Al(III) speciation distribution and transformation in high concentration PACl solutions

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Abstract: Effects of Al(III) concentration and pH on the speciation of Al(III) in polyaluminum chloride (PACl) solutions especially on the Al_{13} fraction were investigated. A series of PACl samples were prepared over the range of Al(III) concentration from 0.01 to 2.0 mol/L with the B (OH/Al ratio) value from 1.0 to 2.5 by forced hydrolysis of $AlCl_3$. The samples were characterized by ferron assay, pH and ^{27}Al NMR. It was shown that the Al(III) concentration had a dramatic effect on the hydrolysis processes and the species distribution of PACl was in relate to the decrease of pH. The fraction of Al species, Al_b (or Al_{13}) decreased and Al_c increased with increase of total Al(III) concentration. Under the condition of Al(III) 2.0 mol/L, $B = 2.5$, the pH value was 2.73 and no Al_{13} could be detected. During diluting and aging, the species distribution evolved. The Al_{13} could then be detected again and the amounts increased with time. If the diluted samples were concentrated by freeze dry at $-35^\circ C$ or heating at $80^\circ C$, the pH value and Al_{13} content would decrease with the increased concentration. It demonstrated that the key factor for formation of Al_{13} in concentrated PACl was pH value.

Keywords: PACl; Al_{13} ; B value; pH; speciation

Introduction

Since water pollution has become a worldwide problem, many countries suffered from lack of quantity of source water to high quality and safe water or both. Increased attention has been paid to the purification of water in recent years. The effective coagulants must play a more important role in water and wastewater treatment. The inorganic polymer flocculant (IPF) of polyaluminum chloride (PACl) gained broadest use in the world because of its high efficiency and low toxicity compared with the organic reagents (Stumm and Morgan, 1962; Tang, 1998; Parthasarathy and Buffle, 1985; Wang and Tang, 2001; Wang *et al.*, 2002). Researches concerning PACl started to be an active topic in the field of environmental science and technology.

The hydrolysis reaction of aqueous Al(III) has been the subject of innumerable investigations over the passed century. Especially in recent 30 years, the great progress in characterizing the species of PACl and their transformation has been achieved due to the application of the advanced methods of timed-complexation absorption and ^{27}Al NMR spectroscopy. It is accepted prevalently that the Al(III) ions in partially neutralized solution exhibit strong hydrolysis reactions and various polynuclear or polymer species in metastable state can be formed (Tang, 1998; Wang and Tang, 2001; Wang *et al.*, 2002; Bersillon *et al.*, 1980; Parker and Bertsch, 1992; Hsu, 1988; Akitt and Alan, 1981; Bottero *et al.*, 1987, 1988; Brosset, 1952; Rowsell and Nazar, 2000; Allouche *et al.*, 2000; Klopogge *et al.*, 1993). The ferron assay can divide

the Al(III) species into Al_a , Al_b and Al_c categories. The ^{27}Al NMR spectroscopy can identify the monomer, oligomer and tridecamer (Al_{13}) species in special. The species distribution of PACl depends on the preparing conditions, such as OH/Al molar ratio (B), total concentration of Al, rate of base addition, and temperature and so on.

It was gradually recognized that Al_{13} is the most effective species for charge neutralization and particle bridging actions in coagulation and flocculation processes (Bottero, 1988; Tang, 1998; Xu *et al.*, 2003; Wang *et al.*, 2004; Tang and Luan, 1996). However, Al_{13} is only one kind of the complicated hydrolyzed Al (III) species, which coexists with other species in PACl and its content depends greatly on the preparation conditions. For the PACl prepared in laboratory with concentration less than 0.5 mol/L Al(III), the content of Al_{13} can usually reach 70% more. But Al_b content can be less than 30% in current industrial liquid PACl products at concentration above 2 mol/L Al(III) (Xu *et al.*, 2003; Wang *et al.*, 2004; Tang and Luan, 1996). Therefore, how to produce PACl with high Al_{13} content becomes an important target of PACl production and polymeric solution chemistry of Al(III) as well. However, most of the previous studies focused on the solutions of low concentration of 10^{-4} – 10^{-1} mol/L and few concerned with the high concentration about 1–2 mol/L. It is necessary to further investigate the cause of very low Al_{13} or Al_b content in high Al(III) concentration PACl.

This investigation was focused on the series speciation characterization in concentrated and diluted Al(III) solutions by using ferron assay and ^{27}Al NMR

spectroscopy. It was aimed to enhance our understanding of the characteristics of PACl with high concentration and the mechanism of decrease of Al_{13} content.

