Separation of $\text{Al}_{13}$ from polyaluminum chloride by sulfate precipitation and nitrate metathesis

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Abstract

A methodology of preparing high purity $\text{Al}_{13}$ through chemical precipitation/separation was developed. Polyaluminum chloride (PACl) with medium high concentration (0.1–1.1 mol/L as Al) was used as the source of $\text{Al}_{13}$. The factors that affect separation process were thoroughly examined. Intermediate and final products of $\text{Al}_{13}$ were characterized morphologically and structurally using SEM, XRD, and solid-state $^{27}\text{Al}$ NMR. The purity of obtained $\text{Al}_{13}$ product was verified using both ferron assay and $^{27}\text{Al}$ NMR. It was found that the separation of $\text{Al}_{13}$ from medium high concentration PACl was feasible and the purity of $\text{Al}_{13}$ product could be higher than 95%.

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Keywords: $\text{Al}_{13}$; Polyaluminum chloride (PACl); Separation; Purification

1. Introduction

$\text{Al}$ solution chemistry has been investigated by researchers for over a century and the research fields span over pharmaceutical, catalysis, ceramic, environmental, geochemical, soil sciences, engineering, etc. [1–7]. Much of the efforts are aimed to elucidate the transformation mechanisms among different $\text{Al}$ species, such as the formation of $\text{Al}$ hydroxides from various metastable hydrolysis products. Partially neutralized $\text{Al}$ solution is a very complicated system consisting of many different constituents, including monomers, oligomers, polymers and/or colloidal species. Further, the speciation of such $\text{Al}$ solution can be influenced by many factors, for example, the solution concentration, neutralization degree, neutralization speed, base strength, agitation intensity and temperature.

Besides the complexity of partially neutralized $\text{Al}$ solutions, another great challenge is the difficulty to identify each individual species. Only few species are confirmed experimentally to date [5]. Due to the ambiguity on $\text{Al}$ speciation, there exist different understandings about the $\text{Al}$ hydrolysis–polymerisation–precipitation pathways. Some researchers contend that the $\text{Al}$ species with six-member ring structure, known as $\text{Al}_6[\text{Al}_6(\text{OH})_{12}(\text{H}_2\text{O})_{12}]^{6+}$, plays the most important role in $\text{Al}$ hydrolysis processes and acts as precursor of the $\text{Al}$ hydroxide formation [5–7]. The $\text{Al}$ atoms in the ring structure are octahedrally coordinated and connected to each other by two $\text{OH}$ bridges. The continuous polymerization and bidimensional growth of this structure could finally form crystalline $\text{Al}$ hydroxides, such as gibbsite and bayerite. With the development of modern instrumental technologies, the existence of $\text{Al}_{13}[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{2\times+}$ has been confirmed by using $^{27}\text{Al}$ and $^{17}\text{O}$ nuclear magnetic resonance spectroscopy (NMR) [8,9]. The structure of $\text{Al}_{13}$ is highly symmetric with an $\text{AlO}_4$ tetrahedral surrounded by 12 octahedrally coordinated $\text{Al}$ (the so called Keggin structure). Since the confirmation of $\text{Al}_{13}$, some researchers argue that the formation of crystalline $\text{Al}$ hydroxide is through the aggregation and structure rearrangement of $\text{Al}_{13}$ species [5,10,11]. $\text{Al}_{13}$ has been widely reported to be the predominant species in partially neutralized $\text{Al}$ solutions. Recently, it has been proposed that both the six-member ring $\text{Al}_6$ and Keggin $\text{Al}_{13}$ structures exist in partially neutralized $\text{Al}$ solution and their formation and transformation to aluminum hydroxide follow different pathways [7].

$\text{Al}_{13}$ is receiving more and more attention due to its special structure and chemical properties. The content of $\text{Al}_{13}$ is believed to be associated with the performances of many $\text{Al}$ containing chemical products, such as catalysts, toxicant-adsorbents [1–4]. In the water treatment areas, studies...
on the coagulation/flocculation mechanisms of polyaluminum chloride (PACl) have indicated that Al13 is the most effective species, which can efficiently neutralize the surface charge of colloids and bridge small particles into large aggregates [10–12]. However, most of the current studies about Al13 are conducted either based on partially neutralized Al solutions or commercial PACl products. Al13 in these products is limited, particularly for commercial products (usually less than 40%).

Therefore, to obtain pure Al13 products will not only provide a novel perspective to study Al solution chemistry but also will help understand the specific roles it can play in many application areas. Using pure Al13 in experiments can avoid confounding effects of other species and will significantly increase the experimental reliability.

