
24 h	0.50	2.40	0.0233	4.65	0.0058	1.16	0.1756	35.12	0.2954	59.07	0.1814	36.28
48 h	0.50	2.40	0.0243	4.86	0.0064	1.27	0.1924	38.48	0.2770	55.39	0.1988	39.75
40 min	1.00	2.30	0.0695	6.95	0.1036	10.36	0.0743	7.43	0.7526	75.26	0.1779	17.79
12 h	1.00	2.30	0.0723	7.23	0.0671	6.71	0.0882	8.82	0.7724	77.24	0.1553	15.53
24 h	1.00	2.30	0.0838	8.38	0.0072	0.72	0.1473	14.73	0.7617	76.17	0.1545	15.45
48 h	1.00	2.30	0.0811	8.11	0.0021	0.21	0.1602	16.02	0.7566	75.66	0.1623	16.23
40 min	0.20	1.80	0.0456	22.80	0.1128	56.38	0.0301	15.04	0.0116	5.78	0.1428	71.42
12 h	0.20	1.80	0.0467	23.34	0.0057	2.86	0.0808	40.39	0.0668	33.41	0.0865	43.25
24 h	0.20	1.80	0.0513	25.65	0.0089	4.46	0.0715	35.74	0.0683	34.15	0.0804	40.20
48 h	0.20	1.80	0.0498	24.90	0.0115	5.73	0.0270	13.52	0.1117	55.85	0.0385	19.25

MCA: Molar concentration of aluminum in HPA solutions; RTA: ratio of total aluminum concentration; un: undetected by ^{27}Al NMR method.

Table 2

Al species distribution measured by Al-Ferron methods in HPA solutions which were synthesized at 80 °C and then heated at 95 °C for different duration

Heating times	Species distribution			Al _a /Al _m	Al _b /Al ₁₃	Al _b /(Al ₁₃ + Al ₃₀)	Al _c /Al _u	<i>k</i> (min ⁻¹)
	Al _a (%)	Al _b (%)	Al _c (%)					
40 min	8.43	78.27	13.30	1.78	0.96	0.96	0.96	0.0282
5 h	10.30	65.98	23.72	2.53	1.30	0.80	1.75	0.0294
12 h	6.57	23.13	70.30	1.80	1.40	0.25	22.90	0.0283
24 h	11.27	14.58	74.15	2.11	2.26	0.18	4.90	0.0235
48 h	9.39	7.44	83.17	1.87	6.95	0.10	3.75	0.0180
40 min	11.35	43.70	44.95	2.18	0.90	0.76	1.21	0.0246
6 h	10.77	20.29	68.94	1.98	1.02	0.49	1.29	0.0240
12 h	10.65	7.82	81.53	1.80	1.61	0.21	1.45	0.0104
24 h	9.90	4.51	85.59	2.13	3.89	0.12	1.45	0.0145
48 h	6.87	5.52	87.61	1.41	4.35	0.14	1.58	0.0126
40 min	13.04	41.01	45.95	1.88	3.96	2.31	0.61	0.0287
12 h	8.65	8.50	82.85	1.20	1.27	0.55	1.07	0.0296
24 h	6.08	4.00	89.92	0.73	5.56	0.26	1.18	0.0168
48 h	4.96	5.38	89.66	0.61	25.62	0.33	1.19	0.0119
40 min	23.96	62.54	13.49	1.05	1.11	0.88	2.34	0.0314
12 h	23.90	10.83	65.27	1.02	3.79	0.25	1.95	0.0292
24 h	25.75	9.25	65.00	1.00	2.07	0.23	1.90	0.0292
48 h	24.08	10.50	65.42	0.97	1.83	0.55	1.17	0.0267

There are various other species except for Al₁₃ and A₃₀ species in HPA solutions, *e.g.* Al_m, oligomer and Al_u. Although the amounts of these species are small, the existing of these species imposes great influence on the Al speciation and stability [25]. As the basicity of Al inter- or intra-species are different [43], the species which is over basified may act as a basifier, and the species which is under basified may act as Lewis acid. Acid–base neutralization reaction facilitates the capping of Al_m on the trimer of Al₁₃, and forming ε-Al₁₄. Thermal treatment promotes the isomerization of ε-Al₁₄ into δ-Al₁₄ [25]. At the same time, the internal structure in some species are dissociated and rearranged [44]. As a result, the Al hydrolysis ratios and dimension inter- or intra-species are averaged by thermal treatment. The homogenization slowed up the reaction-limited aggregation, and enhanced the stability of solutions [45].

