Species analysis methods for hydrolysis
polymerization of aluminum

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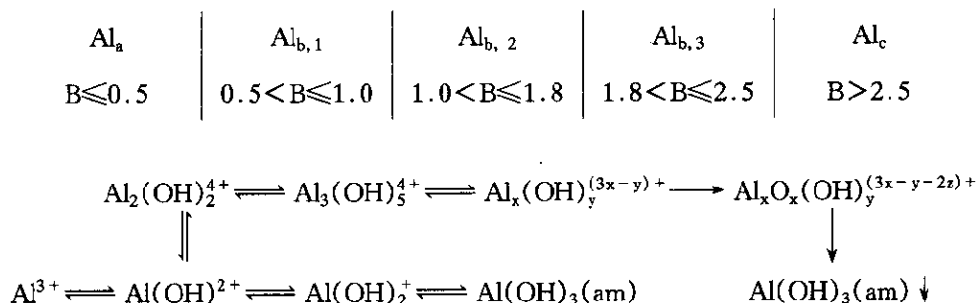Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Abstract—Al-Ferron timed complex colorimetric method (AFM) and ^{27}Al NMR spectroscopy method (ANM) were discussed. For the former, the different colorimetric reagent preparation methods' results indicate that there are some differences between them, and the combined method can be used as a simplified procedure. For the latter, the small tube method is more accurate. Eventually, the Al_{13}(ANM) was compared to the Al_b(AFM).

Keywords: hydrolysis-polymerization species of Al; ^{27}Al NMR; Al-Ferron timed complex colorimetric method.

1   Introduction

Polyaluminium chloride (PAC) is a kind of inorganic polymer flocculant. It has been widely used in the treatment of water and wastewater in Japan, China and other countries since 1970s. Aluminum salts as flocculant can occur hydrolysis polymerization reaction after they are put into water. The polynuclear hydroxy-complex and high polymer resulted in hydrolysis are regarded as the main species of impelling colloidal particles to coagulate and flocculate(Tang, 1990; Stumm, 1968; CRO' Melia, 1975).

Many researchers think that in hydrolysis polymerization processes hydrolysis and polymerization occur alternately at the same time and finally tend to product poly-hydroxy-complex ions with high charge. The species of this products will transform from linear→round→bodily form with B(OH/Al) increasing. The Al(III) hydrolysis polymerization precipitation processes and species transformation model are shown as follows(Luan, 1988):

Al_a	$Al_{b,1}$	$Al_{b,2}$	$Al_{b,3}$	Al_c
$B \leqslant 0.5$	$0.5 < B \leqslant 1.0$	$1.0 < B \leqslant 1.8$	$1.8 < B \leqslant 2.5$	$B > 2.5$

$$Al_2(OH)_2^{4+} \rightleftharpoons Al_3(OH)_5^{4+} \rightleftharpoons Al_x(OH)_y^{(3x-y)+} \longrightarrow Al_xO_x(OH)_y^{(3x-y-2z)+}$$

$$Al^{3+} \rightleftharpoons Al(OH)^{2+} \rightleftharpoons Al(OH)_2^+ \rightleftharpoons Al(OH)_3(am) \qquad Al(OH)_3(am) \downarrow$$

Because species resulted in Al(III) hydrolysis polymerization processes are complicated and varied, we can not give a precise explanation, especially poly-hydroxy-complex ions. Most results based on experimental suggest and there is few direct appraisal. At present, the often used research methods are Al-Ferron timed complex colorimetric method (AFM) improved by Smith(Smith,

1971) and ^{27}Al NMR spectroscopy method (ANM) advanced by Akitt(Akitt, 1969). The former can quantitatively measure Al_a, Al_b and Al_c ($Al_T = Al_a + Al_b + Al_c$); the latter can quantitatively measure certain Al ions species, for example $Al_{mon.}$, Al_2 and Al_{13}(Akitt, 1969; 1972). This paper presents this two kinds of measuring methods and compared their relation in order to provide reliable experimental basis for further research the hydrolysis polymerization species of Al(III).

2   Materials and methods

2.1   Material

2.1.1   Preparation of PAC

2.1.1.1   Micro-injection of base method (MIBM)

Quantitative $AlCl_3$ solution was slowly titrated with NaOH solution till fixed B(OH/Al) value using 655 Dosimat micro-titration apparatus, the titration rate was 0.04 ml/min.

2.1.1.2   Instantaneous injection of base methods (IIBM)

Quantitative NaOH solution was rapidly added into fixed dose of $AlCl_3$ solution till fixed B (OH/Al) value, then heated and stirred till dissolved.

All prepared PAC were used after 24h.

