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Magnetic field coupled with electrochemical process for enhancing Al_{13} formation

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ABSTRACT

Rare earth Nd-Fe-B magnetic field was used to enhance the conventional electrochemical process for preparing the polyaluminum chloride (PACl) of high Al_{13} polymer. It was found the formation process of Al_{13} polymer was obviously influenced by electrobath's voltage (V_i), magnetic field intensity (B_i), current density (d_i), the distance of two adjacent electrodes (d_{adj}), and the circulating rate. The concentration polarization was inhabited by external magnetic field and out-circulating pump, therefore, the comfortable surroundings for the formation of adequate $Al(OH)_4^-$ precursor was formed. The Al_{13} polymer content of PACl with Al_T (total aluminum concentration) = 0.8 M and B (basicity) = 2.2 reached 79.8 % of Al_T when the V_i, Bi, d_i, d_{adj} and circulating rate was 2.0 V, 0.4 T, 3.34 A/dm², 20 mm and 23.7 L/h, respectively. For aging 15 d, it increased to 84.6%. In comparison with the conventional electrolysis process, the content of Al_{13} polymer was improved by 8.7% and 8.9%, respectively.

Keywords: Magnetic field; Electrochemical process; Polyaluminum chloride (PACl); Al_{13} polymer; Flocculants; Polarization

1. Introduction

Coagulation processes are often used in water and wastewater treatment to destabilise and remove colloids and dissolved impurities from water. Polyaluminum chloride (PACl) is a kind of the most often used inorganic macromolecule flocculants. It has attracted many researchers attention in recent years because of its lower costs and higher efficiency compared with other traditional coagulants [1–6]. It is generally thought the higher efficiency of this flocculants mainly depends on the formation of the highly charged polymeric Al_{13} ($[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$) species [1,5,7]. Al_{13} is composed of one tetrahedral center surrounded by 12 octahedral Al units, known as Keggin structure [8,9]. It was assumed by several authors [2,5] that the process of Al_{13} formation requires the presence of $Al(OH)_4^-$ as a precursor. It is highly influenced by the solution composition and synthesizing conditions. Bertsch et al. [5] found that the base injection rate was an important parameter influencing Al_{13} polymer formation at high basicity (B value, OH/Al molar ratio). Xu [10], Wang [11] and Bottero et al. [12] presented some different methods for preparing PACl of high Al_{13} polymer content. However, the drawbacks of these preparation processes were tedious; time consuming and impossible for the industrial production. Lu [13] and Liu [3] illustrated the principles of PACl preparation by conventional electrolysis and demonstrated the optimum conditions for Al_{13} polymer formation. When the electrolysis was carried out with direct current, Al^{3+} and OH^- ions were generated from the anode and cathode respectively. The Al^{3+}, OH^- and $Al(OH)_4^-$ ions were drove to the bulk solution to form the Al_{13} polymer by an out-circulating pump. In this process, however, current density decreased critically for the reason of electrodes polarization and passivation. In order to sustain a stable current density, electrobath's voltage was turned up. Byproducts generated from electrodes increased rap-

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idly under the higher cell's voltage, which decreased the efficiency of current and electrobath's energy transformation. The Al_{13} polymer accounted for only 70% of Al_T (PACl of Al_T =2.0 M and B =2.0) was obtained, as Qu [14] reported.

Our recent research [15] showed that the concentration polarization in electrochemical process was inhabited distinctly by external magnetic field. The purpose of this investigation was to enhance the conditions for Al_{13} polymer formation in the electrolysis process by external magnetic field.

2. Materials and methods

2.1. Characteristics of reactor

A diagram of lab-scale reactor for PACl preparation is illustrated in Fig. 1. It consisted of four parts — a power supply (Kl-1, China), an electrobath (three sheets of 100×20 mm Al as anodes; three sheets of 100×20 mm Fe as cathodes), PACl storage box (organic glass) and some monitors (pH meter, ampere meter, volt meter and gauss meter). The distance of the adjacent electrodes (d_{adj}) could be regulated from 40 to 10 mm. A pump with max lift of 35.8 L/h was used to circulate the electrolyte to increase mass transfer rate. Magnetic field direction was parallel to the ground and the surface of the electrodes, the intensity of magnetic field could be adjusted from 0 to 0.8 T. Some 0.3 M NaCl (for increasing the conductivity of the solution) was added to the 0.22 M $AlCl_3$ solution to form the electrolyte.