Three types of Al species measured by Al-Ferron method and rate constant (*k*) as well as the comparison between ²⁷Al NMR and Al-Ferron methods are listed in Table 2. As the heating time increases, the content of Al_a changes very little, Al_b decreases continuously, while Al_c increases continuously. The increase in Al_c indicates that the reactivity of Al species in solution reduces by thermal treatment. This indicates thermal treatment promotes the transformation of Al species into high polymers and slow reacting species. The species transformation mainly proceeds through the inter-species polymerization and the intra-species structure adjustment or rearrangement.

Comparing the data listed in Tables 1 and 2, the changing tendency of Al species derived from Al-Ferron method is consistent with that obtained from ²⁷Al NMR. Many previous experiments carried out in diluted solutions have demonstrated that Al_b and Al₁₃ are almost equivalent. But there exists a sizable difference between the data (Al_m, Al₁₃ and Al_u vs. Al_a, Al_b and Al_c) obtained by these two methods. As can be seen from Table 2, Al_b/Al₁₃ > 1.0, and the ratio increases with the

prolonging of heating due to the more rapid decrease of Al₁₃. Al_b/(Al₁₃ + Al₃₀) < 1.0, and the ratio decreases with the prolonging of heating. This suggests that most of Al₁₃ have reacted with Ferron within 1–120 min. While Al₃₀ is more stable against the decomposition promoted by H⁺ and ligand, so it cannot react with Ferron within 1–120 min. The *k* values of all samples are in the same order of magnitude, and range from 0.0104 min⁻¹ to 0.0314 min⁻¹. The *k* values observed in current research agree reasonably well with the determinations made by several investigators for Al₁₃ polymer [40,46]. The consistency of *k* values indicates that the species reacting with Ferron within 1–60 min condense with a similar pattern and polymerization degree.

Our other research indicates that appropriate thermal treatment can enhance the stability of HPA solutions, and prevent gelling and precipitating. A clear solution almost cannot be obtained without thermal treatment or synthesized at high temperature especially for the samples with Al_T higher than 1.0 mol L⁻¹. Wang et al. [33] reported that the hydrolytic Al solutions prepared at 70 °C have better stability than those prepared at 25 °C upon aging. When HPA solutions are prepared at low temperature, the hydrolytic ratios and dimensions inter- and intra-species are different due to the limitation of diffusion kinetic limitation. The reactivity of Al species is high because there exist many structural defects and active site on Al species, and which favors gelatinization of solutions. However, these defects are remedied by structural rearrangement and adjustment during thermal treatment. So the reactivity between Al species and Ferron reagent decline, and the content of Al_c increases. It should be noted that the reactivity is not only related to the polymerization degree of Al species, but also related to the internal structure of Al species. Thermal treatment imposes greater influence on the later than on the former. Fitzgerald and Johnson [30] also reported that heating treatment could lead the decomposition of large molecular weight polymeric species to intermediate