1 Material and methods

1.1 Preparation of PACl

All PACl samples were prepared in a 500-ml double-walled, heat-resistant glass vessel. The solution in the reactor was maintained at 80°C by circulating water from a thermostatically controlled water bath. 2.0 mol/L Al stock solution was prepared by dissolving $AlCl_3 \cdot 6H_2O$ in deionized water. The amount of deionized water and Na_2CO_3 added were determined according to the final Al(III) concentration and B value desired. Na_2CO_3 was added into the $AlCl_3$ solution with a certain slow rate. The species distribution of PACl was characterized by ferron assay and ^{27}Al NMR spectroscopy. The total Al(III) (Al_T) concentration was measured by ICP.

1.2 Dilution of high concentration PACl

In this investigation, the 2.0 mol/L PACls at B value of 1.5, 2.0, 2.5 prepared by the above-mentioned method were diluted with deionized water to the final concentration of 1.0, 0.5, 0.2, 0.1 and 0.05 mol/L at 25°C, respectively. The species distribution of diluted PACl was characterized by ferron assay and ^{27}Al NMR spectroscopy as well. The transformation of species of PACl in one month of aging at 25°C after dilution has also been studied.

1.3 Reconcentrating of PACl

The reconcentrating of PACl was carried out in two ways of vacuum freeze-dry or heating dry. The samples were prepared by diluting 2.0 mol/L PACl ($B = 2.5$) to 0.1 mol/L and then concentrated reverse in vacuum desiccators at -35°C or in water bath at 80°C. The final Al concentrations were approached to 0.5, 1.0 and 2.0 mol/L respectively. The concentrated PACl samples were characterized by ferron assay, pH and ^{27}Al NMR spectroscopy.

1.4 Ferron assay

Based on the kinetic difference of the reactions between the Al species and ferron reagent (8-hydroxy-7-iodoquinoline-5-sulfonic acid), the Al species can be divided into Al_a , Al_b and Al_c categories, respectively (Wang *et al.*, 2002). The timed absorbance measurements were carried out on UV-Vis 800 Spectrometer at 366 nm and the readings were picked at 1 min and 120 min after mixing the sample with ferron reagent. It was operationally divided that the 1 min absorbance as Al_a , and 1 min to 2 h as Al_b , then the concentration of Al_c was obtained from the remainder of Al_T .

1.5 ^{27}Al NMR spectroscopy analyses

The measurements were carried out on a Bruker Advance 500 NMR spectrometer at 52.14 MHz and

the methods was addressed in details elsewhere (Xu *et al.*, 2003). The other spectral parameters were: temperature 293 K, number of scan 128, pulse width 14.0 μs . The 0.05 mol/L $NaAlO_2$ solution diluted with D_2O was used as reference with respect to the chemical shift (δ) for all solutions, which causes the resonance peak at chemical shift $\delta = 80$ in spectrum. The concentration of Al_{13} was calculated by the integral of resonance peak at about 62.5 (δ) multiply 13. The concentrations of Al-monomer and Al-oligomer were taken from the integral intensities of corresponding resonance peaks at about 0 and 4 (δ). The undetectable Al was obtained from the remainder of the Al_T .

1.6 General methods

The measurement of pH value was carried out on Orion pH meter (Model 828) with glass-electrode system. The measurement of Al_T was carried out on YJ ULTIMA ICP-AES. Deionized water prepared by RO processing free from trace organic compounds. All the chemicals used in this study were of analytical grade unless otherwise pointed out.

2 Results and discussion

2.1 Speciation characterization in PACl of high concentration

The distribution of Al species of various PACl samples characterized by ferron assay is summarized in Table 1. All the samples were prepared as described in Section 1 over the range of concentration from 0.01