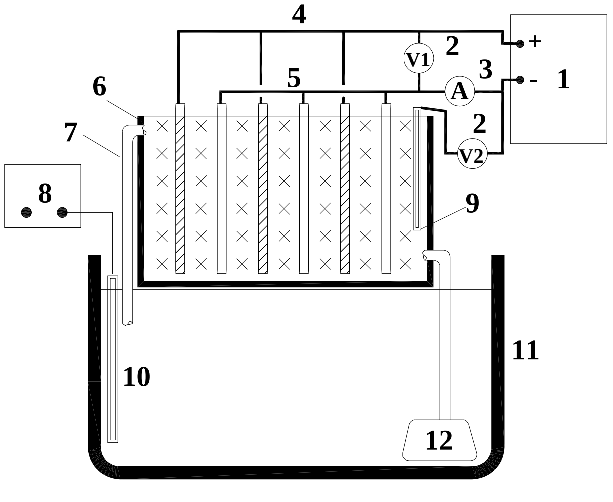

Fig. 1. A diagram of lab-scale electrolysis reactor. (1) power supply; (2) volt meter; (3) ampere meter; (4) wire of anode; (5) wire of cathode; (6) electrobath; (7) circulating pipe; (8) pH meter; (9) reference electrode; (10) pH electrode; (11) PAC storage box; (12) circulating pump; × direction of magnetic field.

2.2. Al_{13} formation process

When the electrolysis process is carried out at direct current in the above reactor, the following reactions will bring out on the anode and cathode.

Anode reaction:

$$2Al - 6e^- \rightarrow 2Al^{3+} \qquad E^0 = -1.706\ V \tag{1}$$

Excessive overpotential of anode results in the following side-reactions.

$$2H_2O - 4e \rightarrow 4H^+ + O_2\uparrow \tag{2}$$

$$2Cl^- - 2e \rightarrow Cl_2\uparrow \tag{3}$$

Cathode reaction:

$$6H_2O + 6e^- \rightarrow 3H_2\uparrow + 6OH^- \qquad E^0 = 0.0\ V \tag{4}$$

Relative low overpotential of cathode leads to other side-reactions.

$$2H^+ + 2e \rightarrow H_2\uparrow \tag{5}$$

$$Al^{3+} + 3e \rightarrow Al\downarrow \tag{6}$$

It was confirmed that some of the OH^- ions reacted with the Al^{3+} ions to form the $Al(OH)_4^-$ precursor on the metal–solution surface; others were gradually transferred to the bulk solution to react with $Al(OH)_4^-$ precursor, forming the Al_{13} polymer further.

$$Al^{3+} + 4OH^- \rightarrow Al(OH)_4^- \tag{7}$$

However, the amount of Al^{3+}, OH^- and $Al(OH)_4^-$ near the metal surface was much higher than those in the bulk solution, which resulted in the concentration polarization. Although the out-circulating pump could alleviate the concentration polarization, the alleviation degree was limited. The magnetic field conducted on the two sides of the electrobath was beneficial to alleviate the concentration polarization by increasing the mass transfer rate of these ions to the solution body.

The following relation was used to calculate the desired B values.

$$B = \frac{OH^-}{Al_T} = \frac{3Al_d}{Al_d + Al_0} \tag{8}$$

Al_0 and Al_d represented the quantities (mol) of Al^{3+} from the added $AlCl_3$ solution and the precipitated from Al sheets. In solution, the Al_T of PACl was determined by titrimetric methods using nitric acid to depolymerize the polymerized Al species. The content of the Al_d was calculated according to the known Al_0: $Al_d = Al_T + Al_0$. And then based on the current intensity through the electrolysis reactor and Faraday law, the electrolysis time was calculated.