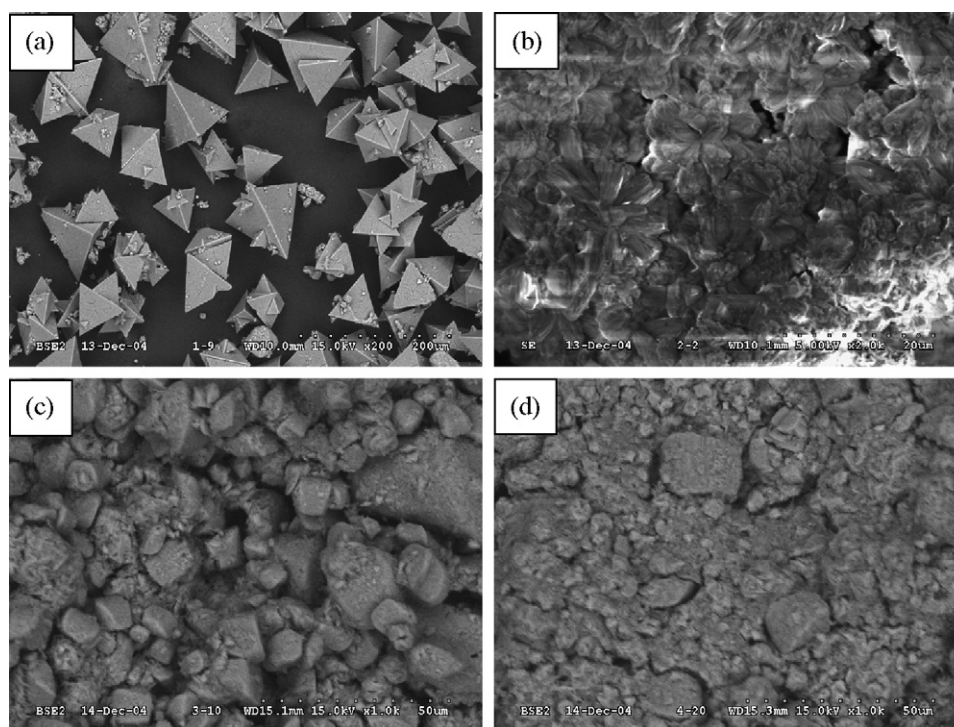


Fig. 2. Scanning electron micrographs of sulfate precipitates obtained from the samples with $Al_T = 0.2 \text{ mol L}^{-1}$ and $B = 2.4$, which was heated at 95°C for different periods after being synthesized at 80°C . (a) 40 min; (b) 12 h; (c) 24 h; (d) 48 h.

molecular weight polymeric species in highly hydrolyzed, concentrated Al chlorohydrate solutions. This is likely one of the reasons that the stability of the concentrated HPA solutions is enhanced by thermal treatment. But it should be pointed out that excessive thermal treatment at high temperature will lead to irreversible polymerization and precipitation, and deteriorate the stability of solutions.

Fig. 2 shows the scanning electron micrographs of sulfate precipitates obtained from samples with $Al_T = 0.2 \text{ mol L}^{-1}$ and $B = 2.4$. The samples were heated at 95°C for different duration after synthesized at 80°C . The tetrahedral shaped crystal in Fig. 2a is the typical crystal of Al_{13} -sulfate. The ovoid-shaped crystal in Fig. 2b is assigned to crystals of Al_{30} -sulfate [23]. Fig. 2c and d are mainly composed of large sized irregular particles and amorphous fine powders. The amount of fine powders increases with the prolonging of heating. These fine powders are possibly attributed to the sulfate of high polymerization degree and low charge species.

3.2. Effect of Al_T and B values on Al speciation during thermal treatment

Comparing the spectra with $Al_T = 0.2 \text{ mol L}^{-1}$, 0.5 mol L^{-1} and 1.0 mol L^{-1} and $B = 2.3\text{--}2.4$ in Fig. 1, we can see that Al speciation in HPA solutions is affected by Al_T . The NMR signal at 4 ppm cannot be observed in samples with $Al_T = 0.2 \text{ mol L}^{-1}$ and $B = 2.4$. But there exist clear NMR signal at 4 ppm in samples with $Al_T = 0.5 \text{ mol L}^{-1}$ and 1.0 mol L^{-1} and $B = 2.3\text{--}2.4$. The intensity of resonance peak at 4 ppm increases with the increas-

ing of Al_T , which indicates that the concentration of oligomers such as dimer and trimer increase with the increase in Al_T . At the same time, the intensity of 4 ppm weakens during thermal treatment. Another faint NMR signal is found at 75.6 ppm in samples with $Al_T = 0.5 \text{ mol L}^{-1}$ and 1.0 mol L^{-1} which were heated for more than 12 h at 95°C . The NMR signal was attributed to other high polymer that containing tetrahedral coordinated Al [22,23]. But the peak area cannot be integrated due to the weak signal intensity.