The principles of Al13 precipitation/separation from PACl are based on the reaction kinetics of various Al species with sulfate: Al monomers (including some oligomers) react with sulfate to form soluble complexes; medium polymerized species, such as Al13 react with sulfate to form crystalline solids gradually; while large Al aggregates or colloidal species react with sulfate to form amorphous solids much faster. These reaction characteristics have been successfully applied to distinguish Al species into three different categories [13–17]. The possibility of achieving Al13 separation was also reported [18]. However, most of the previous studies were focused on rather diluted Al concentrations. PACl, as the source of Al13, its concentration and Al13 content are two key factors affecting the efficiency of separation processes. On one hand, PACl solution with low concentration (less than 0.1 mol/L) could achieve high percentage of Al13, but it is not economically favorable for large-scale production; on the other hand, PACl solution with high concentration (greater than 1.0 mol/L) is preferred in large-scale production, but the Al13 content is usually too low (it is the case in most commercial PACl products). Based on these considerations, both low and high concentration PACls is not economically feasible as Al13 sources for industrial production. Therefore, the feasibility of Al13 separation utilizing medium high concentration PACls needs to be investigated.

This work first examined the speciation distribution of PACl within medium high concentration range. The effect of temperature on Al speciation was also evaluated. Bench-scale Al13 separation procedures include: PACl preparation, Al13 precipitation/separation by sulfate, Al13 re-dissolution by barium nitrate metathesis, and dehydration to obtain solid Al13 products. The optimum separation conditions were determined and products of every step were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD) and solid-state 27Al nuclear magnetic resonance. The verification of Al13 product purity was conducted using both ferron assay and 27Al NMR.

2. Experimental

2.1. Preparation of PACl

Reagents used in this study are of analytical grade, and deionized water was used to prepare all solutions. PACl solution was prepared using aluminum chloride (AlCl3·6H2O) and sodium carbonate (Na2CO3) solid powder. Pre-weighed amount of aluminum chloride was dissolved into a 500 mL glass reactor, and then under condition of intense agitation, sodium carbonate was slowly added. The sodium carbonate dosing speed was carefully adjusted to avoid occurrence of appreciable turbidity. The amount of sodium carbonate was determined according to target basicity (B value, OH/Al molar ratio). Temperature was controlled by a circulating water bath. After sodium carbonate addition, the reaction system was cooled down to room temperature and the solution volume was adjusted to pre-designed concentration. After preparation, all PACl solutions were set for at least 24 h of aging at room temperature, and then stored in refrigerator. Concentrations of the PACls (as Al) were within the medium range of 0.1–1.1 mol/L. The B values of all PACls were 2.40. The Al speciation was determined using ferron assay.

2.2. Al13 precipitation/separation

PACl prepared under optimum condition was chosen to conduct separation operations. Hundred milliliter of PACl solution was transferred into a 300 mL glass beaker, and then a pre-calculated amount of Na2SO4 solution was introduced with target SO4/Al molar ratios under the condition of magnetic stirring. The concentration of Na2SO4 solution was adjusted according to the target total Al concentration (denoted as Alt) in the reaction system. Samples were taken at different reaction time and filtered using 0.45 μm Millipore membrane. The residual Al concentration in filtrate was determined using inductively coupled plasma-optical emission spectrophotometer (ICP-OES, 1100–1155 V, Jarrell-Ash, USA). By observing residual Al concentration changes with time under different SO4/Al ratios and Alt, the optimum precipitation conditions were determined. Precipitate obtained under optimum condition was dried at room temperature and stored for the next metathesis operation. Since the precipitate mainly consisted of compound formed by Al13 and sulfate, this product was denoted as Al13-(SO4)h in this study.

To obtain soluble Al13 product, further ion metathesis reaction was carried out to release Al13 from solids into solution. Ba(NO3)2 was chosen to conduct this metathesis process. Ten grams of Al13-(SO4)h solid was put into a 200 mL glass beaker, and 20 mL of water was added to pre-disperse the solid, then under condition of intense agitation, a certain amount of Ba(NO3)2 solution was mixed with Al13-(SO4)h suspension. The concentration of Ba(NO3)2 was 0.306 mol/L. After metathesis reaction, insoluble product and soluble Al13 were separated by 0.45 μm membrane filtration. The filtrate Al concentration and speciation was measured using ICP-OES and ferron assay, respectively.