2.3. Analytical methods

^{27}Al-NMR spectroscopy (UNITY INOVA 600, Varian

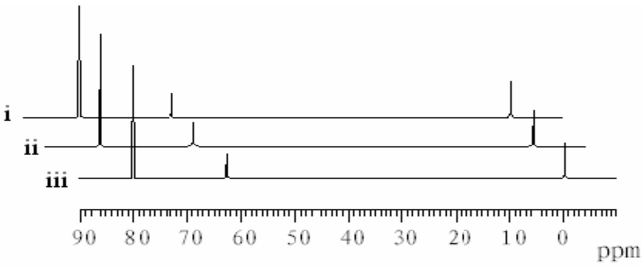

Fig. 2. ^{27}Al NMR spectra of PACl solutions on aging time. Lines i, ii and–r! represent aging for 0 d, 1 d and 7 d, respectively.

Inc., USA) was utilized to verify the existence of Al$_{13}$ Keggin structure. The instrumental settings were: 6mm Chemagnetics TM solid double-resonance probe; resonance frequency 156 MHz; rotation frequency 5 KHz; recycling delay time 1 s. Fig. 2 represents the ^{27}Al NMR spectra of PACl solutions along with aging time. For PACl solution, the intensities of 0 ppm resonance represented the quantities of the monomeric Al(Al$_m$); that of 63 ppm resonance represented the quantities of the Al$_{13}$ polymer. Al$_c$ represented the colloidal, solid-phase or polymeric Al except the Al$_m$ and Al$_{13}$ polymer. The relation of the three species was Al$_T$ = Al$_m$+ Al$_{13}$+ Al$_c$. Some added Na aluminate resulted in the resonance of 80 ppm. A pH meter (Orion 210A, USA) was used to measure the pH value of the solution. Al$_T$ was determined by titrimetric methods [16].

3. Results and discussion

3.1. *Effects of magnetic intensity* (B$_i$) *on current density* (d$_i$)

The current density (d_i) changes as a function of magnetic field intensity (B_i = 0, 0.25, 0.4 and 0.6 T, respectively) is illustrated in Fig. 3 when the d_{adj} = 15 mm and Al$_0$ = 0.22 M. Fig. 3 shows that the d_i was only 2.67 A/dm^2 when the V_i (electrobath's voltage) = 3.0 V and B_i = 0 T. In comparison with the electrolysis process coupled with external magnetic field with the intensity of 0.25 T, 0.4 T and 0.6 T, the V_i was only 1.8 V, 1.5 V and 1.3 V when the d_i reached to 2.67 A/dm^2. Especially, d_i was obviously increased when the V_i >1.4 V. However, B_i had slight inference on d_i when V_i < 0.8 V. This was also confirmed by some other researchers [17]. According to Eqs. (1) and (4), maintaining the eletrobath's voltage under 2.0 V is beneficial for precipitatation of Al^{3+} and OH$^-$ ions from electrodes. Max d_i reached 3.34 A/dm^2 when B_i = 0.4 T and V_i–2.0 V.

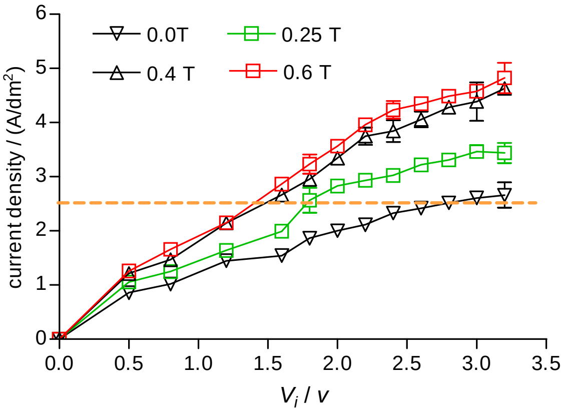

Fig. 3. Magnetic field intensity vs. current density of electrodes.

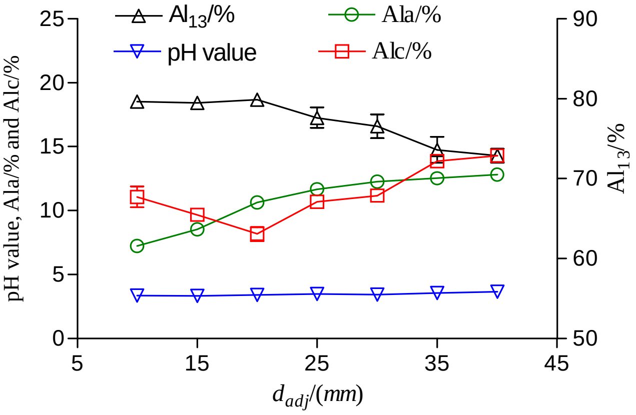

Fig. 4. The influence of d_{adj} on the performance of Al$_{13}$ polymer (aging time: 24 h).

