Separation of Al_{13} from polyaluminum chloride by sulfate precipitation and nitrate metathesis

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Abstract

A methodology of preparing high purity 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 Al_{13} . The factors that affect separation process were thoroughly examined. Intermediate and final products of Al_{13} were characterized morphologically and structurally using SEM, XRD, and solid-state ^{27}Al NMR. The purity of obtained Al_{13} product was verified using both ferron assay and ^{27}Al NMR. It was found that the separation of Al_{13} from medium high concentration PACl was feasible and the purity of Al_{13} product could be higher than 95%.

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Keywords: Al_{13} ; Polyaluminum chloride (PACl); Separation; Purification

1. Introduction

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 Al species, such as the formation of Al hydroxides from various metastable hydrolysis products. Partially neutralized 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 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 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 Al speciation, there exist different understandings about the Al hydrolysis–polymerisation–precipitation pathways. Some researchers contend that the 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 Al hydrolysis processes and acts as precursor of the Al hydroxide formation [5–7]. The Al atoms in the ring structure are octahedrally coordinated and connected to each other by two OH bridges. The continuous polymerization and bidimensional growth of this structure could finally form crystalline Al hydroxides, such as gibbsite and bayerite. With the development of modern instrumental technologies, the existence of $\text{Al}_{13}[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ has been confirmed by using ^{27}Al and ^{17}O nuclear magnetic resonance spectroscopy (NMR) [8,9]. The structure of Al_{13} is highly symmetric with an AlO_4 tetrahedral surrounded by 12 octahedrally coordinated Al (the so called Keggin structure). Since the confirmation of Al_{13} , some researchers argue that the formation of crystalline Al hydroxide is through the aggregation and structure rearrangement of Al_{13} species [5,10,11]. Al_{13} has been widely reported to be the predominant species in partially neutralized Al solutions. Recently, it has been proposed that both the six-member ring Al_6 and Keggin Al_{13} structures exist in partially neutralized Al solution and their formation and transformation to aluminum hydroxide follow different pathways [7].

Al_{13} is receiving more and more attention due to its special structure and chemical properties. The content of Al_{13} is believed to be associated with the performances of many Al containing chemical products, such as catalysts, toxicant-adsorbents [1–4]. In the water treatment areas, studies

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on the coagulation/flocculation mechanisms of polyaluminum chloride (PACl) have indicated that Al_{13} 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 Al_{13} are conducted either based on partially neutralized Al solutions or commercial PACl products. Al_{13} in these products is limited, particularly for commercial products (usually less than 40%).

Therefore, to obtain pure Al_{13} 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 Al_{13} in experiments can avoid confounding effects of other species and will significantly increase the experimental reliability.

The principles of Al_{13} 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 Al_{13} 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 Al_{13} separation was also reported [18]. However, most of the previous studies were focused on rather diluted Al concentrations. PACl, as the source of Al_{13} , its concentration and Al_{13} 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 Al_{13} , 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 Al_{13} 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 Al_{13} sources for industrial production. Therefore, the feasibility of Al_{13} 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 Al_{13} separation procedures include: PACl preparation, Al_{13} precipitation/separation by sulfate, Al_{13} re-dissolution by barium nitrate metathesis, and dehydration to obtain solid Al_{13} 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 ^{27}Al nuclear magnetic resonance. The verification of Al_{13} product purity was conducted using both ferron assay and ^{27}Al 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 ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) and sodium carbonate (Na_2CO_3) 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. Al_{13} precipitation/separation

PACl prepared under optimum condition was chosen to conduct separation operations. Hundred millilitre of PACl solution was transferred into a 300 mL glass beaker, and then a pre-calculated amount of Na_2SO_4 solution was introduced with target SO_4/Al molar ratios under the condition of magnetic stirring. The concentration of Na_2SO_4 solution was adjusted according to the target total Al concentration (denoted as Al_t) 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 SO_4/Al ratios and Al_t , 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 Al_{13} and sulfate, this product was denoted as $\text{Al}_{13}-(\text{SO}_4)_n$ in this study.

To obtain soluble Al_{13} product, further ion metathesis reaction was carried out to release Al_{13} from solids into solution. $\text{Ba}(\text{NO}_3)_2$ was chosen to conduct this metathesis process. Ten grams of $\text{Al}_{13}-(\text{SO}_4)_n$ 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 $\text{Ba}(\text{NO}_3)_2$ solution was mixed with $\text{Al}_{13}-(\text{SO}_4)_n$ suspension. The concentration of $\text{Ba}(\text{NO}_3)_2$ was 0.306 mol/L. After metathesis reaction, insoluble product and soluble Al_{13} 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 Al_{13} product was acquired by freeze-drying. The Al_{13} 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 Al_{13} product was collected and sealed in a glass bottle.

