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Interaction of PACls with sulfate

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Abstract: This article discusses the influential factors on Al_{13} separation considering the interaction of sulfate with various polyaluminum chloride (PACl). The experimental results showed that the basicity (B = [OH]/[Al]), the concentration of PACl and Al/SO_4 ratio exhibited significant roles in the PACl-sulfate reaction. It indicated that different species in various PACl underwent different reaction pathway with sulfate. The Al_c, colloidal species, formed precipitation quickly with sulfate, while Al_b, oligomers and polymers, underwent slow crystallization. And Al_a, monomers, reacted with sulfate to form soluble complexes. The kinetic difference of reaction made it possible to realize the separation of Al_b and further purification. The decrease of Al_a resulted in the limit of ferron method was also mentioned.

Keywords: PACl; sulfate; Al_{13}; kinetic; separation

Introduction

Polyaluminum chloride (PACl) as a main kind of inorganic polymer flocculants is a new higher effective water and wastewater treatment reagent. Based on the traditional low-molecular aluminum, it has been developed worldwide since the 1960s (Tang, 1994; 1990; 1987). PACl is the intermediate product of the hydrolysis-polymerization-ageing process of Al(III) under suitable conditions. At present, it is generally known that there are many possible species exist in the Al(III) solution, such as monomers, oligomers, Al_{13} [$AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$] and colloidal solid phase (Tang, 1998; Bertsch, 1987). Among them, the Al_{13} species has been received more and more attention. And the Al_{13} or Al_b as shown in ferron assay was considered to be the most important species (Parthasarthy, 1985; van Benschoten, 1990; Tang, 1996; Wang, 2002).

However, most of the researches have been carried out or based on using of the partially hydrolysed Al (III) solution. The results were unavoidably reached as the simultaneous effect of the various coexisting species, while Al_{13} is only one of the most important components. Undoubtedly, finding the methods to separate the various species (especially the Al_{13}) from the hydrolysed solution, and to investigate their structure and physicochemical properties is of significant importance. The main purpose of this work is to investigate the characters of the interaction of the PACls with sulfate. In this preliminary study, we aim to get some important information on the separation of Al_{13} from other hydrolyzed species. Further work will then be concerned with higher effective purification of Al_{13} and its coagulation mechanisms.

1 Materials and methods

1.1 Preparation of PACl

The reagents adopted in this paper are all of analytical grade except those being pointed out specifically. The method to prepare PACl is adopted as literature (Wang, 2002). The various PACl samples were prepared by using a slow base titration at room temperature. A solution of $AlCl_3 \cdot 6H_2O$ was titrated slowly with NaOH under rapid stirring conditions. The amount of NaOH added varied with the target [OH]/[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 PACls was 0.1 mol Al/L. The samples after aging for one week were analyzed by an assay procedure using ferron reagent (Wang, 1994; 2001). The ferron assay was the same as that applied by Hsu and Cao (Hsu, 1991) and allows the various Al species to be classified according to a conventional scheme. Al_a represents mainly monomers, the Al_b fraction consists mainly of oligomers and small polymeric species and Al_c has some colloidal material. It needs to point out that the species distribution of PACls depend largely on the preparation methods and conditions such as the concentration of primary materials, titration speed and mixing condition. 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

Notes: Al_a (monomers); Al_b (oligomers and polymers) and Al_c (colloidal hydroxides)

1.2 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.

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Then samples were taken from the reaction solution at different time period for subsequent speciation and total aluminum concentration analysis by ferron assay.

2 Results and discussion

2.1 Characterization the PACl-sulfate reaction

For these experiments, the concentration of aluminum was set at 0.02 mol/L, while the Al/SO_4 ratio was 1∶1. Then supernatant solution was taken from the reaction solution at different time period for subsequent speciation analysis by ferron assay. The results are shown in Fig.1.

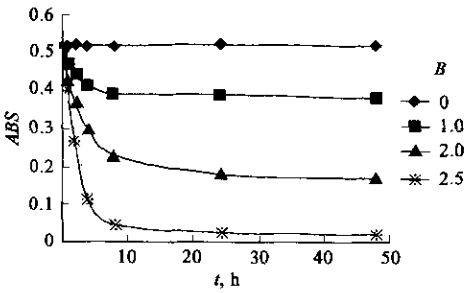

Fig.1 The effect of basicity on the reaction of PACls with sulfate

It is observed that sulfate reacts quite differently with PACl, corresponding well with the various components in PACl. For $PACl_0$ ($B=0$), with mostly Al_a and no Al_c, the speciation keeps stable during the experimental period. It indicated that sulfate forms soluble complexes with simple Al (III). With the increase of B, the components of Al_b and Al_c increase. The decrease of total aluminum with time is obviously and becomes more rapidly as B increases.