3.2. *Effects of distance between the two adjacent cathodes* (d$_{adj}$) *on Al$_{13}$ formation*

All the experiments were carried out at d_i = 3.34 A/dm^2, Al$_T$ = 1.0 M, B_i = 0.4 T, V_i = 2.0 V, B = 2.2 and circulating rate of 20.0 L/h. Fig. 4 indicates that Al$_{13}$ polymer content of PACl was influenced heavy by d_{adj}. Al$_{13}$ polymer accounted for 79.8% of Al$_T$ in the electrolyte was achieved when d_{adj} = 20 mm at the end of electrolysis. However, the prepared PACl solution obtained only 76.6% and 72.9% of Al$_{13}$ polymer when d_{adj} was 30 and 40 mm. Comparing Al$_{13}$ polymer content of PACl prepared at d_{adj} = 10 and 40 mm, an increase of 6.8% of Al$_{13}$ appeared when d_{adj} decreased from 40 mm to 10 mm. On the one hand, more electrodes were applied in the reactor when d_{adj} decreased, the total area of the electrodes would increase in the same reactor, and then more Al(OH)$_4^-$ was created at more interface of metal–solution. On the other hand, the magnetic field accelerated the Al^{3+} and OH$^-$ precipitated from electrodes to the bulk solution to react with the Al(OH)$_4^-$ to form Al$_{13}$ polymer, therefore, the accumulation behavior of Al^{3+} and OH$^-$ on the interface of metal–solution was alleviated. d_{adj} was controlled to 20 mm in the following experiments.

3.3. Effects of current density (d_i) *on* Al_{13} *formation*

In electrolysis process, the current density (d_i) determined the speed of adding OH^- into the bulk solution. Higher current density generated more OH^- than that could be consumed by the formation of Al_{13} polymer, the excess $Al(OH)_4^-$ re-equilibrated with the bulk solution to result in colloidal or precipitated $Al(OH)_3$ [5]. Obviously, controlling an ideal d_i was beneficial to keep the reaction of Al^{3+} and OH^- in the stage of Al_{13} polymer. For PACl (B = 2.2) of the same Al_T, Fig. 5 indicates that the amount of Al_{13} polymer increased as a function of *di*, and then passed through a peak value before it decreased at the higher *di*. For different Al_T, the optimum *di* for high content of Al_{13} polymer was different. PACl of $Al_T = 0.4$ M, the optimum *di* was 2.4 A/dm^2 and the content of Al_{13} accounted for 77.5% of the Al_T. The maximum Al_{13} polymer yield (79.6% of Al_T) was obtained when *di* = 3.3 A/dm^2 and $Al_T = 0.8$ M at the end of electrolysis process. Fig. 5 also indicates that the highest Al_{13} polymer content for PACl of different Al_T was not coincident. In order to get more amount of Al_{13} polymer, the optimum Al_T was from 0.8 M to 1.2 M.

3.4. Effects of circulating rate and B_i *on* Al_{13} *formation*

Fig. 6 represents the force analysis of Al^{3+} and OH^- generated from the electrodes. Al^{3+} and OH^- took electric force of $F_1 = qE$ and magnetic force of $F_2 = qvB$ (the resultant is F_3) to escape from the interface of metal-solution to bulk solution, the accumulation behavior of charged ions surrounding electrodes was controlled strictly. Also, the charged particles in electrolyte were accelerated under the above mentioned resultants. High circulating rate caused high mass transfer rate of Al^{3+}, OH^- and $Al(OH)_4^-$ to the bulk solution to form more Al_{13} polymer.

