Optimization of the separation and purification of Al_{13}

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Abstract

The optimum process for the separation and purification of Al_{13} was investigated in detail in this paper. The various influencing factors were discussed. The experimental results show that the concentration and basicity (B , OH/Al ratio) of polyaluminum chloride (PACl), Al/SO_4 ratio, Ba/SO_4 ratio and ultrasonic reaction have different roles in the separation and purification of Al_{13} . Moderate concentration of PACl with the basicity around 2.0 gives some benefits in the separation of Al_{13} . An optimization condition has then been found to obtain high purity Al_{13} by involving Al/SO_4 and Ba/SO_4 ratios of 1:1, and 3 h ultrasonic time. Further indication on the separation of Al_{13} is also discussed.

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1. Introduction

In aqueous solution, $\text{Al}(\text{III})$ exhibits strong trend of hydrolysis. After dosing into water solution, it will undergo serial hydrolysis, polymerization, aggregation and precipitation processes. As results, various possible species existing in a metastable state or transient state can be formed in the bulk solution [1,2]. Among them, the Al_{13} species has received more and more attention. Al_{13} species has been applied in many fields such as water and wastewater treatment, manufacture of pharmaceuticals, as the main components in certain catalysts, and modification reagents for soil [3–6]. It has also been considered to play significant role in the case of acid precipitation and global chem-

ical cycling [7]. Especially in water and wastewater treatment, the main kind of inorganic polymer flocculants (IPFs)-polyaluminum chloride (PACl) has been rapidly developed based on the traditional metal salts, the Al_{13} or Al_b as shown in ferron assay was considered to be the most important species [3,8–10].

However, most of the researches have been carried out or based on using of the partially hydrolysed $\text{Al}(\text{III})$ solution. These show the simultaneous effect of the various coexisting species, since Al_{13} is only one of the most important components. Furthermore, the formation mechanism of the various hydrolysed species, their structure and physicochemical properties remain to be verified. Therefore, purified Al_{13} species are greatly needed. Meanwhile, the commercial PACl products contain only little amount of Al_{13} . To obtain PACls with high yield of Al_{13} becomes the current objective of the research of IPFs. The methods to

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separate the various species from the hydrolysed solution are expected to become one of the hot topics in this area. The optimum process for the separation and purification of Al_{13} becomes therefore the major objective of this paper.

It is observed that various possible species such as monomers, oligomers, polymers including Al_{13} , polymer aggregates and colloids, could coexist in a typical hydrolyzed $\text{Al}(\text{III})$ solution. To separate Al_{13} from the other species in the complicated bulk solution, it needs a method with high selectivity. A previous study has been carried out to compare several kinds of reagents such as sulfate, phosphate, silicate, some organic anions and organic polymers as well. Only sulfate exhibits some special feature by forming Al_{13} -sulfate crystals as has been early reported by Johansson [11]. Therefore, the sulfate ion is adopted here as the selective reagents to separate Al_{13} from the other hydrolyzed species.

2. Experimental

2.1. Material

The reagents adopted in this paper are all of analytical grade except those pointed out specifically. The method to prepare PACl is adopted as in the literature [12]. The various PACl samples were prepared by using a slow base titration at room temperature. A solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was titrated slowly with NaOH under rapid stirring conditions. The amount of NaOH added varied with the target $[\text{OH}]/[\text{Al}]$ ratio (B values). The chosen B values were 0, 1.0, 2.0, 2.2 or 2.5, and the resulting samples were denoted respectively as PACl_0 , PACl_{10} , PACl_{20} , PACl_{22} and PACl_{25} . The final concentration of aluminum was 0.1 mol/l. The samples after aging for one week were analyzed by an assay procedure using ferron reagent [13,14]. It should be noted that the species distribution of PACls depends largely on the preparation methods and conditions such as the concentration of primary materials, titration speed and mixing conditions. With the above conditions established as shown in this study, the species distribution of PACls can easily be repeated within difference less than 5%. The typical speciation distribution of PACls by ferron assay is shown in Table 1.

Table 1

The speciation distribution of PACls by ferron assay

PACl	B	Al_a (%)	Al_b (%)	Al_c (%)
PACl_0	0	90.1	9.90	0.0
PACl_{10}	1.0	60.1	38.5	1.40
PACl_{20}	2.0	26.1	70.3	3.60
PACl_{22}	2.2	15.1	69.7	15.2
PACl_{25}	2.5	7.4	57.5	35.1

Note: Al_a (monomers), Al_b (oligomers and polymers) and Al_c (colloidal hydroxides).