The change of Al_a during PACl-sulfate reaction is shown in Fig.2. It can be seen that the curves follow a rapid drop initially and tend to stable plateau. It illustrates that the Al_a keeps unchanged during PACl-sulfate reaction. The rapid drop initially is indicative of the reaction of Al_b and Al_c with sulfate. Being complexed and precipitated with sulfate, the surface aluminum previously exposed in bulk solution is no longer available for the color-developing reagent ferron. Therefore, the rapid reaction part of Al_a contains a small part of contribution from Al_b and Al_c during ferron assay. The speciation method of ferron assay needs some further modification to divide more precisely the amount of Al_a, Al_b and Al_c.

It was observed that in the reaction of sulfate with PACl rapid precipitation occurs in the initial period. This indicates that the Al_c species, i.e. colloidal aluminum hydroxides, can be coagulated rapidly by sulfate. While the Al_b species, mainly Al_{13}, form crystal precipitates slowly with sulfate. The kinetic difference of reaction makes it possible to separate Al_{13} from colloidal Al_c. The initial rapid precipitates formed by Al_c can be removed through filtration or centrifugation, while the Al_{13} crystals can then be formed slowly with further aging.

3.2 Effect of Al/SO_4 ratio and basicity

The interaction of sulfate with PACl depends on ionic

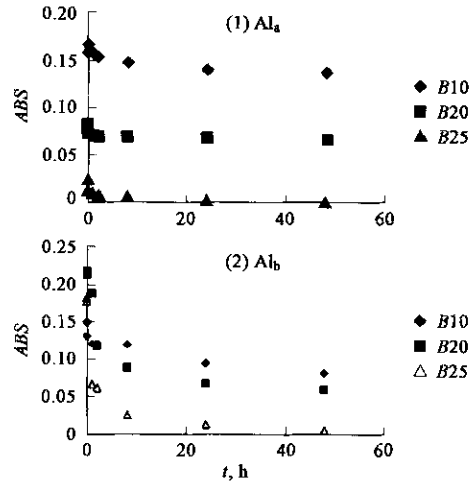

Fig.2 The change of speciation during PACl-sulfate reaction

association. At the low sulfate concentration, the mainly association occurs at the outer layer. While with the increase of the ionic intensity of solution and sulfate concentration, more and more complexation ions come into the inner layer, which is an important factor for the form of basic aluminium sulfate. Therefore, the effect of Al/SO_4 ratio on the reaction of sulfate with PACl was examined. The concentration of aluminum was set at 0.02 mol/L, while the sulfate concentration was varied according to an Al/SO_4 ratio from 5∶1 to 1∶5. The results of $PACl_{10}$, $PACl_{20}$ and $PACl_{25}$ as exhibited from the residual total aluminum are shown in Fig. 3 to Fig.5.

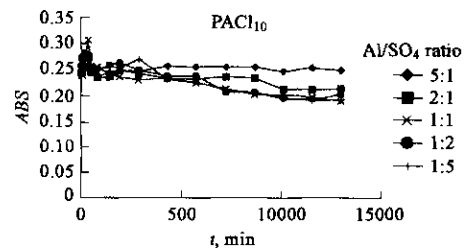

Fig.3 The effect of Al/SO_4 ratio on the reaction of $PACl_{10}$ with sulfate

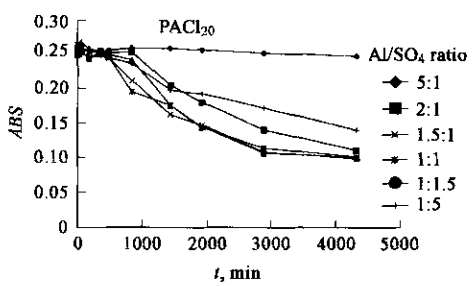

Fig.4 The effect of Al/SO_4 ratio on the reaction of $PACl_{20}$ with sulfate

It can be seen that the Al/SO_4 ratio has significant role in the reaction of sulfate with PACl. In the case of $PACl_{20}$, it is indicated that too less or too more concentration of sulfate is not favor for the PACl-sulfate reaction as shown in Fig.4. Especially in the lower concentration of sulfate, no visible reaction has been observed during experimental period. An

