

Features and mechanism for coagulation - flocculation processes of polyaluminum chloride

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Abstract—The coagulation - flocculation experiments for kaolinite suspension were carried out with polyaluminum chloride of various basicities. The microelectrophoresis mobility and adsorption of aluminum species were determined simultaneously. The quantitative relations between the surface coverage, zeta potential change and coagulating species were investigated to draw up a coagulation - stability diagram. The mechanism of high efficient coagulation effects for pre - produced polyaluminum chloride was discussed on the basis of the experimental results.

Keywords: polyaluminum chloride; coagulation - flocculation; microelectrophoresis.

1 Introduction

The principle and mechanism of coagulation - flocculation processes with aluminum salts in water/waste treatment units have been studied for several decades (Stumm, 1968; Amirtharajah, 1982). To set up a theoretical or operational model qualitatively may be the aim for progressing researches (Letterman, 1985; 1990; Dentel, 1988). In recent years, a new challenging and stimulating factor has been put forward by the development of inorganic polymer flocculants. The mechanism of their high efficient coagulation effect has not been studied systematically so far. This weakness becomes a key point for constructing their quantitative model and improving the technology of production and application.

Pre - produced polyaluminum, in fact, is the intermediate products in the controlled processes of hydrolysis, polymerization, gelation and precipitation for aluminum species. In previous paper (Luan, 1990), the chemical species distribution and transformation scheme polyaluminum with different basicities were identified and discussed. In this successive paper, their coagulation - flocculation behaviors were investigated and the mechanism were discussed tentatively.

2 Methods and materials

2.1 Suspension system

Sieved kaolinite particles were dispersed into deionized water to make a suspension of 100 mg/L. The ionic strength of 1×10^{-3} mol/L and available buffer capacity were regulated with $\text{NaHCO}_3 + \text{NaNO}_3$. The pH was regulated to designed value with acid or base and measured by

pH meter (Orion Model 901). The particle size distribution was determined by the Coulter Counter TII. The number average size was $1.96 \mu\text{m}$ with the maximum of $12.0 \mu\text{m}$, its 98.4% was $<5.0 \mu\text{m}$ and 83.52% $<2.0 \mu\text{m}$. The specific surface area was $23.2 \text{m}^2/\text{g}$ determined by nitrogen adsorption (BET). The total surface sites was $N = 2.07 \times 10^{-4} \text{mol/g}$ determined by a titroprocessor (Metrohm model 682), then the specific surface sites was calculated as $N_s = 8.92 \times 10^{-6} \text{mol/m}^2$.

2.2 Coagulation procedure

It was conducted on a jar tester (Japanese SUGIYAMA made) with the suspension volume of $500 \text{ml} \times 6$. Rapid mixing ($140-160 \text{ r/min}$) for 2 min after dosing and then slow mixing (40 r/min) for 5 min., settling in subsidence for 10 min were operated and samples for determination of turbidity and pH were collected under the surface of supernatant. A light scattering turbidmeter was used.

2.3 Microelectrophoresis mobilities (EM)

It was determined by a precision zeta meter (Japanese KYOWA ZP -- OM). Samples were collected just after rapid mixing. 10 particles at each direction were measured. Zeta potentials were calculated by the EM values.

2.4 Coagulants

Analytical grade of AlCl_3 was used for comparison as basicity $B^* = 0$. Polyaluminum chloride (PAC) with different basicities were pre-produced as those in previous paper (Buffle, 1985). Their characteristics are listed in Table 1. Species Al_a , Al_b , Al_c were identified by the Ferron method as before.

Table 1 Polyaluminum coagulants used in experiments

Type	B	Speciation, %			NMW, $\times 10^3$	Dominant species	possible formulas
		Al_a	Al_b	Al_c			
A_0	0	>80	<20	0	<0.1	Al_a	$\text{Al}^{3+}, \text{Al}(\text{OH})^{2+}$
A	0.5	72	28	0	<1	Al_a	$\text{Al}_2(\text{OH})_4^{2+}$
B	1.0	55	45	0	1-5	Al_b	$\text{Al}_3(\text{OH})_8^+$
C	2.0	22	72	6	5-10	Al_b	$\text{Al}_3(\text{OH})_7^{3x+y}+$
D	2.5	4.6	82	13.4	10-50	Al_b	$\text{Al}_3\text{O}_4(\text{OH})_{3x+y-2x}+$