As can be seen from Table 1, with the increase in Al_T , the content of Al_m increases slightly, and the content of Al_{13} , Al_{30} and the sum of Al_{13} and Al_{30} decrease, respectively. But Al_u content increases. Increase of Al_T accelerates the polymerization of Al species. And the changing tendency of Al species is consistent with the results measured by Al-Ferron method (Table 2). Al_a content in the samples heated for 40 min increases with the increase in Al_T . But the content of Al_a in samples heated for 48 h decreases with the increase in Al_T . Al_b content decreases, and Al_c content increases with the increase in Al_T . This suggests that the polymerization reaction of Al species caused by thermal treatment is speed up by the increase in Al_T .

The influences of thermal treatment on the Al species distribution in HPA solutions weakens with the increase in Al_T . Thermal treatment imposes a great influence on the species distribution of samples with $Al_T = 0.2 \text{ mol L}^{-1}$, but has less effect on the samples with $Al_T = 0.5 \text{ mol L}^{-1}$ and 1.0 mol L^{-1} . The Al species distribution in HPA solutions is governed by multifold factors. Both heating and increasing Al_T accelerate the polymerization of Al species. In samples with relative low Al_T (e.g.

0.2 mol L⁻¹), thermal treatment governs the species distribution, but for samples with relative high Al_T (e.g. 1.0 mol L⁻¹), Al_T becomes the dominant factor which affect the Al species distribution.

Although Al_m changes very little during the process of thermal treatment, the molar concentration of Al_m in HPA solutions increases with the increase of Al_T due to the increase in Al_T and the slightly increase in the content of Al_m. From the molar concentration listed in Table 1, we can see that the initial concentration (*i.e.* 40 min samples) of Al₁₃ and Al₃₀ are different for samples with different Al_T, but the final concentration of Al₁₃ and Al₃₀ are less different when heated for 48 h at 95 °C. The final concentration of Al₁₃ ranges from 0.0021 mol L⁻¹ to 0.0064 mol L⁻¹, and Al₃₀ ranges from 0.1435 mol L⁻¹ to 0.1924 mol L⁻¹. Although the Al species in HPA solutions are the kinetic intermediate products during Al salts hydrolysis, the above results indicate there exist evident pseudo-equilibrium between Al₁₃ and Al₃₀ as well as Al_m and undetected Al species. Thermal treatment speeds up the conversion rate of metastable species to more stable species. The final equilibrium may be independent on Al_T, but the time needed to reach equilibrium is related to heating temperature.

Comparing the variation of Al species distribution in samples with Al_T=0.2 mol L⁻¹, *B*=1.8 and *B*=2.4, it can be seen that Al_m content increases greatly when *B* value decreases. With the prolongation of thermal treatment, the majority of Al₁₃ are converted to Al₃₀ in samples with Al_T=0.2 mol L⁻¹, *B*=2.4, and the content of Al_u and AlO₄ change slightly. But the high content of Al_m accelerates the conversion of Al₁₃ to Al₃₀ for samples with Al_T=0.2 mol L⁻¹, *B*=1.8, as a result, the content of Al₃₀ reaches 15.04% when heating for 40 min. At the same time, the conversion of Al₁₃ and Al₃₀ to other species also increases. So Al_u species increases continuously and the total content of Al₁₃ and Al₃₀ decreases. Because there exist large difference between *B* value (*B*=1.8) of the solutions and the theoretic *B* value of Al₁₃ (*B*=2.46) and Al₃₀ (*B*=2.4), Al₁₃ and Al₃₀ in solutions with *B*=1.8 are located in extremely non-equilibrium chemical environment. On one hand, thermal treatment accelerates the polymerization of Al₁₃ species, on the other hand, the acidic decomposition of Al₁₃ and Al₃₀ are also accelerated by thermal treatment. The later becomes the dominant reaction for samples with a low *B* value upon heating, so the total content of Al₁₃ and Al₃₀ decreases, and Al_u increases.