Table 1 Speciation distribution of PACl samples by ferron assay

No.	Value B	Al_T , mol/L	Al_a , %	Al_b , %	Al_c , %	pH
1	1.5	0.01	39.5	52.8	7.7	3.98
2	2.0	0.01	26.5	71.3	2.2	4.27
3	2.5	0.01	5.4	81.9	5.0	5.44
4	1.0	0.1	59.4	35.1	2.9	3.46
5	1.5	0.1	44.4	52.1	3.5	3.60
6	2.0	0.1	25.3	72.6	2.1	3.78
7	2.5	0.1	4.5	73.6	21.9	5.32
8	0	0.5	100	0	0	2.71
9	1.0	0.5	66.7	29.3	4.0	3.40
10	1.5	0.5	45.7	38.1	16.2	3.44
11	2.0	0.5	30.2	50.1	19.7	3.51
12	2.2	0.5	20.2	54.7	20.1	3.59
13	2.4	0.5	13.1	59.7	27.2	3.75
14	2.5	0.5	6.8	63.2	30.0	4.19
15	2.5	1.1	4.7	19.7	75.6	3.44
16	2.5	1.8	4.2	10.0	85.8	3.12
17	0	2.0	100	0	0	0.63
18	1.0	2.0	75.5	18.3	6.2	—*
19	1.5	2.0	56.1	13.4	30.5	2.18
20	2.0	2.0	32.9	8.8	58.3	2.39
21	2.3	2.0	11.5	7.5	81.0	2.42
22	2.5	2.0	6.9	8.0	85.1	2.73

Note: * The data was not detected

to 2.0 mol/L. The pH of samples is also listed. The distribution of Al species is plotted vs. Al(III) concentration and *B* values respectively (Fig.1). From Fig.1, it can be recognized that the Al_b fraction decreases and the Al_c fraction increases sharply with the increasing of Al (III) concentration especially from 0.5 mol/L while the Al_a fraction increases moderately at the same

B value. For the high concentration PACl at 2.0 mol/L Al (III), the Al_a fraction begins to decrease rapidly while the Al_c fraction increases rapidly with increase of *B* value. The Al_c becomes the predominant species over *B* = 2.0. It shows that the Al_b fraction is very limited in high concentration of Al.

Fig.1 Species distribution of PACl characterized by ferron assay
a. various concentration of Al(III); b. various *B* value

The fractions of Al₁₃, Al-monomer and Al-oligomer of samples by ²⁷Al NMR spectrum are calculated from the integral intensities of corres-

ponding resonance peaks and summarize in Table 2. The Al₇ and undetectable Al fraction are listed as well.

Table 2 Speciation characterization of PACl by ²⁷Al NMR spectra

Al(III) conc., mol/L	<i>B</i> value	Intensity				Fraction, %			
		δ = 0	δ = 4	δ = 10	δ = 63	Al _{mon}	Al _o	Al ₁₃	Al _{un}
0.1	1.0	4.19	0.05	-	0.2	44.0	2.1	20.2	33.7
0.1	1.5	3.52	-	-	0.41	36.9	-	49.3	13.8
0.1	2.0	1.48	-	-	0.51	15.2	-	63.1	21.7
0.1	2.5	-	-	-	0.34	-	-	39.6	60.4
0.5	2.0	8.56	0.75	-	1.03	17.2	1.7	29.6	51.5
0.5	2.2	4.26	0.20	-	1.50	8.7	0.6	41.6	49.1
0.5	2.4	1.74	-	-	1.92	3.7	-	52.6	43.7
0.5	2.5	0.45	-	-	2.08	1.2	-	56.7	42.1
2.0	1.5	45.83	4.61	-	-	22.8	2.3	-	74.9
2.0	2.0	23.22	1.65	-	-	11.6	0.9	-	87.5
2.0	2.5	4.34	-	-	-	2.2	-	-	97.8

Notes: Al_{mon}, Al-monomer; Al_o, Al-oligomer; δ, chemical shift

Fig.2 shows the ²⁷Al NMR spectra of 0.5 mol/L PACl over the range of *B* from 2.0 to 2.5 and 2.0 mol/L PACl over the range of *B* from 1.5 to 2.5 respectively. Comparison of Fig.2b with Fig.2a, it can be recognized that no Al₁₃ can be detected in PACl at 2.0 mol/L Al(III) concentration. The concentration of monomer and oligomer decreases with the increase of *B* value, which is similar to the situation in PACl at 0.5 mol/L Al(III) concentration. However, the concentration of undetectable species is increasing rapidly

with the increasing of *B* value (Table 2).