2.2   Method

2.2.1   Al-Ferron timed complex colorimetric method(AFM)

2.2.1.1   Separated method(SM)(Smith, 1971)

0.2% Ferron, 0.01% 1, 10-phenanthroline (covering Fe(III)), 35% NaOAC, 10% NH_2OHHCl (containing fixed dose of 1:1 concentrated HCl) solutions were prepared separately. When Al_a, Al_b and Al_c were measured, all of these solutions were added according to their order.

2.2.1.2   Combined method(CM)(Akitt, 1972)

500 ml combined colorimetric buffer was prepared once only, which contained 250ml 0.2% Ferron (including 0.01% 1, 10-phenanthroline), 100 ml 35% NaOAC, 100ml 10% NH_2OHHCl (including 4 ml 1:1 concentrated HCl). The combined solution was used after four or five days. It would be best if it was used within one month. When Al_a, Al_b and Al_c were measured, got fixed dose of this kind of combined solution.

Measured solutions' pH were needed within 5.2 for this two kinds of methods, that is to say, Congo red test paper became red.

2.2.2 ^{27}Al NMR spectroscopy method(ANM)

Samples were measured using FX90Q Pulse-Fourier-Variety NMR spectroscopy instrument, the resonance frequency was 23.31 MHZ. One capillary that contained $NaAlO_4$ solution as background sample was inserted in the tube containing PAC sample, and their concentrations were similar. The lower the content of Al, the more the number of sampling and accumulating.

There were two kinds of measuring methods: big tube measuring method (BTMM), i.e. background sample and PAC sample were separately inserted in ϕ5mm and ϕ10mm tubes; small tube measuring methods(STMM), i.e. they were separately inserted in capillary and ϕ5mm tube.

3   Result and discussion

3.1   Comparison SM with CM for AFM

3.1.1   Draw up the standard curve

    The quantitative colorimetric buffer were added in the fixed dose soured Al standard solutions and the distilled water was used as blank. Absorbance (A) of Al-Ferron solutions were measured using UV-120-02 spectrophotometer with 370 wavelength. The abscissa showed the concentration of Al(mol/L) and the ordinate showed A, then drew up the standard curve. The result of comparison SM with CM is shown in Fig.1.

    The curve equation was:

$$Y = 0.009460 + 0.075821X, \quad r = 0.9996, \quad (1)$$
$$Y = -0.0001754 + 0.10753X, \quad r = 0.9999. \quad (2)$$

Where, X is the concentration of Al(mol/L); Y is the absorbance; r is the related coefficient.

3.1.2   Draw up the working curve

    Al species of PAC solution($Al_1 = 0.1$ mol/L, $B = 2.0$) prepared by IIBM was measured by AFM. The abscissa showed t (min) and the ordinate showed A, then drew up the working curves. The results of SM and CM are shown in Fig.2.
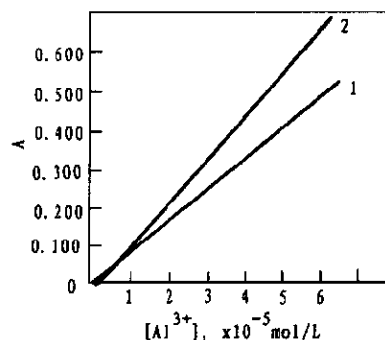

Fig.1   The standard curve of Al-Ferron timed complex colorimetric method

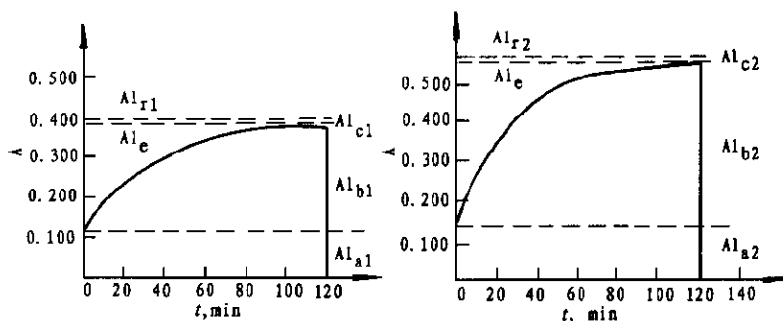1. Separated method;

2. Combined method

Fig.2   The working curve of Al-Ferron timed complex colorimetric
1. Separated method; 2. Combined method

    Al is divided into Al_a, Al_b and Al_c based on the complex rate of hydric Al with Ferron reagent. Al_a is the part which reacts with Ferron within 1 min, generally thinking that Al_a consists of monomers, for example, Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$; Al_b is the part which reacts with Ferron from 1 min to 120 min, thinking that Al_b consists of polymers, for example $Al_2(OH)_2^{4+}$, $Al_2(OH)_2^{4+}$, $Al_{13}(OH)_{34}^{5+}$ and so on. Some researchers divided Al_b into Al_{b1}, Al_{b2}, Al_{b3} (Luan, 1988); Al_c is the part which does not react with Ferron, for example, $Al(OH)_3$ species.