Comparing the content of Al_u and Al_c in samples with Al_T=0.2 mol L⁻¹, *B*=1.8 and *B*=2.4 listed in Tables 1 and 2, respectively, the content of Al_u in samples with *B*=1.8 are larger than that with *B*=2.4 when heated for more than 12 h, but the content of Al_c in samples with *B*=1.8 are lower than that with *B*=2.4. This indicates that Al_u in these two samples are different on the aspects of chemical structure and polymerization degree. The Al_u species in samples with *B*=2.4 are composed of high polymers, but the Al_u species in samples with *B*=1.8 are composed of oligomers. This can be verified by the obvious resonance signals at 4 ppm in Fig. 1d, and the signals at 4 ppm intensifies upon heating. However, there is no visible resonance signal at 4 ppm in Fig. 1a.

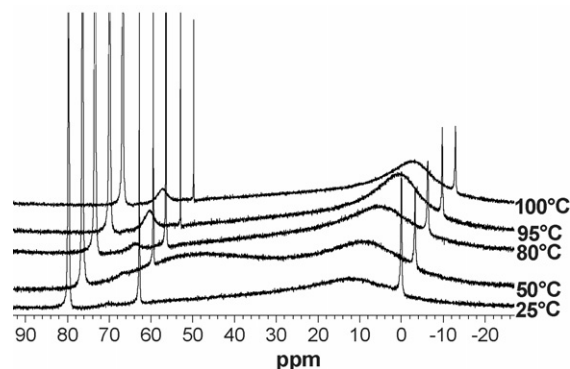


Fig. 3. ²⁷Al NMR spectra of HPA solutions which were heated for 12 h at different temperatures after being synthesized at 80 °C (Al_T=0.2 mol L⁻¹, *B*=2.4).

3.3. Effects of heating temperature on the conversion of Al₁₃ to Al₃₀

Fig. 3 shows the ²⁷Al NMR spectra of HPA samples with Al_T=0.2 mol L⁻¹ and *B*=2.4, the samples were prepared at 80 °C, and heated for 12 h under different heating temperature. The effect of heating temperature on Al speciation in HPA solutions measured by ²⁷Al NMR and Al-Ferron method are shown in Figs. 4 and 5, respectively. As can be seen from Fig. 4, Al_m content nearly does not change under all heating temperature, and it maintains between 4.0% and 5.0%. With the increase in heating temperature, Al₁₃ content decreases, and Al₃₀ content increases. This indicates that increasing heating temperature accelerates the conversion of Al₁₃ to Al₃₀. The sum of Al₁₃ and Al₃₀ increases first when heating temperature increases from 25 °C to 80 °C, and reaches a maximum, then decreases as the heating temperature increases further. Increasing heating temperature imposes two opposite effects on the sum of Al₁₃ and Al₃₀. The dissolution of Al sol-gels which enveloping around the AlO₄ undetected by ²⁷Al NMR is enhanced by increasing temperature, at the same time, the polymerization and acidic decomposition of Al₁₃ and Al₃₀ are speed up by increasing

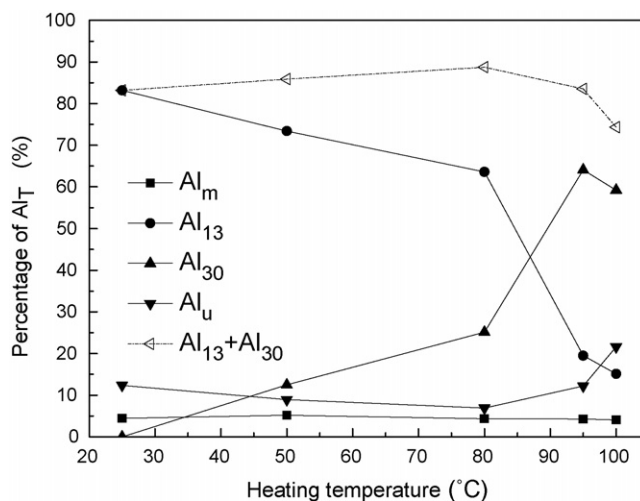


Fig. 4. Effect of heating temperature on Al speciation in HPA solutions measured by ²⁷Al NMR. (Synthesis temperature, 80 °C; heating time, 12 h; Al_T=0.2 mol L⁻¹.)