Fig.3 shows the effect of aging on the species of PACl in high concentration. The ²⁷Al NMR spectrum of PACl (2.0 mol/L, *B* = 2.5) fresh prepared presents only the signal of monomer while aged 2 months the PACl (2.0 mol/L, *B* = 2.5) presents a middle intensity and broad peak at chemical shift about δ = 10 nearby the signal of monomer. With the signal appearing at δ = 10, the peak of monomer decreases. It is believed that the resonance peak at chemical shift about 10(δ)

Fig.2 ^{27}Al NMR spectra of PACl prepared by adding Na_2CO_3 solution to AlCl_3 stock solution at 80°C

a. Al(III) conc. 0.5 mol/L, from far to near represent, $B = 2.0, 2.2, 2.4, 2.5$ respectively; b. Al(III) conc. 2.0 mol/L, from far to near represent $B = 1.5, 2.0, 2.5$ respectively

is caused by octahedral Al(III) connected with tetrahedral Al(III) (Akitt, 1989). It indicates that the tetrahedral Al(III) may exist with asymmetric structure in fresh prepared PACl and it connects with octahedral Al(III) during aging. However, the structure of this species has not been identified yet. It seems different from Al_{30} , the species reported by Allouche *et al.* (2000).

Fig.3 ^{27}Al NMR spectra of 2.0 mol/L PACl prepared by adding Na_2CO_3 into AlCl_3 solution at 80°C with B value of 2.5 by aging

Upon comparison of the results obtained by ferron assay and ^{27}Al NMR spectroscopy methods, it indicates that the increasing of Al_T concentration favors the formation of larger polymer species beyond Al_{13} . The Al_{13} fraction decreases sharply with the increasing of total Al(III) concentration. The influence of total concentration on oligomer is not significant. The amount of monomer increases a little with the increasing of total Al(III) concentration. It indicates the decrease of Al_{13} with the yield of undetectable species in ^{27}Al NMR analysis or Al_e fraction in ferron assay is not a simple aggregation of Al_{13} . It is difficulty for Al(III) to form Al_{13} at high Al(III) concentration.

2.2 Effect of concentration on the formation and transformation of Al_{13} or Al_b species

Fig.4 shows the species evolution in PACl solutions that were diluted from 2.0 mol/L to various concentrations and then aged at 25°C . Figs.4a, 4b and 4c are the PACl solutions with the B value of 2.5, 2.0 and 1.5 respectively. It seems that the transformation of species in high concentration of PACl takes place during dilution. The variation of diluted solution depends largely on the B value of primary solutions. After dilution, the Al_b fraction of all samples starts to

increase. The increments become slowed down after several days in the solutions of $B = 2.0$ (Fig.4b) and $B = 1.5$ (Fig.4c) but continued to increase in the solutions of $B = 2.5$ at lower concentration (< 0.2 mol/L) (Fig.4a).

For Al_a species, the amount is decreasing with decreasing solution concentration. The variety is more obvious for PACl at lower B value. Comparison of Fig.4 with Fig.1 shows a similar tendency of species distribution in the diluted solution and the PACl prepared in the same concentration.

For Al_b species, the fraction is increasing with decreasing solution concentration. The increment of Al_b is larger at higher B value. Although the Al_b fraction formed during dilution is much less than prepared at the same concentration and B value, it shows a similar tendency that the formation and stabilization of Al_b is unfavorable in high concentration. The Al_b fraction is increasing with the increasing of B value at last. It is needed to point out that the rate of Al_b formation and the increment of Al_b during aging vary according to the different B value. For diluted PACl at B value of 1.5 or 2.0, the increment of Al_b fraction is very rapidly during the first 3 h aging and then slows down. It almost reaches equilibrium until 1 d aging and this increment is very limited during the henceforth 29 d aging investigated. For diluted PACl at B value of 2.5, however, the Al_b fraction is increasing continuously during one month aging. The higher Al_a fraction is, the quicker Al_b forms. From Fig.4, it can also be observed that a large part of Al_e species are colloidal Al(OH)_3 , which could not dissolve to form Al_b any more.

Fig.5 shows the transformation of species after dilution and aging as identified by ^{27}Al NMR spectroscopy. It proves that Al_{13} has been formed during the dilution process. Upon comparison of Fig. 5, it could be found that the formation rate of Al_{13} varied depending on the B value. The signal of Al_{13} of PACl at B value of 2.0 appears immediately after dilution. The concentration of Al_{13} is increasing obviously during the period of 150 min monitoring. The rate of Al_{13} formation of PACl at B value of 2.5,

Fig.4 Speciation of PACl at various concentrations and the effect of aging time
a. dilution with $B = 2.5$; b. dilution with $B = 2.0$; c. dilution with $B = 1.5$

however, is much slower. A very weak signal of Al_{13} appears until 60 min aging. It seems that the Al_{13} fractions form via different ways. In the low B value PACl, the pH unequilibrium at interface arising from the addition of deionized water (weak base) during dilution causes the formation of AlO_4^- because of the higher Al_1 content. Therefore the Al_{13} forms rapidly. In the high B value PACl, the disconnection of polymer takes place and the disconnection of polymer containing tetrahedral $Al(III)$ can form AlO_4^- that reacts with Al -monomer or Al -oligomer formed to form Al_{13} . Since the dissolution of the polymer follows a slow kinetic and lasts a long period, the formation of Al_{13} increases gradually during aging. The results of ^{27}Al NMR spectra correspond well with ferron assay.