Fig. 7 shows that the content of Al_{13} polymer for PACl was sensitive to the out-circulating rate and magnetic field intensity (B_i) when OH^- was injected into the solution containing Al^{3+} by magnetic electrochemical process. During the electrolysis process, the speed of OH^- precipitating from the cathode represented the speed of the base injecting into bulk solution when OH^- was dispersed immediately. A pump with max lift of 35.8 L/h was used to circulate the electrolyte to increase the interaction chance between $Al(OH)_4^-$ and aluminum oligomer to form Al_{13} polymer. Al_{13} polymer content of PACl ($Al_T = 0.8$ M, $B = 2.2$) prepared at different circulating rates (from 1.0 to 35.8 L/h) and B_i (0, 0.25, 0.4 and 0.6 T, respectively) is shown in Fig. 7. When the circulating rate was 1.0 L/h, Alc was the optimum aluminum species, Al_{13} polymer accounted for only 20.5% and 24.2% of the Al_T appeared when B_i was 0 and 0.8 T, respectively. For PACl with $Al_T = 0.8$ M and B = 2.2, the content of Al_{13} polymer improved rapidly with increasing the circulating rate from 1.0 to 23.7 L/h and B_i from 0 to 0.8 T. Al_{13} polymer content of

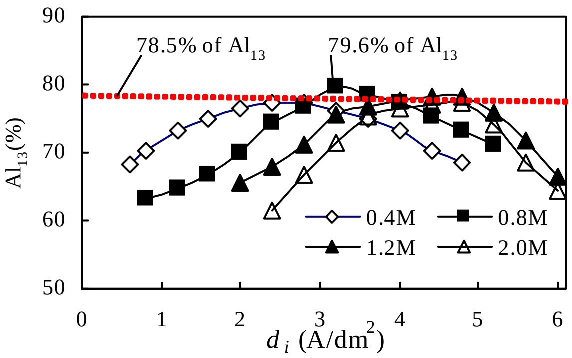

Fig. 5. Al species distribution and transformation in PACl as a function of *di* at the end of electrolysis.

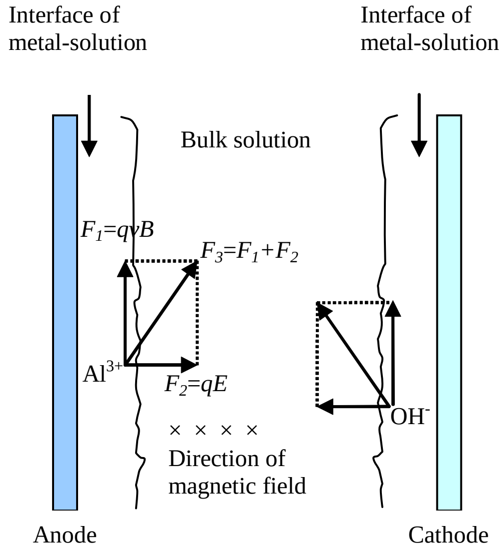

Fig. 6. The principle scheme of force for Al^{3+} and OH^- in the electromagnetic field.

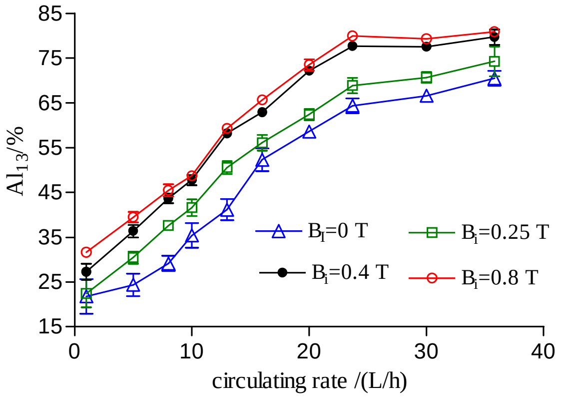

Fig. 7. Circulating rate and B_i effect on the content of Al_{13} species (aging time: 3 d).