Soluble solid Al13 product was acquired by freeze-drying. The Al13 solution after metathesis reaction was frozen into ice state under temperature of −18 °C, and then put it into a vacuum freeze-dryer (Alpha, Martin Christ, Germany) to remove water. Dried Al13 product was collected and sealed in a glass bottle.
2.3. Characterization of intermediate and final Al\textsubscript{13} products

Solid samples were characterized using three different instrumental technologies: SEM, XRD, and solid-state \textsuperscript{27}Al NMR. XRD was performed using an X’Pert PRO MPD diffractometer (PANalytical, Holland). The instrumental settings were: Cu K\textalpha, 40 kV, 40 mA. Data were collected from 2\theta degree of 5–90\degree and the scanning rate was 1\degree(2\theta)/min. The SEM images of solid matters were captured using a S-3000 (Hitachi, Japan) scanning electron microscope. Solid-state \textsuperscript{27}Al NMR (Inova 300, Varian Inc., USA) were utilized to verify the existence of Al\textsubscript{13} Keggin structure. The instrumental settings were: 6mm Chemagnetics TM solid double-resonance probe; resonance frequency 78.17 MHz; rotation frequency 5 KHz; recycling delay time 1 s.

The speciation of PACls and separated Al\textsubscript{13} solutions was determined using ferron assay. Ferron assay is based on the reaction kinetics of different Al species with ferron (8-hydroxy-7-iodo-5-quinoline-sulfonic acid). This assay can differentiate Al species into three categories: Al\textsubscript{a} (monomers), Al\textsubscript{b} (fast-reacting polymers), and Al\textsubscript{c} (slow-reacting colloidal species). In this study, the reagents preparation and operation procedures followed the method described in Wang et al.\cite{19}. As a speciation verification method, liquid-state \textsuperscript{27}Al NMR (Avance 500, Bruker, USA) was run to evaluate the purity of Al\textsubscript{13} product. The instrumental settings were: RF = 500 MHz, NS = 128, P1 = 20 \mu s, PL1 = −3 dB, inner standard 0.05 mol/L NaAlO\textsubscript{2} (75% D\textsubscript{2}O), \textit{T} = 298 K.

3. Results and discussion

3.1. Effect of concentration and temperature on the speciation of PACls

The speciation of PACls within medium high concentration range was investigated. At the same time, two temperature levels were chosen to assess the influence of preparation temperature on the content of Al\textsubscript{13} (Fig. 1). Fig. 1a shows the Al speciation changes with the increase of concentration under preparation temperature of 50\degree C. The Al\textsubscript{a} was relatively stable within this concentration range and kept in a level of lower than 10%. Al\textsubscript{b} was dominant species for all PACls, but its content decreased rapidly when the total Al concentration was greater than 0.6 mol/L. With the decrease of Al\textsubscript{b}, Al\textsubscript{c} species increased accordingly. It has been proved that Al\textsubscript{b} content determined by ferron assay bears good relationship with the Al\textsubscript{13} content determined by \textsuperscript{27}Al NMR, and the ratio of Al\textsubscript{b}/Al\textsubscript{13} is close to 1.0 \cite{20}. So the content of Al\textsubscript{b} in PACl can reasonably be viewed as the equivalent content of Al\textsubscript{13}.

The comparison of Al\textsubscript{b} between two different preparation temperature levels is illustrated in Fig. 1b. It shows the Al\textsubscript{b} content obtained at 70\degree C decreased with the increase of concentration. When the concentration was less than 0.6 mol/L, Al\textsubscript{b} corresponding to 50\degree C was higher than that corresponding to 70\degree C. However, the situation was reversed when concentration was greater than 0.6 mol/L. It should be mentioned that room temperature was not suitable for preparation of PACls within medium high concentration ranges because large amount of Al hydroxide precipitate could occur during the process of base addition if temperature was low. The occurrence and/or accumulation of precipitate were unfavorable for Al\textsubscript{13} formation \cite{5}. Increasing temperature could avoid or mitigate such disadvantages. On the other hand, high temperature (over 80\degree C) could intensively promote the Al hydrolyzing progress or lead to different hydrolyzing pathways, and consequently lead to less Al\textsubscript{13} species \cite{8,10}. Medium high temperature might be favorable for Al\textsubscript{13} formation, and thus 50 and 70\degree C were chosen in this study. Another issue should be addressed here is the utilization of Na\textsubscript{2}CO\textsubscript{3} as base reagent instead of NaOH. NaOH is a strong base and widely used in laboratory to prepare low concentration PACI. But when it was used to prepare medium high concentration PACI, precipitate could form rapidly despite intense agitation and increased temperature.