Fig.6 shows the ^{27}Al NMR spectra of the PACls concentrated by vacuum freeze dry and heating dry. The data of chemical shift and integral intensity of resonance and pH have been listed in Table 3. It is easy to be recognized that the Al_{13} concentration is decreasing with the increasing of $Al(III)$ concentration of PACl while the concentration of monomer is not increasing during concentrating. In addition, the species which causes chemical shift at about $10(\delta)$ is forming during concentration. This chemical shift moves to high field and its integral intensity increases

Fig.5 ^{27}Al NMR spectra of PACl diluted from 2.0 to 0.1 mol/L
a. dilution with $B = 2.5$ aging 5 min, 1 h, 2.5 h, 2 months from near to far respectively; b. dilution with $B = 2.0$ aging 0 min, 30 min, 1.5 h, 2.5 h from near to far respectively

with the increasing of concentration. The Al_{13} species has disappeared completely until the PACl has been

Table 3 Characterization of concentrated PACl by ^{27}Al NMR spectroscopy

C_{Al} , mol/L	pH	Intensity			Method of concentration
		$\delta = 63$	$\delta = 10$	$\delta = 0$	
1.0	3.56	0.21	0.12	1.76	Freeze dry at -35°C
2.0	2.89	-	0.81	2.72	Freeze dry at -35°C
2.0	2.82	-	0.79	3.86	Heating at 80°C

Notes: δ : Chemical shift; * it was concentrated from 0.1 mol/L PACl at pH 4.44

Fig.6 ^{27}Al NMR spectra of the PACl ($B = 2.5$) (diluted from 2.0 mol/L to 0.1 mol/L and aged 2 months and then concentrated from 0.1 mol/L to various concentrations under different conditions)

concentrated to 2.0 mol/L. Little difference can be found between the PACl concentrated by freeze dry at -35°C and by heating at 80°C . The temperature does not play a key role for the disappearance of Al_{13} . It indicates that increasing concentration is unfavorable for the stabilization of Al_{13} .

2.3 Influence of pH on Al_{13}

The above results show that no Al_{13} exists in PACl with concentration exceeding 2.0 mol/L. Since Al_{13} is one of the products of partial hydrolyzed Al(III) solution, pH value will play important role in the formation and stabilization of Al_{13} . Concentration is an indirect cause for the unfavorable formation and stabilization of Al_{13} in high concentration PACl solution. By referring Table 1, various Al(III) concentrations will result in the variety of pH. Therefore, the variety of species distribution of PACl in various concentrations should be caused by the different pH values.

Fig.7 shows the relationship of Al_{13} of PACl in concentration of 0.01, 0.1, 0.5, 2.0 mol/L and pH value. The characteristics indicated that for PACl in Al(III) concentration of 0.01 and 0.1 mol/L, the pH over the B range from 1.0 to 2.5 is from 3.52 and 3.78 to 5.32 and 5.44 respectively. The content of Al_{13} is increasing with the pH value first and then decreasing. The critical point is between 3.78 and 5.32. For PACl in Al(III) concentration of 0.5 mol/L, the pH over the B range from 2.0 to 2.5 is from 3.51 to 4.19. The content of Al_{13} is increasing with the pH value. For PACl in Al(III) concentration of 2.0 mol/L, the pH over the B range from 1.5 to 2.5 is from 2.17 to 2.73. However, no Al_{13} can be detected by ^{27}Al NMR spectroscopy. It indicates that Al_{13} forms under the condition of a certain range of pH values. The optimal

range of pH values is about between 3.5 and 5. Under the condition of pH in the optimal range, Al-monomer or other Al-oligomer species tend to be further hydrolyzed and transform to Al_{13} and the content of Al_{13} increases rapidly with the increasing of B value. It agrees with the reports of previous researchers (Hsu, 1988; Akitt and Alan, 1981; Bottero *et al.*, 1987, 1988; Brosset, 1952; Rowsell and Nazar, 2000; Allouche *et al.*, 2000). In case of the pH over the maximum of the optimal range, the content of Al_{13} decreases due to the condensation or aggregation of Al_{13} . In case of the pH below the minimum of the optimal range it is difficult to produce Al_{13} in PACl. No Al_{13} can form at pH of 2.73. In our recent study on the purification of Al_{13} (Wang *et al.*, 2005), the pH of the Al_{13} solutions obtained are 5.15, 4.96 and 4.81 corresponding the concentrations of 0.42, 1.06 and 2.11 mol/L respectively. It is close to the optimal range of pH for the formation of Al_{13} and much higher than in the PACl prepared by adding base in AlCl_3 solution at the same concentration. It demonstrates that high concentration Al_{13} can exist under the condition of proper pH.