2.5 Adsorption experiments

Kaolinite suspensions of 100mg/L with ionic strength of $1 \times 10^{-3} \text{mol/L}$ and $\text{pH} = 5.2 \pm 0.2$. 50ml of suspension were contained in the polyethylene bottles of 100ml. AlCl_3 and PAC of $B^* = 1.0$ and 2.5 were dosed respectively. The bottles were agitated for 10 min on an agitator at $25 \pm 1^\circ\text{C}$. Standed for 30 min, the pH was determined and the suspensions were filtrated through membrane of $0.45 \mu\text{m}$. Then the filtrates were acidified to $\text{pH} < 2$ and the residues of aluminum were determined by atom adsorption spectrometer (Hitachi model 180-80).

3 Experimental results

3.1 The characters of coagulation by polyaluminum

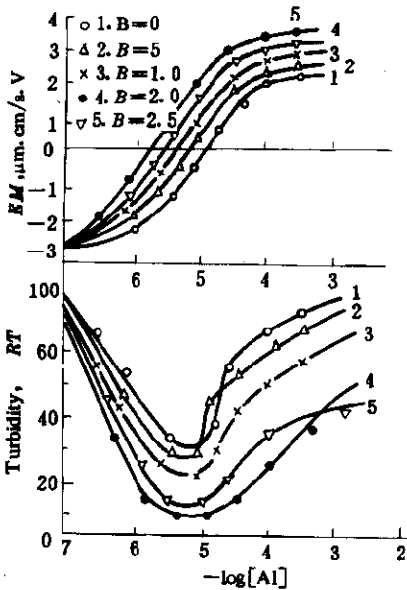


Fig. 1 Turbidity removal and micro-electrophoretic mobility of polyaluminum coagulants

The coagulation of kaolinite suspensions by AlCl_3 ($B^* = 0$) and PAC ($B^* = 0.5 - 2.5$) were accomplished at $\text{pH} = 6.0 - 6.2$. The curves for residual turbidity (RT) and electrophoresis mobility (EM) versus dosing of coagulants were plotted as Fig. 1. It is shown that the positive EM and clarified effects were increased as the basicity and dosing raised. However, the RT and EM for curves of $B^* = 2.5$ were lower than that of $B^* = 2.0$.

All the curves can be divided into three areas: (1) No evident coagulation area, $RT < 50\%$, EM still negative; (2) Destabilized coagulation area, $RT > 50\%$, EM turned to positive. The maximum RT (70%–90%) occurred at about $EM = 0$; (3) Resabilized area, EM raised to high positive and the clarified effect was deteriorated.

The unified critical values of parameters can be summarized by the data for polyaluminum of different basicities. The results are listed in Table 2. The critical coagulation concentration (CCC) was assumed to be located at about $RT = 50\%$ and critical $EM = -2.0$. The optimum destabilization occurred at the range of $EM = +1.0$, which at $EM = 0$, the optimum destabilized concentration (ODC) was related. It was assumed that the restabilization occurred above $EM = +1.0$ and the critical concentration (CRC) was related. In addition, CNC was the aluminum needed for neutralizing the charges on particle surface to $EM = 0$ and EM_H was the saturated maximum positive EM value.

Table 2 Critical dosages and effects for different sorts of polyaluminum

Type	B	CCC			ODC			CNC mol/m ²	CRC			EM_H , μm·cm/s·v
		EM	T, %	mol/L	EM	T, %	mol/L		EM	T, %	mol/L	
A ₀	0	2.0	40	2.0×10^{-6}	0	74	1.2×10^{-5}	5.17×10^{-16}	+1.0	<60	2.0×10^{-5}	+2.46
A	0.5	-2.0	45	2.0×10^{-6}	0	78	1.0×10^{-5}	1.31×10^{-6}	+1.0	<67	2.0×10^{-5}	+2.83
B	1.0	-2.0	48	1.5×10^{-6}	0	81	8.6×10^{-6}	0.71×10^{-6}	+1.0	<70	2.0×10^{-5}	+3.02
C	2.0	2.0	53	1.0×10^{-6}	0	89	4.5×10^{-5}	1.94×10^{-6}	+1.0	<70	2.0×10^{-5}	+3.56
D	2.5	-2.0	54	1.0×10^{-6}	0	90	5.0×10^{-5}	0.16×10^{-6}	+1.0	<70	2.0×10^{-5}	+3.12

By the results shown in Fig. 1 and Table 2, it is evident that the coagulation effects of PAC was much higher than that of AlCl_3 (type A₀). The CCC and ODC of AlCl_3 were the highest but the related removal of turbidity (T%) were the lowest among the coagulants. The CCC and ODC

for the PAC of $B^* = 2.0$ (type C) were only $1/2 - 1/3$ of that for $AlCl_3$ and the corresponding T% was about 15% higher.