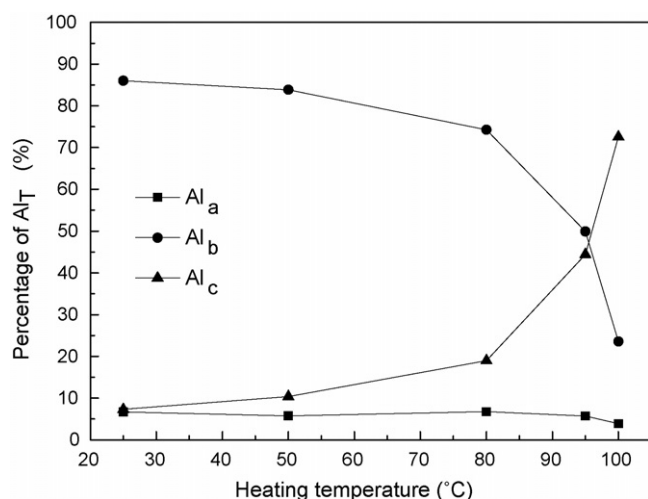


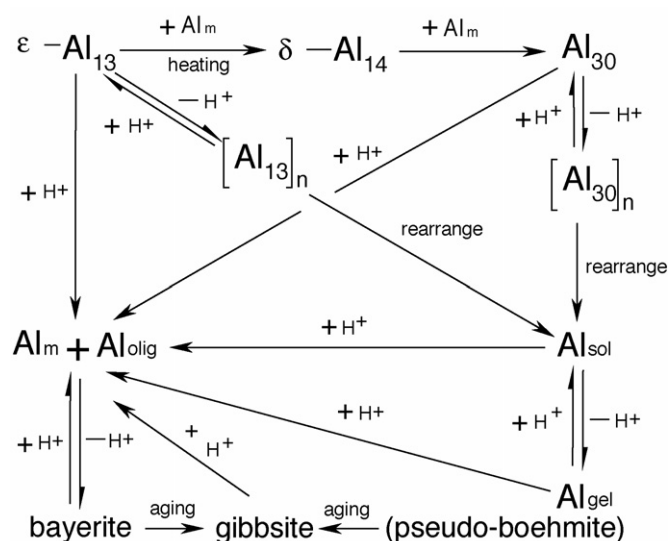
Fig. 5. Effect of heating temperature on Al speciation in HPA solutions measured by Al-Ferron method. (Synthesis temperature, 80 °C; heating time, 12 h; $Al_T = 0.2 \text{ mol L}^{-1}$.)

temperature. When heating temperature increases from 25 °C to 80 °C, the former effect is greater than the later, so the sum of Al_{13} and Al_{30} increases. But when heating at a temperature higher than 80 °C, the depletion reaction of Al_{13} and Al_{30} species become dominant, so the sum of Al_{13} and Al_{30} decreases. This is the reason why the samples were synthesized at 80 °C. Synthesis at this temperature can assure the maximum content of AlO_4 in HPA solutions.

As can be seen from Fig. 5, with the increase in heating temperature, Al_a content decreases slightly, Al_b content decreases, and Al_c content increases largely. The amount of Al that reacts with Ferron reagent within 120 min decreases from 92.69% to 27.45% when heating temperature increased from 25 °C to 100 °C. The transformation of Al species into high polymerization degree and inert species accelerates with the increase of heating temperature. And more dense polymers with compact structure formed. The polymers are more stable against the dissociation promoted by proton and ligand than that of heating at low temperature.