Fig.7 Content of Al_{13} fraction in PACl prepared in various Al(III) concentrations and the corresponding pH values

B value is 1.0, 1.5, 2.0, 2.5 with the increasing of pH respectively in each line except the line of Al (III) concentration of 0.5 mol/L; the B value of Al (III) concentration of 0.5 mol/L is 2.0, 2.2, 2.4, 2.5 with the increasing of pH respectively

By referring back Fig.6, the Al_{13} disappears until the concentration concentrated to 2.0 mol/L where the pH value is about 2.9 (Table 3). It indicates that Al_{13} can not exist for long period and will be decomposed very soon by H^+ at pH below the minimum of optimal range and transform to other species. For PACl in low concentration, the pH value is higher and Al_{13} is

formed; for PACl in high concentration, the pH is lower and no Al_{13} is formed. Although the tetrahedral $\text{Al}(\text{OH})_4^-$ can form at the interface of the base and the bulk solution by adding base into AlCl_3 solution, it reacts with H^+ at once and is decomposed rapidly at the low pH. And H^+ will promote the decomposition of Al_{13} when formed in the interface during base addition (Furrer *et al.*, 1999). The products of decomposition of Al_{13} , such as Al-oligomer can react with OH^- to form Al_6 . Therefore, even if a little Al_{13} has formed at $B = 2.5$ in high concentration PACl, it can not exist for a long period and will be decomposed very soon in low pH. As a result, the content of Al_{13} decreases and Al_6 increases rapidly with the increasing of $\text{Al}(\text{III})$ concentration.

The formation of Al_{13} in diluted solution of 2.0 mol/L PACl is similar with base addition into $\text{Al}(\text{III})$ solution. Fig.8 shows the variation of pH of 2.0 mol/L PACl diluted to various concentrations with aging

time. The pH of PACl is increasing rapidly during dilution. The pH is higher in lower concentration. Based on the deduction of optimal pH range for Al_{13} , i. e. from 3.5 to 5, the pH of PACl in concentration below 0.5 mol/L favors the formation of Al_{13} . Fig.9 shows that the pH value measured in diluted PACl is higher than that by calculation. Since larger polymers are the predominance species in high concentration PACl, the increase of pH is probably attributed to the decreasing of H^+ concentration by dilution and the consumption of H^+ by decomposition of larger polymer mainly. This H^+ consumption causes the micro-interfacial pH gradient and makes the formation of tetrahedral Al-O possible. Once the tetrahedral Al has formed, it can react with oligomer to form Al_{13} . Since the rate of decomposition of larger polymer is very slow at the optimal pH range, the formation of Al_{13} is a continuous process.

Fig.8 Variation of pH value with aging time of PACl in various B during dilution

Fig.9 Comparison of pH increment in diluted PACl

The results suggest the possibility that the preparation of PACl at concentration exceeding 2.0 mol/L with high Al_{13} fraction may be achieved only if

the pH of the system can be maintained at high level, e.g. 4.0 under the condition of B value below 2.5. The processing of electrolysis or concentration by ultra-filtration could be one of the promising techniques to be applied in the high Al_{13} -PACl production because the pH value of the system can be controlled.

3 Conclusions

The effect of total $\text{Al}(\text{III})$ concentration on the hydrolyzed products over the range of concentration from 0.5 to 2.0 mol/L in partial neutralized $\text{Al}(\text{III})$ solution is significant. The pH value of solution plays a very important role. This study demonstrates that the formation and stabilization of Al_{13} are radically influenced by pH which is the function of $\text{Al}(\text{III})$ concentration and B value. The main reason of

disappearance of Al_{13} in high concentration PACl (> 2.0 mol/L) is the very low pH value. The results indicates that the hydrolysis mechanism of Al(III) in high Al(III) concentration is different from that in low Al(III) concentration by base adding into AlCl_3 solution.

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