With the increase of basicities (B^*) the values of CCC and ODC decreased and the T% raised. It can be explained from the species distribution. Directly dosed $AlCl_3$ and slightly basified type A were similar in the species of monomer and dimer i. e. oligomers with lower molecular weight (NMW) and charge. Prepared polyaluminum of type B ($B^* = 1.0$) consisted of low polymers but with more Alb (b_1) of medium NMW and charge. Polyaluminum type C and D belonged to the same category approximately. Both were dominated by Alb with higher NMW and charge and in addition contained to some extent of Alc with high NMW but decreased charge. In type D the content of Alc₃ became significant, therefore their charges and neutralizing ability were lower than type C, that can be verified in comparison of their ODC, CNC and EM_H values. In general, the optimum B^* may be in a range of 1.8–2.3 which can reserve the optimum coagulating form of species in solutions of pH 6–7.

3.2 The effects of pH in coagulation by polyaluminum

In suspensions of different pH the behaviors of different types of coagulants in experiments are shown in Fig. 2, in which $B^* = 0, 1$ and 2 represented type A₀, A, type B and type C, D, respectively. At low pH (5.2–5.5), the curves were similar to Fig. 1 but had narrower coagulation areas i. e. stronger trends of restabilization. As pH raised to above 7.0, the coagulation areas were significantly widened and the restabilization were weakened. As pH raised further to above 9, the coagulation effect of $AlCl_3$ was worsened, while the polyaluminum still get good results at higher dosing. The EM value, correspondingly, for $AlCl_3$ remained to be negative while for polyaluminum could still reverse their sign though barely.

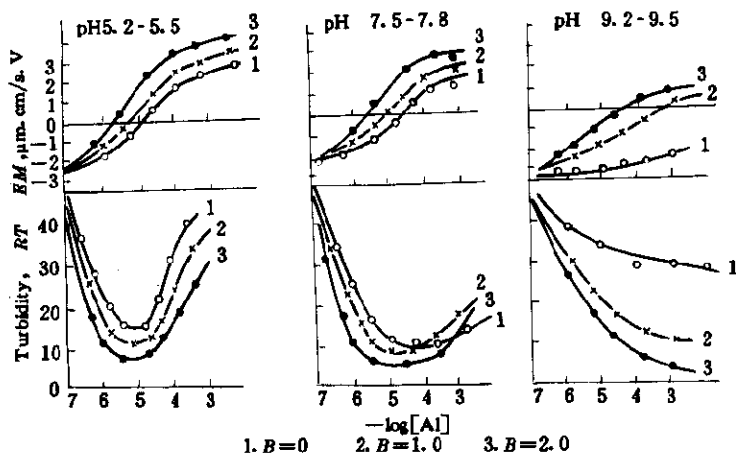


Fig. 2 Coagulation curves under various pH values

Accordingly, at high pH the hydrolysis tendency of coagulants was strengthened. AlCl_3 transformed easily into the low charged gel or amorphous $\text{Al}(\text{OH})_3$ and its sweeping function can be evident only at high dosing. At the other hand, preproduced aluminum polymers could reserve their forms with higher charge after dosing.

The curves for EM as the function of pH with constant dosing of $7.4 \times 10^{-5} \text{ mol Al/L}$ were plotted in Fig. 3, for comparison the curves of $\text{Al}_2(\text{SO}_4)_3$ and kaolinite were also included. It was assumed that the EM of flocs were the synthetic value from that of kaolinite and adsorbed aluminum species.

Under this constant dosing, at pH 4–6 the EM showed positive maximum and increased with B^* . Above pH 6, EM decreased gradually and reached their isoelectric point (IP) in succession above pH 8. For the floc of kaolinite with aluminum sulfate the IP was pH 7.6–7.8, with aluminum chloride, pH 8.0–8.2, and with polyaluminum, pH 8.5–9.4 which moved to higher pH with B^* . It meant that at pH above 7.5 the charges of hydrolysis products for aluminum chloride or sulfate decreased evidently but for polyaluminum remained to have more charges.