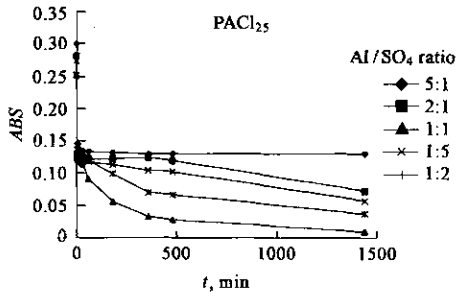

Fig.5 The effect of Al/SO_4 ratio on the reaction of $PACl_{25}$ with sulfate

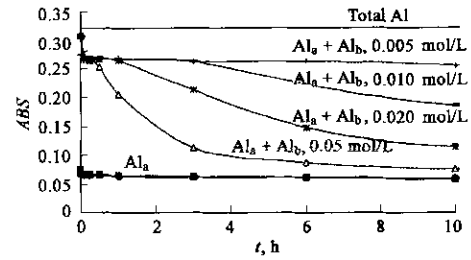

Fig.6 The effect of concentration of PACl on the reaction of $PACl_{20}$ with sulfate

Al/SO_4 ratio around 1.0 exhibits the efficient reaction kinetic. So are the case of $PACl_{10}$ and $PACl_{25}$ observed. Fig. 3 is the result of $PACl_{10}$. Because there are not any Al_{13} and Al_c in $PACl_{10}$, several days later the decrease of total aluminum begin to happen. More attention should be paid to $PACl_{25}$, the results in Fig.5 show that the reaction of sulfate with $PACl_{25}$ can be divided into two typical periods with various Al/SO_4 ratios. A rapid precipitation occurs in the initial period, followed by different reaction kinetics in accordance with the Al/SO_4 ratio. This can help to separate Al_{13} from colloidal Al_c.

3.3 Effect of concentration of PACl and basicity

At a constant Al/SO_4 ratio of 1:1, a range of concentration of PACl from 0.05, 0.02, 0.01 to 0.005 mol Al/L respectively, the effect of concentration of PACl and basicity was further tested. The typical results of $PACl_{20}$ from ferron assay are shown in Fig.6. The change of residual Al_a, Al_{a+b} (Al_a plus Al_b) during reaction period is exhibited. The data are normalized in the same scale. It can be seen that the concentration of PACl has marked effect on the PACl-sulfate reaction in relation well with the speciation components. Decrease the concentration of PACl, the reaction kinetic decreases continuously. The interesting feature of the curves is that there exists three typical parts, i.e. a rapid drop of the curve follows a transient zone, then decreases gradually to a lower plateau. The rapid drop of curve is indicative of the coagulation of Al_c by sulfate. The subsequent plateau indicated the induction period for Al_{13}-sulfate crystallization. As exhibited from all the curves, the quantity of precipitated aluminum (rapid drop of curve) and the initial concentration for the subsequent crystallization calculated (subsequent plateau), 15% and 62%, is in rough correlation of Al_c and Al_b of $PACl_{20}$.

From Fig. 6, it can also be seen that the lower the concentration of PACl (and thus Al_{13}), the longer the induction period needed. With further aging, the Al_{13}-sulfate crystal precipitates resulting in the gradual drop of the curve again. It indicated that a certain control of PACl concentration will be beneficial for the separation of Al_{13} from Al_c as exhibited from the induction zone. The similar trend has also been observed for $PACl_{10}$, $PACl_{22}$ and $PACl_{25}$ (data not shown). However, due to low concentration of Al_{13} in the low basicity PACl and high Al_c in the high basicity PACl, the basicity around 2.0 with high yield of Al_{13} would be more suitable for the application in the separation of Al_{13}.

4 Conclusions

Preliminary results reported herein that sulfate reacts quite differently with PACls in relating to the various co-existing species. The results showed that sulfate forms soluble complexes with the monomer species (i.e. Al_a), 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. The optimum process for the separation of Al_{13} is the moderate concentration and basicity around 2.0 of PACl, and Al/SO_4 ratio around 1.0.

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