2.2. General methods

The PACl samples were mixed with Na_2SO_4 solution in a 25 ml tube according to the target Al/SO_4 ratio. Deionised water was then rapidly added to dilute the solution to 25 ml. Then samples were taken from the reaction solution at different time period for subsequent speciation and total aluminum concentration analysis by ferron assay.

For the case of final product analysis, the precipitates after 48 h aging were collected using 0.45 μm Millipore membrane. The precipitates were cleaned using deionised water several times until no more sulfate ion could be removed and then dried under constant temperature of 60 °C. The powder was analysed for the total aluminum by ferron assay. The content of sulfate in the powder was analysed using ion-chromatography (Dionex 4500i). The concentration of Na^+ was analysed by atomic absorption spectroscopy (HITACHI Z-6100). Then the quantity of OH was calculated via material balance. The morphology of powder was observed using SEM (HITACHI S-570).

For the purification of Al_{13} , the PACl_{22} was adopted as the primary material. The amorphous precipitate formed rapidly by mixing PACl_{22} with sulfate was removed by filtration after 10 min reaction. The filtrates were then aged for further crystal formation for another 48 h. The crystals were filtered, washed and dried as above. To separate thoroughly the Al_{13} species, the sulfate in the Al_{13} -sulfate crystals was permuted through reacting with Ba^{2+} under ultrasonic vibration. The final powder crystals were weighed and dosed into predetermined deionised water and mixed with certain amount of 0.1 mol/l $\text{Ba}(\text{NO}_3)_2$ solution under ultrasonic vibration at the target Ba/SO_4 ratio. The reaction solution was then analysed for the

speciation distribution by ferron assay. The purified Al_{13} solution was further examined by using 500 MHz ^{27}Al NMR spectroscopy (Brookhaven, USA). The experimental conditions are: NS = 128, P1 = 20 μs , PL1 = -3 dB. Solvent: D_2O , and $T = 298\text{ K}$. The inner standard is 0.01 mol/l NaAlO_2 solution.

3. Results and discussion

3.1. Basis for the PACl-sulfate reaction

The general pathway of sulfate reaction with PACl as exhibited from the residual total aluminum is shown in Fig. 1.

It can be seen that sulfate reacts quite differently with PACl, corresponding well with the various components in PACl. For PACl_0 ($B = 0$), no decrease of total aluminum has been observed during the experimental period. It indicates that sulfate forms soluble complexes with simple $\text{Al}(\text{III})$. With the increase of B , the components of Al_b and Al_c increase. The decrease of total aluminum with time is clear and becomes more rapid as B increases. It is indicative that there exists kinetic difference of reaction of various species with sulfate corresponding well with their structure and quantity.

The different reaction phenomena have also been observed during experiments. On increasing the B

value of PACl, crystal precipitates occur. However further increase of B to 2.5, i.e. PACl_{25} , voluminous bulk amorphous precipitates appear. It indicates the significant effect of Al_c . The reaction products are then examined using SEM and chemical analysis as well. The SEM figures are shown in Fig. 2. It can be seen that the morphology of PACl-sulfate reaction products differs markedly in accordance with the basicity of PACl, i.e. the primary speciation component. The products of PACl_{10} are very complicated containing elongated prismatic crystals, and small spherical crystals in addition to the large tetrahedral ones. Similar results have also been observed by Hsu and co-workers although they adopted a more dilute solution [13,15,16]. While in PACl_{20} and PACl_{22} , the products are dominated by Al_{13} tetrahedral crystals. It is interesting to point out that some of the crystals are combined together due to high initial concentration during crystal formation. As exhibited from the speciation results (Table 1), the main components in PACl_{20} and PACl_{22} are Al_b (Al_{13}) species. It becomes complicated again in the case of PACl_{25} . The irregular solids appear in PACl_{25} in addition to the large tetrahedral ones.

The powder products were further analysed for their chemical components, as shown by the formulae, $\text{Na}_{0.03}\text{Al}(\text{OH})_{2.33}(\text{SO}_4)_{0.35}(\text{H}_2\text{O})_x$ ($B = 1.0$), $\text{Na}_{0.06}\text{Al}(\text{OH})_{2.40}(\text{SO}_4)_{0.33}(\text{H}_2\text{O})_x$ ($B = 2.0$), $\text{Na}_{0.12}\text{Al}(\text{OH})_{2.46}(\text{SO}_4)_{0.33}(\text{H}_2\text{O})_x$ ($B = 2.2$), $\text{Na}_{0.35}\text{Al}$

Fig. 1. The change of total aluminum concentration with time during reaction of sulfate with PACl (ABS indicates the absorption value; the concentration of PACl and SO_4^{2-} is 0.1 mol/l, i.e. Al/SO_4 ratio at 1.0).