PACl showed no obvious changes when the circulating rate was higher than 23.7 L/h and $B_i > 0.4$ T. When the out-circulating rate was 30.0 L/h, the content of Al_{13} polymer of PACl increased by only 1.8% when B_i changed from 0.4 to 0.8 T. For $B_i = 0.8$ T, an increase of 1.9% for Al_{13} was obtained when the out-circulating rate varied from 35.0 L/h to 23.7. The possible reason was that the out-circulating pump with rotational speed of 2900 r/min made some low-polymeric Al disperse to monomeric Al, resulting in a decrease of Al_{13} polymer content. Therefore, 23.7 L/h and 0.4 T were considered as the optimum circulating flux and B_i for preparing PACl of $Al_T = 0.8$ M and $B = 2.2$.

3.5. Comparison of the influence of different methods on Al_{13} formation

In order to compare the influence of magnetic field on catholic electrochemical process for preparing PACl, catholic electrolysis without the magnetic field was also conducted. For 800 ml PACl of $Al_T = 0.8$ M and B = 2.2, the preparing parameters were as follows: $Al_0 = 0.22$ M, $di = 3.34$ A/dm^2, $d_{adj} = 20$ mm, $B_i = 0.4$ T ($B_i = 0$ T when the catholic electrolysis process was conducted), $V_i = 2.0$ V, electrolyzing time was 11.0 h, circulating rate was 23.7 L/h. At the end of both electrolysis processes, the PACl solutions were aqueous suspensions because some dissolved aluminum ions from the anode sheet dif not react with OH^- completely. It would continue to hydrolyze and the solutions would become clear over a short span of 1–3 d. Al_T and the changes of Al_m, Al_{13} and Al_c species are shown in Fig. 8 when the aging time lasted for 15 d. Fig. 8 shows that Al_{13} species accounted for 79.8 % of the Al_T at the end of magnetic electrolysis process. The content of Al_{13} polymer increased to 82.3%, 82.8% and 84.6% when the PACl was aged for 1, 4 and 15 d, respectively. In comparison with the catholic electrolysis process, an increase of 6.9%, 6.7% and 7.1% was obtained, respectively. The content of Al_{13} polymer was improved by 7.8% than that of the PACl prepared by catholic electrolysis, as reported by Qu [14]. However, it was 10.2% 13.6% lower than the content of Al_{13} separated by the ultrafiltrate method [4] and chemical precipitation [18].

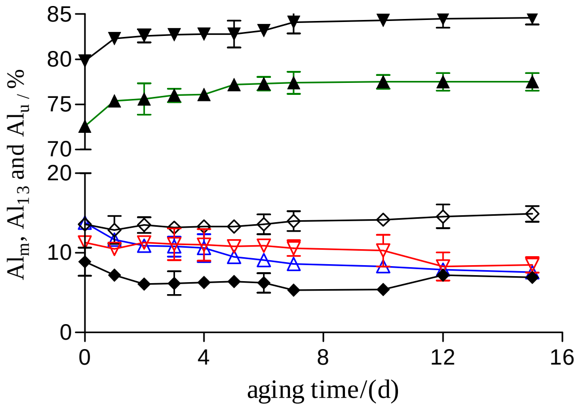

Fig. 8. Distribution and transformation of Al species with aging time for PACl prepared by different approaches. △, ▽, ○ represent the content of Al_m, Al_{13} and Al_c of the PACl prepared by the catholic electrolysis process; ▲, ▼, ● represent the content of Al_m, Al_{13} and Al_c of the PACl prepared by the magnetic electrolysis process.

4. Conclusions

The electrochemical process coupled with magnetic field was employed to prepare PACl with high content of Al_{13} polymer. The influencing parameters were studied through lots of experiments to determine their optimum conditions on Al_{13} polymer formation. It was observed that Al_{13} polymer formation was dependent on Al_0, di, d_{adj}, B_i and V_i. For obtaining as much as Al_{13} polymer by magnetic electrochemical process, the optimum Al_0, di, d_{adj}, B_i and V_i were 0.22 M, 3.34 A/dm^2, 20 mm, 0.4 T and 2.0 V respectively when the circulating rate was 23.7 L/h. 0.8 M Al_T PACl prepared in these conditions, the content of Al_{13} polymer reached 79.8 %, 82.3%, 82.8% and 84.6% for aging 0, 1, 4 and 15 d, meanwhile, it was only 72.6%, 75.4%, 76.1% and 77.5% at the same aging time for PACl prepared by the catholic electrolysis process.

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