Fig. 1 shows that Al_a measured by CM is smaller than that by SM, that is to say, the former can make Al fast complex with Ferron than the latter.

Table 1   Al species distribution measured by AFM

Method	Al_a, %	Al_b, %	Al_c, %
SM	26.77	66.35	6.48
CM	21.94	74.20	3.86

Table 1 shows Al species distribution measured by these two kinds of colorimetric buffer methods. It expresses that the content of Al_a measured by CM is lower than by SM, but the content of Al_b is opposite. The content of Al_a measured by SM does not completely express the part which reacts instantaneously with Ferron, because the time of injection of colorimetric buffer needed by SM is longer than by CM. CM needs shorter adding time and may measure the content of Al_a at the right time, so the measured content of Al_b is relatively higher. Therefore, CM may be a kind of simplified, fast and accurate method.

3.2   The spectra analysis of ^{27}Al NMR and quantitative calculation of species distribution

3.2.1   The spectra analysis

^{27}Al NMR spectra of PAC solution ($Al_T = 0.1$ mol/L) prepared by different methods and with different B(OH/Al) are shown in Fig. 3.
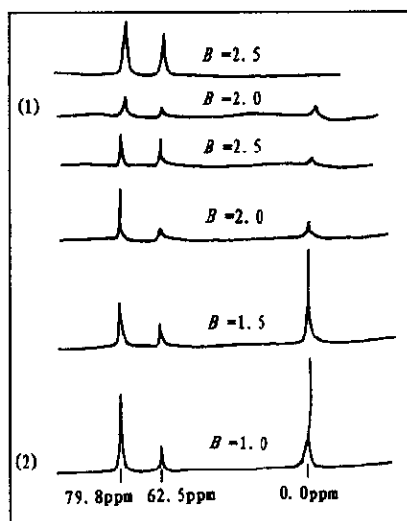
Fig. 3 evidently expresses three resonance peaks (RP): 0.0ppm RP is monomers RP, for example, Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ and so on; 62.5 ppm RP is polymer RP which is supposed as $Al_{13}O_4(OH)_{24}^{7+}$ RP. $Al_{13}O_4(OH)_{24}^{7+}$ consists of twelve hexaligands and one surrounded quadligand Al atomic groups, and they link up through hydrogenbond. But only the quandligand Al being in symmetric environment can occur RP, the hexaligand Al being in unsymmetric environment can not occur RP. So Al_{13} content should be thirteen times as much as peak area; 79.8 ppm RP occurred by background sample indicates quadligand $Al(OH)_4^-$ RP. According to Bottero (Bottero, 1980), ^{27}Al NMR method can evidently distinguish not only Al monomers RP and Al_{13} RP, but also Al_2RP (4.5 ppm). The higher B ($B > 2.0$), the lower Al_2 content, so it is difficult to distinguish Al_2. In order to compare with the results by AFM, this paper only gave $Al_{monomers}$ and Al_{13} contents measured by ANM.

Fig. 3 ^{27}Al NMR spectra of PAC solutions prepared by different method
1. $B = 2.0$, 2.5 prepared by HBM;
2. $B = 1.0$—2.5 prepared by MIBM

3.2.2   Quantitative calculating method of Al species distribution

Suppose the background sample's concentration, volume: C_0 (mol/L), V_0 (ml); PAC

sample's total concentration, total volume: $C_T(mol/L)$, $V_T(ml)$; the background sample's RP area, $Al_{monomers}$ RP area and Al_{13} RP area: S_0, $S_{monomers}$ and S_{13}, then

$Al_{monomers}\% = (C_0 V_0 S_{monomers}/S_0)/(C_T V_T) * 100\%$,

$Al_{13}\% = (13 * C_0 V_0 S_{13}/S_0)/(C_T V_T) * 100\%$,

$Al_{other}\% = 1 - Al_{monomers}\% - Al_{13}\%$.