2.3. Characterization of intermediate and final Al_{13} products

Solid samples were characterized using three different instrumental technologies: SEM, XRD, and solid-state ^{27}Al NMR. XRD was performed using an X'Pert PRO MPD diffractometer (PANalytical, Holland). The instrumental settings were: Cu $K\alpha$, 40 kV, 40 mA. Data were collected from 2θ degree of $5-90^\circ$ and the scanning rate was $1^\circ(2\theta)/min$. The SEM images of solid matters were captured using a S-3000 (Hitachi, Japan) scanning electron microscope. Solid-state ^{27}Al NMR (Inova 300, Varian Inc., USA) were utilized to verify the existence of Al_{13} Keggin structure. The instrumental settings were: 6mm Chemagetics 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_{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_a (monomers), Al_b (fast-reacting polymers), and Al_c (slow-reacting colloidal species). In this study, the reagents preparation and operation procedures followed the method described in Wang et al. [19]. As a speciation verification method, liquid-state ^{27}Al NMR (Avance 500, Bruker, USA) was run to evaluate the purity of Al_{13} product. The instrument settings were: RF = 500MHz, NS = 128, P1 = 20 μ s, PL1 = -3 dB, inner standard 0.05 mol/L $NaAlO_2$ (75% D_2O), $T = 298$ 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_{13} (Fig. 1). Fig. 1a shows the Al speciation changes with the increase of concentration under preparation temperature of $50^\circ C$. The Al_a was relatively stable within this concentration range and kept in a level of lower than 10%. Al_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_b , Al_c species increased accordingly. It has been proved that Al_b content determined by ferron assay bears good relationship with the Al_{13} content determined by ^{27}Al NMR, and the ratio of Al_b/Al_{13} is close to 1.0 [20]. So the content of Al_b in PACl can reasonably be viewed as the equivalent content of Al_{13} .

The comparison of Al_b between two different preparation temperature levels is illustrated in Fig. 1b. It shows the Al_b content obtained at $70^\circ C$ decreased with the increase of concentration. When the concentration was less than 0.6 mol/L, Al_b corresponding to $50^\circ C$ was higher than that corresponding to $70^\circ C$. 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

Fig. 1. The speciation evolution of PACl with concentration (a) and the comparison of Al_b content at different preparation temperatures (b).

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_{13} formation [5]. Increasing temperature could avoid or mitigate such disadvantages. On the other hand, high temperature (over $80^\circ C$) could intensively promote the Al hydrolyzing progress or lead to different hydrolyzing pathways, and consequently lead to less Al_{13} species [8,10]. Medium high temperature might be favorable for Al_{13} formation, and thus 50 and $70^\circ C$ were chosen in this study. Another issue should be addressed here is the utilization of Na_2CO_3 as base reagent instead of NaOH. NaOH is a strong base and widely used in laboratory to prepare low concentration PACl. But when it was used to prepare medium high concentration PACl, precipitate could form rapidly despite intense agitation and increased temperature.

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

3.2. Precipitation/separation of Al_{13} from PACl

The residual Al concentration changes with precipitation reaction time at different SO_4/Al ratios and different Al_i concen-

trations are shown in Fig. 2. It can be seen that 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_2SO_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_a in original PACl (Al_a less than 10%). In order to confirm if the sulfate was sufficient, $\text{Ba}(\text{NO}_3)_2$ was added to the solutions after filtration. It was observed that BaSO_4 was formed immediately with the addition of $\text{Ba}(\text{NO}_3)_2$. 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.

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 $\text{Al}_{13}-(\text{SO}_4)_n$ precipitate.

According to previous study, there existed a transition period between the reactions of sulfate with Al_c and Al_b [18]. That means, upon the addition of sulfate, Al_c reacted with sulfate rapidly and then after a period of non-precipitation, the precipitation of sulfate with Al_b 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, Al_c and Al_b could be separated. Fig. 2a shows that there exists only a small plateau zone between reaction time of 1 and 2 min with SO_4/Al ratios of 0.4 and 0.6, which might be resulted from the time lag between the reactions of sulfate with Al_c and Al_b . However, when Al_t 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 Al_b species could be accelerated dramatically and the transition period between the reactions of sulfate with Al_c and Al_b tended to diminish.

Due to the greatly shortened and even diminished transition period between sulfate with Al_c and Al_b , 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 SO_4/Al ratio 1.0, reaction time 10 min, and Al_t 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 Al_{13} 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 Al_c in PACl. XRD and solid-state ^{27}Al NMR technologies 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

Fig. 5. Solid-state ^{27}Al NMR spectrum of $Al_{13}-(SO_4)_n$ precipitate.