3.3 Adsorption of aluminum coagulants

Adsorption of different aluminum coagulants were carried out in the kaolinite suspension of $\text{pH} = 5.0 \pm 0.2$. The experimental results for AlCl_3 and polyaluminum of $B^* = 1.0$ and 2.5 were shown in Fig. 4 as isotherms of adsorbed species $G(\text{mol Al/m}^2)$ versus equilibrium concentration of residual aluminum in solution $C(\text{mol Al/L})$. In the same initial concentration of aluminum, the adsorbed species on the surface of kaolinite were increased with B^* .

The adsorption curves were plotted by Langmuir isotherm:

$$G = G^0 C / (A + C), \tag{a}$$

or
$$1/G = 1/G^0 + (A/G^0) (1/C), \tag{b}$$

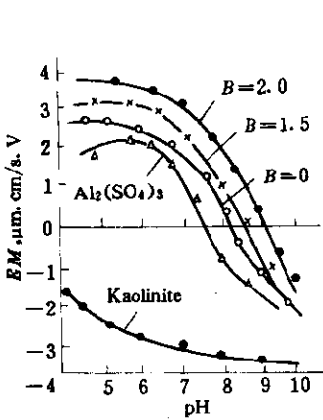


Fig. 3 The micro-electrophoretic mobility change of particles

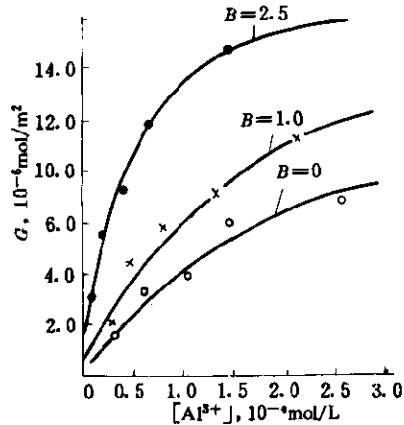


Fig. 4 The adsorption isotherm of polyaluminum coagulants

where, G^0 is the saturated adsorption value and A is a coefficient which is reverse related to the

adsorption strength. The calculated parameters by Equation (b) and the regression coefficient r are listed in Table 3.

Table 3 The adsorption characteristic for different sorts of polyaluminum

Type	B	$G^0, \text{mol/m}^2$	$A, \text{mol/L}$	r
A_0	0	9.65×10^{-6}	1.38×10^{-4}	0.9987
B	1.0	1.36×10^{-5}	1.01×10^{-4}	0.9970
D	2.5	2.11×10^{-5}	5.36×10^{-5}	0.9960

It is evident that with the increasing B^* , G^0 increased and A decreased i. e. , the adsorption tendency was strengthened. The G^0 for polyaluminum of type D were twice as large as that of type A_0 . It means that the pre-produced species were adsorbed much stronger on the surface of particles.

4 Discussion

4.1 Optimum coagulating species and stability

On the basis of experimental data for species distribution and coagulation - adsorption processes, some comprehensive parameters can be set as shown in Table 4.

Table 4 Comprehensive parameters of adsorption and coagulation for polyaluminum

Type	B	$Al_b(\%)$	$G(\%)$	$G^0, \text{mol/m}^2$	$\frac{G^0}{Ns}$	$\frac{G_{CNC}}{Ns}$	$\frac{\Delta \xi (\text{mV})}{\Delta G (\text{mol})}$
A_0	0	<20	40-60	9.65×10^{-6}	1.08	0.35	5.72×10^6
B	1.0	45-54	50-70	1.36×10^{-5}	1.52	0.30	6.83×10^6
D	2.5	72-82	80-90	2.11×10^{-5}	2.37	0.25	9.10×10^6

In Table 4 $Al_b\%$ is the portion of Al_b species before dosing and $G\%$ is the portion of adsorbed species. These two values for type B and D are similar but $G\%$ is bigger slightly. It is assumed that the adsorbed species are mainly Al_b because of they have both larger molecular and higher charge. For type A_0 , $G\%$ is much bigger than $Al_b\%$, the adsorbed extra Al_b may be produced after dosing by hydrolysis of $AlCl_3$ in solution.