With all the above factors being considered, PACI prepared at temperature of 50\degree C with concentration of 0.5 mol/L was selected as Al\textsubscript{13} source for the next separation steps. Fig. 1a depicts that the Al\textsubscript{13} content of this PACI reached as high as 80\%, and its colloidal species (Al\textsubscript{c}) was as low as 10\%.

3.2. Precipitation/separation of Al\textsubscript{13} from PACI

The residual Al concentration changes with precipitation reaction time at different SO\textsubscript{4}/Al ratios and different Al\textsubscript{b} concen-
The precipitation reactions were significantly influenced by SO$_4$/Al and Al$_t$. For SO$_4$/Al of 0.2, no appreciable precipitate was observed during the whole experimental period. In the cases of SO$_4$/Al ratios greater than 0.2, the residual Al decreased obviously with time. By comparing the reaction characteristics with Al$_t$ 0.10 and 0.25 mol/L (Fig. 2a and b), the dilution effect on precipitation was evaluated. Clearly the precipitation reactions in less diluted system were faster than those in more diluted system. It is particularly observed for the case of SO$_4$/Al ratio 0.4: when the Al$_t$ value was 0.25 mol/L, the reaction curve approached an almost level phase after 8 min; but when the Al$_t$ value was 0.10 mol/L, even after 20 min there was no such level phase observed. Another interesting phenomenon was that precipitates did not occur immediately after Na$_2$SO$_4$ was added for some cases (SO$_4$/Al ratio 1.0 in Fig. 2a, SO$_4$/Al ratios of 0.4 and 0.6 in Fig. 2b). This phenomenon might be explained by the lack of crystal seeds at the beginning in the reaction system.

Except for the reactions with SO$_4$/Al ratio of 0.2 at both Al$_t$ values and SO$_4$/Al ratio of 0.4 at Al$_t$ of 0.1 mol/L, all other reaction curves reached an almost level phase after a period of rapid reaction. The level phases of these curves did not imply precipitation reactions were completed. Calculation demonstrated that even for the case of SO$_4$/Al 1.0, after 20 min of reaction the residual Al still accounted for 40 and 24% of total Al, with Al$_t$ 0.10 and 0.25 mol/L, respectively. It was much higher than the amount of Al$_b$ in original PACl (Al$_b$ less than 10%). In order to confirm if the sulfate was sufficient, Ba(NO$_3$)$_2$ was added to the solutions after filtration. It was observed that BaSO$_4$ was formed immediately with the addition of Ba(NO$_3$)$_2$. Thus, it can be deduced that some Al$_b$ species could form temporarily soluble compounds with sulfate and further formation of solids could take much longer time.

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**Fig. 2.** The residual Al concentration changes with time during reaction of PACl with sulfate. (a) Al$_t$ 0.10 mol/L; (b) Al$_t$ 0.25 mol/L (R-Al: Residual Al concentration).

**Fig. 3.** The SEM images of Al$_{13}$-(SO$_4$)$_n$ precipitate.
According to previous study, there existed a transition period between the reactions of sulfate with Alc and Alb [18]. That means, upon the addition of sulfate, Alc reacted with sulfate rapidly and then after a period of non-precipitation, the precipitation of sulfate with Alb started at much lower rate. The latter precipitation period could take as long as tens of hours. The duration of such transition period was found dependent on the Al concentration. The more diluted the system was, the longer the transition period would last. Taking advantage of this transition period, Alc and Alb could be separated. Fig. 2a shows that there exits only a small plateau zone between reaction time of 1 and 2 min with SO4/Al ratios of 0.4 and 0.6, which might be resulted from the time lag between the reactions of sulfate with Alc and Alb. However, when Al increased to 0.25 mol/L, no obvious transition period was observed (Fig. 2b).

These results indicate that with the increase of PACl concentration and/or the total Al concentration of precipitation reaction system, the precipitation of Alb species could be accelerated dramatically and the transition period between the reactions of sulfate with Alc and Alb tended to diminish.

Due to the greatly shortened and even diminished transition period between sulfate with Alc and Alb, the precipitates formed here were supposed to be a mixture of these two species. SEM was used to examine the precipitate morphology. Fig. 3 presents the images of precipitate formed under the conditions of SO4/Al ratio 1.0, reaction time 10 min, and Al 0.25 mol/L. Fig. 3a is one of the most representative images viewed at relatively low magnification, which demonstrated that tetrahedral-shaped crystals were the dominant components in the precipitate. Fig. 3b shows the appearance of a larger precipitate particle, which was consisted of a cluster of many small tetrahedral crystals.