Fig. 2. The morphology of basic sulfate aluminum observed by SEM: (a) $B = 1.0$; (b) $B = 2.0$; (c) $B = 2.2$; (d) $B = 2.5$.

$(\text{OH})_{2.69}(\text{SO}_4)_{0.30}(\text{H}_2\text{O})_x$ ($B = 2.5$), respectively. It can be seen that the content of $-\text{OH}$ and Na^+ increases with the increase of basicity, while sulfate decreases with the increase of basicity. It indicates that the various species in PACl exhibit significant role in the final morphology and composition. Increasing the basicity of PACl, cause the Al_c to increase and the average charge for the hydrolysed species decreases. Therefore the sulfate needed to neutralize the charge of hydrolysed species decreases. In the meantime, the increased Al_c results in amorphous precipitates containing a large quantity of salts. It is difficult to

clean the salts by simple washing. The analysis results of PACl_{20} and PACl_{22} are very close to previously reported data of the similar products [15,16].

Therefore, further experiments were carried out to optimize the process for Al_{13} separation and purification.

3.2. Effect of Al/SO_4 ratio and basicity

The effect of Al/SO_4 ratio and basicity on the reaction of sulfate with PACl is examined first. The concentration of aluminum was set at 0.02 mol/l, while

Fig. 3. Effect of Al/SO₄ ratio on reaction of sulfate with PACl₂₀.

the sulfate concentration was varied according to an Al/SO₄ ratio from 5:1 to 1:5. The results of PACl₂₀ and PACl₂₅ as exhibited from the residual total aluminum are shown in Figs. 3 and 4.

It can be seen that the Al/SO₄ ratio has significant role in the reaction of sulfate with PACl. In the case of PACl₂₀, it is indicative that too little or too much sulfate is not favorable for the PACl-sulfate reaction. Especially at lower sulfate concentration, no visible reaction has been observed during experimental period. An Al/SO₄ ratio around 1.0 gives efficient reaction kinetics. Similar behavior is observed in the case of PACl₂₅. However, it is interesting to point out that the reaction of sulfate with PACl₂₅ can be divided into two typical periods for all Al/SO₄ ratios.

A rapid precipitation occurs in the initial period, followed by different reaction kinetics in accordance with the Al/SO₄ ratio. From the results in Fig. 4, the rapid drop part of curve accounts for 40% of the initial concentration of aluminum, which corresponds roughly with the amount of Al_c in PACl₂₅. It indicates that the Al_c species, i.e. colloidal aluminum hydroxides, can be coagulated rapidly by sulfate. While the Al_b species, mainly Al₁₃, form crystal precipitates slowly with sulfate. The kinetic difference of reaction makes it possible to separate Al₁₃ from colloidal Al_c. The initial rapid precipitates formed by Al_c can be removed through filtration or centrifugation, while the Al₁₃ crystals can then be formed slowly with further aging.

Fig. 4. Effect of Al/SO₄ ratio on reaction of sulfate with PACl₂₅.

Fig. 5. Effect of concentration of PACl on the PACl-sulfate reaction (The final concentration of PACl is 0.05, 0.02, 0.02 and 0.005 mol Al/l, respectively).

3.3. Effect of concentration of PACl and basicity

Experiments were carried out further to examine the effect of concentration of PACl and basicity. At a constant Al/SO₄ ratio of 1:1, a range of concentration of PACl from 0.05, 0.02, 0.01 to 0.005 mol Al/l respectively, has been tested. The typical results of PACl₂₂ from ferron assay are shown in Fig. 5. The change of residual Al_a, Al_{a+b} (Al_a plus Al_b) and Al_T during reaction period is shown. It can be seen that the concentration of PACl has a marked effect on the PACl-sulfate reaction which corresponds well with the speciation components. As the concentration of PACl is decreased, the reaction rate decreases continuously. The interesting feature of the curves is that there exist three typical parts, i.e. a rapid drop of the curve followed by a transient zone, and then a gradual decrease to a lower plateau. The rapid drop of curve is indicative of the coagulation of Al_c by sulfate. The subsequent plateau indicates the induction period for Al₁₃-sulfate crystallization. As shown by the curves, the calculated quantity of precipitated aluminum and the initial concentration for the subsequent crystallization (15 and 62%) is in rough correlation with Al_c and Al_b for PACl₂₂.