4.2 Adsorption and charge neutralization

The charge neutralization effects for kaolinite particle are achieved by the adsorption of aluminum species with different sign. The coverage of aluminum species on the surface can be represented by G/Ns , Ns is the density of surface adsorption sites (mol/m^2). In Table 4, G^0/Ns represents the coverage of saturated adsorption. It is shown that $G^0/Ns=1$ approximately for type A_0 . It seems that a monolayer coverage has been approached for the saturated adsorption. However, G^0/Ns are significantly larger than unit for type B and D . That may be explained as the multilayer adsorption at saturation. In fact, it can be understood as the polymeric species combined to the surface sites with only a part of Al atoms directly.

In Fig. 5, the curve of adsorption G versus electrophoresis EM for polyaluminum of type B was plotted. It may be divided into 3 areas; (1) charge neutralization; particle surface was covered by Al species partly. EM increased as the negative charge was neutralized successively. When $EM = 0$, the isoelectric point was achieved and the optimum coagulation was obtained. The coverage at this time was $G_{cnc}/N_s = 0.30 \pm 0.05$ for type B and also for type A_0, D (Table 4). It means that the optimum coagulation occurred at surface coverage of about 1/3; (2) charge overload; EM continued to increase with G and the charge reverse to positive value. As $EM = 2.0$, the coverage approached 1.0, about all the adsorption sites were occupied, the restabilization became evident; (3) charge constant; if adsorption G continued to increase and oversaturated, the EM would achieved to a constant value which represent that of the multilayer adsorbed Al species. This surface constant charge are described in Table 2 by the parameter EM_H , the values of which are different between the types of aluminum species. Type C had the maximum value and type D had less due to the more content of lower charged Alc.

When $EM < 2.0$, $G/N_s < 1.0$, Al species adsorbed on partial surface with monolayer and EM vs. G changed linearly with a constant slope as $\Delta EM / \Delta G$, then a constant ratio between G and charge was reserved in this case. Assume that $\xi(\text{mV}) = 14.1 EM$, $\Delta \xi(\text{mV}) / \Delta G(\text{mol})$ can be calculated and represented the change of zeta potential affected by adsorbed Al species, in turn it represented the reverse charge of Al species. It is shown in Table 4 that the values of $\Delta \xi / \Delta G$ increased to about twice from type A_0 to type B and D . In fact the species transformed in the hydrolysis and polymerization processes as (Jardine, 1985): Al^{3+} , $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_7(\text{OH})_{16}^{5+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$.

The tendencies of species transformation, charges evolution and the effects of neutralization are corresponding each other.

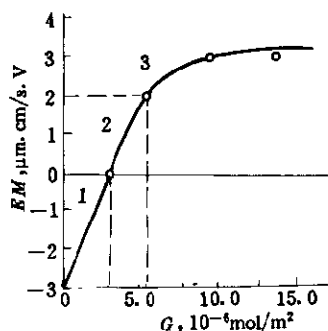


Fig. 5 The EM as a function of adsorption

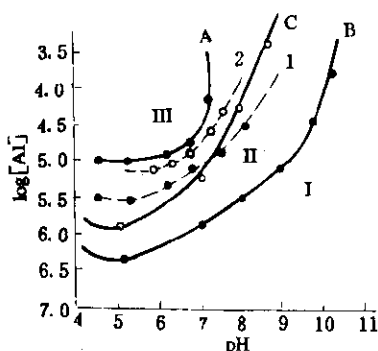


Fig. 6 The coagulation diagram for polyaluminum coagulants

4.3 The coagulation - stability diagram

According to the experimental results, if assume the residual turbidity lower than 30% was

the good coagulation area, a diagram of coagulation - stability can be drawn as Fig. 6, in which the dosing vs. pH was plotted for both type A_c and type C , $D(B^* = 2.0 - 2.5)$. The area between curves A and B was good coagulation zone for polyaluminium, and curves 1 in it was its optimum of $EM=0$. At the other hand, the area between curves A and C was good coagulation zone for $AlCl_3$ with curve 2 as its optimum of $EM=0$. It was shown that all of this zone was included in the coagulation zone II for polyaluminum. In the left side of diagram was the zone of restability III and at the lower right side of curve B was the bad coagulation zone I due to insufficient dosing. It was also evident that a large area out of curve C , i. e. in the bad coagulation zone for $AlCl_3$ was still in the good zone for polyaluminum.

This rough diagram demonstrates clearly the different efficiency and mechanism between $AlCl_3$ and polyaluminum. The much broader good working area and lower dosing for optimum coagulation indicate the significant efficiency of pre - produced inorganic polymer flocculants.

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(Received November 23, 1993)