3.4. Species transformation mechanism

The schematic diagram on the formation and transformation of Al species in HPA solutions upon thermal treatment are shown in Scheme 1. Thermal treatment has two opposite effects on Al speciation in HPA solution. Thermal treatment accelerates the agglomeration and polymerization of Al species in HPA, results in the formation of inert and high polymers. At the same time, thermal treatment facilitates the dissociation and dissolution of Al species by H^+ in solutions. But the former is more significant than the later for samples with high B values. As can be seen from Scheme 1, since thermal treatment provides the activation energy for the isomerization of $\epsilon-Al_{13}$ to $\delta-Al_{14}$, and facilitates the isomerization reaction, the conversion of Al_{13} to Al_{30} via $\delta-Al_{14}$ is accelerated by thermal treatment. At the same time, the clustering and agglomeration of Al_{13} and Al_{30} are also accelerated by thermal treatment and



Scheme 1. Schematic diagram on the formation and transformation of Al species in HPA solutions upon thermal treatment.

elevated Al_T . The clusters of $[Al_{13}]_n$ and $[Al_{30}]_n$ consist primarily of a repeating Keggin structural unit. These clusters grow with a fractal structure, and transform into amorphous sol–gels with a pseudo-boehmite structure by a cluster–cluster aggregation. The sol–gels then slowly transform to gibbsite through solid squeezing and structural self-assembling [47,48]. The coordination number of the tetrahedral Al increases through the cleavage of Al–O–Al bond of AlO_4 during the process of transformation [48]. The rate of cluster–cluster aggregation increases with the increase in Al_T . The clusters also can be dissociated and rearranged at high temperature, and transform into a more compact structure with a high fractal dimension. As Al_{30} species is more stable than Al_{13} species at high temperature [23], the content of Al_{30} increases upon thermal treatment. But Al_{13} does not convert to Al_{30} quantitatively, since the species such as Al_{13} and Al_{30} in HPA solutions can dissociate to monomers and oligomers by H^+ besides polymerizing into high polymers. The dissociation is irreversible. Bayerite can form by recrystallization of these monomers and oligomers and ultimately convert to gibbsite by aging [47].

4. Conclusions

The combination of high-field ^{27}Al NMR and time-developed Al-Ferron complex colorimetry are effective methods to investigate Al species distribution in HPA solutions quantitatively, especially for Al_{13} and Al_{30} species with a Keggin structure. Thermal treatment has an important influence on the formation and transformation of Al_{13} and Al_{30} species in highly concentrated HPA solutions ($0.2\text{--}1.0 \text{ mol L}^{-1}$). The metastable Al_{13} species in HPA tends to polymerize and convert to Al_{30} and other high polymeric species. The rates of polymerization and transformation are speed up by heating at high temperature. The optimal heating temperature for the formation of Al_{30} is ca. 95 °C. Al_{13} content in HPA solution decreases upon thermal treatment, and Al_{30} content increases. But Al_{13} does not convert

to Al_{30} quantitatively due to the clustering, agglomeration and acidic dissolution of Al_{13} and Al_{30} . The Al_{13} species is a dominant nanosized species in freshly prepared HPA solutions, and its content reaches above 80.0% in HPA with $\text{Al}_\text{T} = 0.2 \text{ mol L}^{-1}$ and optimal B values (ca. 2.3–2.4). The content of Al_{30} becomes higher than that of Al_{13} when this solution is heated at 95°C for 12 h. And Al_{30} becomes the dominant nanosized Al species in HPA solutions. Its content reaches 76.8% in samples with $\text{Al}_\text{T} = 0.2 \text{ mol L}^{-1}$ and $B = 2.4$.

The influence of thermal treatment on the Al species distribution depends on Al_T and B value. The content of Al_{13} species decreases with the increase of Al_T and with the increase of difference between B value of solution and theoretic B values of Al_{13} . And correspondingly, the contents of Al_{30} and the sum of AlO_4 decrease. The effect of Al_T on Al speciation increases with the increase in Al_T . For HPA solutions with $B = 1.8$, the acidic dissolution of Al species exceeds polymerization upon heating treatment.

Although Al_{30} is more stable than Al_{13} , it is also a metastable species during the process of Al hydrolysis, polymerization and precipitation. The decomposition and polymerization of Al_{30} were also sped up by rising the heating temperature. Thermal treatment facilitates the inter-species polymerization and the intra-species structural rearrangement. Al species in HPA solutions tend to transform into more stable and inert species, which were more tolerated to the proton and ligand promoted decomposition. Al_b contents decrease, and Al_c contents increase. Al_{30} does not react with Ferron within 120 min.

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