From Fig. 5, it can also be seen that the lower the concentration of PACl (and thus Al₁₃), the longer the induction period needed. With further aging, the Al₁₃-sulfate crystal precipitates, resulting in the gradual drop of the curve again. It indicates that a certain control of PACl concentration will be beneficial for the

separation of Al₁₃ from Al_c as exhibited from the induction zone. Similar trends have also been observed for PACl₁₀, PACl₂₀ and PACl₂₅ (data not shown). However, due to low concentration of Al₁₃ in the low basicity PACl and high Al_c in the high basicity PACl, the basicity around 2.0 with high yield of Al₁₃ would be more suitable for the application in the separation of Al₁₃.

3.4. Effect of Ba/SO₄ ratio and reaction time

As shown above, the Al₁₃-sulfate crystals were separated from the other species by different precipitation from bulk solution. To separate thoroughly the Al₁₃ species, the sulfate in the Al₁₃-sulfate crystals need to be permuted. Therefore, a further purification procedure by involving the BaSO₄ permutation from the Al₁₃-sulfate crystals through ultrasonic reaction was investigated. The effect of Ba/SO₄ ratio and reaction time was then examined. The results are shown in Fig. 6. It can be seen that the Ba/SO₄ ratio and ultrasonic reaction time have important effects on the final yield of Al₁₃. A Ba/SO₄ ratio of 1:1 exhibits enough separation of Al₁₃. Meanwhile, increasing the reaction time, increases the yield of Al₁₃ which reaches a plateau with further increase of time. From Fig. 6, a reaction time of 3 h would be suitable.

With the conditions being established, the final yield of Al₁₃ solution was examined by the ²⁷Al NMR technique. The primary solution of PACl₂₀ was also analysed for a comparison. The results are shown

Fig. 6. Effect of Ba/SO₄ ratio and reaction time on the yield of Al₁₃.

in Fig. 7. It needs to note that the different resonance peaks of ²⁷Al NMR spectroscopy on 80, 63 and 0 ppm are assigned to the inner standard (NaAlO₂), the AlO₄ unit of Al₁₃ and Al³⁺, respectively. It can be seen the separated Al₁₃ sample exhibits only a feature sharp response in the ~63 ppm. While the resonances associated with Al³⁺ (at 0 ppm), Al₁₃ (at

~63 ppm) of the primary PACl₂₀ sample are clearly visible.

3.5. Further indication

A general schematic reaction pathway of PACl-sulfate reaction can then be proposed as shown in

Fig. 7. The ²⁷Al NMR spectra of (a) 0.0192 mol Al/l pure Al₁₃ solution and (b) 0.10 mol Al/l PACl₂₀ solution (the resonance peaks of ²⁷Al NMR spectroscopy on 80, 63 and 0 ppm are assigned to the inner standard NaAlO₂, the AlO₄ unit of Al₁₃ and Al³⁺, respectively).

Eqs. (1)–(3)

The monomer species react with sulfate to form soluble complexes. While Al_b and Al_c react with sulfate to form crystal and amorphous precipitates respectively. There exists significant kinetic difference in the two precipitation processes depending on the primary concentration.

However, several researches have proposed generally two sets of polymer species, i.e. Al_{b1} and Al_{b2} , according to the difference in rate coefficients for the Al_b -ferron reaction. The first exhibits a rapid reaction rate corresponding with the Al_{13} species, while the latter have a slower reaction rate. There exist two possible sources for the latter species. One is the $\text{Al}(\text{OH})_3$ -fragment structure, which is more stable in the aged solutions and can be converted from the Al_{13} during aging [15]. The other could very probably be the aggregate of polymer species such as Al_{13} , as exhibited from ferron assay by several researches [17–19]. In this investigation, the PACI solutions are all freshly prepared. Therefore the polymers of $\text{Al}(\text{OH})_3$ -fragment structure nature can be neglected. However, the aggregation of Al_{13} might account for the fraction of Al_{b2} . Being aggregated, they could also be coagulated rapidly by sulfate contributing to the amorphous precipitates. As shown in Figs. 4 and 5, the initial rapidly precipitated species contain part of species out of the total amount of Al_c , while the totally crystallized species contain less than the amount of Al_b . It indicates that to obtain high yield of purified Al_{13} , the aggregation of Al_{13} during preparation should be avoided. Generally, it could be reached by controlling the basicity less than 2.4–2.5.

Furthermore, there has been continued discussion and debate concerning Al hydrolytic reactions in aqueous solutions. Many of the seemingly inconsistent and conflicting results reported are derived from utilization of both different experimental methods and approaches [1,2]. By using the purified Al_{13} samples, many of the speculations and debates could be clarified. The stability and further transformation mechanism of Al_{13} could then be studied. While the various

reaction coefficients such as Al-ferron reaction can also be illustrated by using purified Al_{13} and/or Al_{13} aggregates with different particle size distribution. It can also be of potential use in the demonstration of ^{27}Al NMR technique.

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