3.3 Compare big measuring method (BTMM) with small tube measuring method (STMM)

3.3.1 Result of BTMM(Table 2)

Table 2   Al species distribution (prepared by MIBM) measured by AFM and ANM (BTMM)

Al_r, mol/L	B	Al_a, %	Al_m, %	Al_b, %	Al_{13}, %	Al_c, %	Al_{13}/Al_b
0.100	1.0	66.83	64.15	32.68	43.64	0.48	1.34
0.125	1.5	48.92	44.40	50.42	60.11	0.66	1.19
0.111	2.0	22.81	4.72	73.39	79.87	3.80	1.09
0.100	2.5	12.48	4.00	82.85	90.18	4.67	1.09

3.3.2 Result of STMM(Table 3)

Table 3   Al species distribution (prepared by MIBM) measured by AFM and ANM(STMM)

Al_r, mol/L	B	Al_a, %	Al_m, %	Al_b, %	Al_{13}, %	Al_c, %	Al_{13}/Al_b
0.100	1.0	66.83	61.43	32.68	32.88	0.49	1.01
0.125	1.5	48.92	39.28	50.42	51.18	0.66	1.01
0.111	2.0	22.81	16.46	73.39	74.76	3.80	1.02
0.100	2.5	12.48	9.75	82.85	82.92	4.67	1.00

Notes: Al_a, Al_b and Al_c were measured by AFM; $Al_{monomers}$, Al_{13} were measured by ANM in Table 2 and Table 3.

Table 2 shows that $Al_{monomers}\% + Al_{13}\%$ (measured by ANM) $>100\%$ and $Al_{13}/Al_b>1$ at B $=1.0$, 1.5, so this results is not very reliable. But Table 3 shows that $Al_{monomers}\% + Al_{13}\% < 100\%$ and $Al_{13}/Al_b \approx 1$ at $B = 1.0—2.5$. So big tube measuring method has bigger error than small one, and the latter has higher sensibility and reliability. Therefore, if quantitative calculating, we should adopt STMM.

3.4 Compare AFM's with ANM's result

Fig.4 shows ^{27}Al NMR spectra of PAC solutions prepared MIBM and IIBM. Comparison AFM's with ANM's result is shown in Table 3(MIBM) and Table 4(IIBM).

Table 4   Al species distribution (prepared by IIBM) measured by AFM and ANM (STMM)

Al_T, mol/L	B	Al_a, %	Al_m, %	Al_b, %	Al_{13}, %	Al_c, %	Al_{13}/Al_b
0.1	2.0	26.77	20.35	66.35	66.96	6.48	1.01
0.1	2.5	15.36	—	55.38	59.59	29.26	1.07

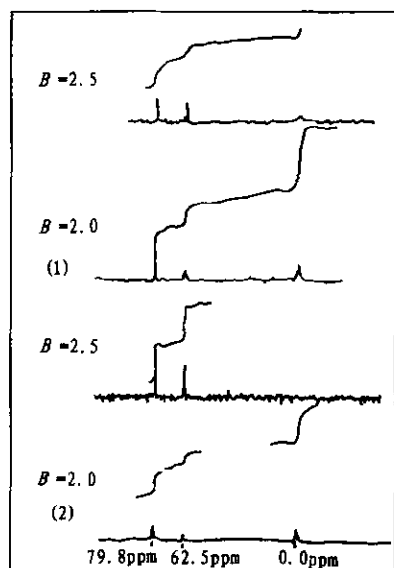Table 3 and Table 4 show that for PAC solutions prepared by this two kinds of methods, at B

Fig. 4 ^{27}Al NMR spectra of PAC solutions prepared by different method

1. $B = 2.0$, 2.5 prepared by MIBM;

2. $B = 2.0$, 2.5 prepared by IIBM

$= 1.0-2.5$; $Al_a\%$ measured by AFM is $5\%-9\%$ bigger than $Al_{monomers}\%$ measured by ANM, but $Al_b\%$ is similar to $Al_{13}\%$, and the relative difference is only 1%. In addition, in Table 3 $Al_{monomers}\% + Al_{13}\%$ is about $90\%-94\%$, $Al_a\% + Al_b\%$ about $95\%-99\%$, and the difference is about 5%. This two kinds of measuring methods' difference may lead all of these results' differences. On the other hand, ANM can not quantitatively measure Al_2 and certain unmeasurable parts, and AFM may contain Al_2 in Al_a because of the artificial definition for Al-Ferron complex rate and time. In this paper, because PAC sample were prepared only by MIBM and IIBM, and so far we can not be sure that Al hydrolysis polymerization species Al_b measured by AFM is Al_{13} by ANM, and Al_a is $Al_{monomers}$ or $Al_{monomers}$ contains Al_2. This research shows that to a certain degree, this two kinds of measuring methods have relativity. Specially, for quantitatively measuring Al hydrolysis polymerization species of PAC prepared by MIBM and IIBM, they have better consistence.

Therefore, they can quantitatively expresses Al species from different aspects.

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