Former studies reported that precipitate formed by sulfate and Al13 could take on tetrahedral crystal shape, but the formation process of such crystals was very slow [18,21,22]. Some irregular matter in the precipitate could also be observed (Fig. 3c and d), but their occurrence within the whole specimen was very rare, which was in agreement with the low percentage of Alc in PACl. XRD and solid-state 27Al NMR were used to further characterize the precipitate (Figs. 4 and 5). XRD pattern proves that the precipitate was mainly consisted of well-formed crystalline solid, which corresponded to the matter with tetrahedral structure observed in SEM images. This diffraction pattern matched well with the reference compound given by International Diffraction Center: Na[AlO4(OH)24(H2O)12]·SO4·xH2O. This formula gives the composition of those tetrahedral crystals, which include one Al13 unit, four sulfates, one sodium ion and uncertain amount of combined water molecules. The existence of Al13 Keggin structure in the precipitate was also confirmed by solid-state 27Al NMR (Fig. 5). Clearly, there is only one peak at chemical shift of 61.5 ppm, which was attributed to the resonance of the central Al atom within the Al13 Keggin structure [14]. It indicated that the original Al13 structure in PACl was not affected by its combination with sulfate during the precipitation/separation process.

In the aim of achieving high production efficiency, the Al13 precipitation/separation conditions were chosen as follows (0.5 mol/L PACl was used): SO4/Al molar ratio 1.0, Na2SO4 concentration 0.5 mol/L, precipitation reaction time 10 min. Precipitate collected was dried and stored for the next step of metathesis operation.

3.3. Transformation of Al13-(SO4)n into water soluble Al13 product

The Al13-(SO4)n product itself can be used to synthesize some special materials, such as nano-sized alumina [22]. However, in most cases, soluble Al13 product is required. It can be achieved by metathesis reaction between Al13-(SO4)n and Ba(NO3)2. This reaction can be expressed as:

\[
\text{Al13-(SO4)}_n + n\text{Ba(NO3)}_2 \rightarrow \text{Al13-(NO3)}_{2n} + n\text{BaSO}_4
\]

Through this reaction, more insoluble barium sulfate (BaSO4) is produced, at the same time, Al13 is released in the form of free polycations. Then, soluble Al13 and BaSO4 can be separated by filtration. In order to obtain high concentration Al13, a 0.306 mol/L Ba(NO3)2 solution was prepared, which is close to the solubility of Ba(NO3)2 at room temperature.

The metathesis reaction kinetics was investigated first and it was observed that the reaction could be completed in 30 min (data are not shown). The proportion of the two reactants could affect the purity of Al13. If excessive amount of Ba(NO3)2 is introduced, there will be residual barium ions left in Al13 solution; on the other hand, Al species in the form of Alc might also be released into Al13 solution. Thus, excessive amount of Ba(NO3)2 should be avoided. The Ba/NO3 molar ratio could be

![Fig. 4. XRD pattern of Al13-(SO4)n precipitate.](image)

![Fig. 5. Solid-state 27Al NMR spectrum of Al13-(SO4)n precipitate.](image)
used as an operation index to determine the optimum barium nitrate dosage in the metathesis reaction. It was observed that when Ba/\(\text{SO}_4\) ratio was greater than 1.0, \(\text{Al}_\text{b}\) was released, which was indicated by low \(\text{Al}_{13}\) purity and the existence of colloidal particles. It should be noted that the upper limit of Ba/\(\text{SO}_4\) ratio is not a constant, its value depends on the specific composition of \(\text{Al}_{13}-(\text{SO}_4)_n\) solid product.

Ba/\(\text{SO}_4\) ratio of 0.8 was chosen to perform further metathesis reactions. The obtained solution after metathesis and filtration was examined using ferron assay. The total Al concentration is 0.69 mol/L, and the content of \(\text{Alb}\) can be reached as high as 98.7%. It is hardly possible for a traditionally prepared PACl to achieve this high \(\text{Alb}\) content at the same concentration level.

The residual insoluble matter after metathesis and filtration were collected and dried at room temperature. XRD and solid-state \(^{27}\text{Al}\) NMR were used to characterize its components (Fig. 6). The XRD pattern matched well with the standard diffraction pattern of barium sulfate, which demonstrated that barium sulfate was the main component of the insoluble matter. While the solid-state \(^{27}\text{Al}\) NMR spectrum obviously indicated that there existed \(\text{Al}_{13}-(\text{SO}_4)_n\) left in the solid matter. The existence of \(\text{Al}_{13}-(\text{SO}_4)_n\) could be explained by the insufficiency of barium nitrate.