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: $Na[AlO_4(OH)_{24}(H_2O)_{12}][SO_4]_4 \cdot xH_2O$. This formula gives the composition of those tetrahedral crystals, which include one Al_{13} unit, four sulfates, one sodium ion and uncertain amount of combined water molecules. The existence of Al_{13} Keggin structure in the precipitate was also confirmed by solid-state ^{27}Al 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 Al_{13} Keggin structure [14]. It indicated that the original Al_{13} 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 Al_{13} precipitation/separation conditions were chosen as follows (0.5 mol/L PACl was used): SO_4/Al molar ratio 1.0, Na_2SO_4 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 $Al_{13}-(SO_4)_n$ into water soluble Al_{13} product

The $Al_{13}-(SO_4)_n$ product itself can be used to synthesize some special materials, such as nano-sized alumina [22]. However, in most cases, soluble Al_{13} product is required. It can be achieved by metathesis reaction between $Al_{13}-(SO_4)_n$ and $Ba(NO_3)_2$. This reaction can be expressed as:

Through this reaction, more insoluble barium sulfate ($BaSO_4$) is produced, at the same time, Al_{13} is released in the form of free polycations. Then, soluble Al_{13} and $BaSO_4$ can be separated by filtration. In order to obtain high concentration Al_{13} , a 0.306 mol/L $Ba(NO_3)_2$ solution was prepared, which is close to the solubility of $Ba(NO_3)_2$ 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 Al_{13} . If excessive amount of $Ba(NO_3)_2$ is introduced, there will be residual barium ions left in Al_{13} solution; on the other hand, Al species in the form of Al_c might also be released into Al_{13} solution. Thus, excessive amount of $Ba(NO_3)_2$ should be avoided. The Ba/SO_4 molar ratio could be

Fig. 4. XRD pattern of $Al_{13}-(SO_4)_n$ precipitate.

used as an operation index to determine the optimum barium nitrate dosage in the metathesis reaction. It was observed that when Ba/SO₄ ratio was greater than 1.0, Al_c was released, which was indicated by low Al₁₃ purity and the existence of colloidal particles. It should be noted that the upper limit of Ba/SO₄ ratio is not a constant, its value depends on the specific composition of Al₁₃-(SO₄)_n solid product.

Ba/SO₄ 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 Al_b can be reached as high as 98.7%. It is hardly possible for a traditionally prepared PACl to achieve this high Al_b 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 ²⁷Al 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 ²⁷Al NMR spectrum obviously indicated that there existed Al₁₃-(SO₄)_n left in the solid matter. The existence of Al₁₃-(SO₄)_n could be explained by the insufficiency of barium nitrate.

Compared to Al₁₃ solution, solid Al₁₃ is more convenient to transport, store and use. In this work, solid Al₁₃ product was acquired through freeze-drying and evaluated by various methods. First, it was characterized using XRD, SEM and solid-state ²⁷Al 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 Al₁₃ Keggin structure in the solid product.

Fig. 6. XRD pattern (a) and solid-state ²⁷Al NMR spectrum (b) of residual insoluble matter after metathesis reaction.

Fig. 7. XRD pattern of solid Al₁₃ product.

Fig. 8. SEM images of solid Al₁₃ product.

Fig. 9. Solid-state ^{27}Al NMR spectrum of solid Al_{13} product.

Table 1
Al concentration and speciation of re-dissolved solid Al_{13} product

Concentration (mol/L)	Ferron assay (%)			^{27}Al NMR (%)		
	Al_a	Al_b	Al_c	Al_m	Al_{13}	Al_n
0.08	3.4	95.8	0.8	2.2	96.6	1.2

The purity of re-dissolved solid Al_{13} product was verified. A test solution was prepared by dissolving 1.0 g Al_{13} solid into 100 mL water, then its speciation was determined using both ferron assay and liquid-state ^{27}Al NMR, respectively (Table 1). The liquid-state ^{27}Al NMR method can also distinguish Al species into three categories: Al_m (monomeric species), Al_{13} , and Al_n (non-observable species).

Compared to the Al_{13} solution before drying, there was only little decrease of Al_b , and correspondingly little increase of Al_a in the re-dissolved Al_{13} solution. Fig. 10a shows the ^{27}Al NMR spectrum of this re-dissolved Al_{13} solution. There was only a small peak at 0 ppm, which indicated only little amount of

monomeric Al species existed in the re-dissolved Al_{13} solution (the peak at 80 ppm was from the inner standard of $\text{Al}(\text{OD})_4^-$). Speciation calculation based on the NMR spectrum confirmed that the amount of Al_b determined by ferron assay was equivalent to the amount of Al_{13} (corresponding to the peak at 63.1 ppm). Al_{13} accounted for 96.6% of total Al, while other species only accounted for less than 5% of total Al. As a comparison, the ^{27}Al NMR spectrum of original PACl was also presented (Fig. 10b). For PACl, in addition to Al_{13} , the resonance peak at 0 ppm (corresponding to monomeric Al species) was significantly higher than that of re-dissolved Al_{13} solution.

4. Conclusion

High purity Al_{13} 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. Al_{13} separation conducted within medium high concentration ranges led to greatly accelerated precipitation process and as a result co-precipitation of Al_b and Al_c with sulfate occurred. Tetrahedral-shaped crystalline matter was the dominant component of the co-precipitate. For the metathesis operation, the Ba/SO_4 molar ratio was observed to affect the purity of Al_{13} , and excessive amount of barium nitrate should be avoided. Purified Al_{13} solution could be freeze-dried into solid form, and the re-dissolution of solid product exhibited no significant degradation of Al_{13} purity.

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Fig. 10. Liquid-state ^{27}Al NMR spectrum of re-dissolved solid Al_{13} product (a), and original PACl solution (b).

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