Compared to \(\text{Al}_{13}\) solution, solid \(\text{Al}_{13}\) is more convenient to transport, store and use. In this work, solid \(\text{Al}_{13}\) product was acquired through freeze-drying and evaluated by various methods. First, it was characterized using XRD, SEM and solid-state \(^{27}\text{Al}\) NMR (Figs. 7–9, respectively). Both XRD pattern and SEM images demonstrated that this solid product did not have well-formed crystalline structure. The solid particles were irregular and porous (Fig. 8). The chemical shift at 62.1 ppm in Fig. 9 indicated the existence of \(\text{Al}_{13}\) Keggin structure in the solid product.
The purity of re-dissolved solid Al₁₃ product was verified. A test solution was prepared by dissolving 1.0 g Al₁₃ solid into 100 mL water, then its speciation was determined using both ferron assay and liquid-state ²⁷Al NMR, respectively (Table 1). The liquid-state ²⁷Al NMR method can also distinguish Al species into three categories: Alₘₙ (monomeric species), Al₁₃, and Alₙ (non-observable species).

Compared to the Al₁₃ solution before drying, there was only little decrease of Al₅ₐ, and correspondingly little increase of Alₚₖ in the re-dissolved Al₁₃ solution. Fig. 10a shows the ²⁷Al NMR spectrum of this re-dissolved Al₁₃ solution. There was only a small peak at 0 ppm, which indicated only little amount of monomeric Al species existed in the re-dissolved Al₁₃ solution (the peak at 80 ppm was from the inner standard of Al(OD)₄⁻). Speciation calculation based on the NMR spectrum confirmed that the amount of Alₖ determined by ferron assay was equivalent to the amount of Al₁₃ (corresponding to the peak at 63.1 ppm). Al₁₃ accounted for 96.6% of total Al, while other species only accounted for less than 5% of total Al. As a comparison, the ²⁷Al NMR spectrum of original PACl was also presented (Fig. 10b). For PACl, in addition to Al₁₃, the resonance peak at 0 ppm (corresponding to monomeric Al species) was significantly higher than that of re-dissolved Al₁₃ solution.

### Table 1

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<th>Concentration (mol/L)</th>
<th>Ferron assay (%)</th>
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<tr>
<td></td>
<td>Alₖ</td>
<td>Alₗₐ</td>
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<td>0.08</td>
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Compared to the Al₁₃ solution before drying, there was only little decrease of Alₗₐ, and correspondingly little increase of Alₖ in the re-dissolved Al₁₃ solution. Fig. 10a shows the ²⁷Al NMR spectrum of this re-dissolved Al₁₃ solution. There was only a small peak at 0 ppm, which indicated only little amount of monomeric Al species existed in the re-dissolved Al₁₃ solution (the peak at 80 ppm was from the inner standard of Al(OD)₄⁻). Speciation calculation based on the NMR spectrum confirmed that the amount of Alₖ determined by ferron assay was equivalent to the amount of Al₁₃ (corresponding to the peak at 63.1 ppm). Al₁₃ accounted for 96.6% of total Al, while other species only accounted for less than 5% of total Al. As a comparison, the ²⁷Al NMR spectrum of original PACl was also presented (Fig. 10b). For PACl, in addition to Al₁₃, the resonance peak at 0 ppm (corresponding to monomeric Al species) was significantly higher than that of re-dissolved Al₁₃ solution.

### 4. Conclusion

High purity Al₁₃ products (both solution and solid forms) were obtained using sulfate precipitation/separation and consequent barium nitrate metathesis operations from medium high concentration PACl. Both concentration and preparation temperature had significant influences on the speciation of PACls. Al₁₃ separation conducted within medium high concentration ranges led to greatly accelerated precipitation process and as a result co-precipitation of Alₖ and Alₗₐ with sulfate occurred. Tetrahedral-shaped crystalline matter was the dominant component of the co-precipitate. For the metathesis operation, the Ba/SO₄ molar ratio was observed to affect the purity of Al₁₃, and excessive amount of barium nitrate should be avoided. Purified Al₁₃ solution could be freeze-dried into solid form, and the re-dissolution of solid product exhibited no significant degradation of Al₁₃ purity.

### References


