

Component Comparison of Polyaluminum Chloride Produced from Various Methods

Wen Po Cheng, Chia Yun Chung, Ruey Fang Yu, Chao Feng Chen

Abstract—The main objective of this research was to study the differences of aluminum hydrolytic products between two PACl preparation methods. These two methods were the acidification process of freshly formed amorphous $\text{Al}(\text{OH})_3$ and the conventional alkalization process of aluminum chloride solution. According to Ferron test and ^{27}Al NMR analysis of those two PACl preparation procedures, the reaction rate constant (k) values and Al_{13} percentage of acid addition process at high basicity value were both lower than those values of the alkaline addition process. The results showed that the molecular structure and size distribution of the aluminum species in both preparing methods were suspected to be significantly different at high basicity value.

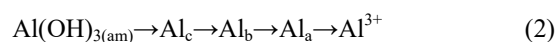
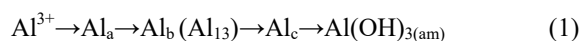
Keywords—Polyaluminum chloride, Al_{13} , amorphous aluminum hydroxide, Ferron test.

I. INTRODUCTION

POLYALUMINUM CHLORIDE (PACl) is broadly used for treating industrial wastewater or purifying drinking water. Including in the PACl, the polymeric aluminum or high valance aluminum species (i.e. Al_{13} species, $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$) can resist the interferences of the background ions in the solution and directly react with the particles in the solution to neutralize the electron charge of particles. Traditionally, the aluminum composition in PACl coagulant was usually analyzed by a Ferron test. According to the complexation time between Ferron reagent and aluminum species, the soluble aluminum species can be operationally defined as monomeric, fast reacting polymeric, or slow-reacting colloidal species denoted simply as Al_a , Al_b , and Al_c , respectively. The previous discussed Al_{13} was identified as Al_b . The Al-Ferron method was not only used for identifying the aluminum formats, but it was also the only method which was capable of identifying the aluminum format in a water treatment process [1]. Hence, this Al-Ferron method gradually became the major method for aluminum species identification in the aluminum hydrolysis solution [2].

Since the percentage of polymeric aluminum species in the PACl can be increased, the flocculation and coagulation efficiencies of the treatment processes may be significantly improved [3]-[5]. Consequently, the formation mechanisms of

high valance aluminum species in the PACl preparation procedure have been the focus of researches in the past several decades [6]. Some scholars used a chemical process at alkali or acidic conditions to dissolve different aluminum minerals [7]-[14]. Another group of scholars mainly concerned about how to improve the alkalinity dosing process or the reaction condition so that the component percentage of the polymeric aluminum could be increased [15], [16]. They found that using the alkali slow addition method could obtain a higher percentage of polymeric aluminum in the PACl than the percentage obtained from the method of alkali be added immediately. Feng et al. [17] focused on the temperature effects on the aluminum formats formed in the PACl preparation process. They found that the best temperature for obtaining the maximum polymeric aluminum was 80 °C. When temperature was 80 °C and B value (basicity, $B = [\text{OH}^-] / [\text{Al}^{3+}]$) was 2.5, the percentage of polymeric aluminum in the PACl was 81.62%. In the past, when the composition of the PACl was studied, the reaction of major preparation method was similar to (1). It was carried out in a laboratory, alkaline solution was slowly added into an aluminum chloride (AlCl_3) solution so that Al^{3+} could react with OH^- to form high Al_{13} content PACl ($\text{PACl}_{\text{base}}$ coagulant) whose concentration was relatively low [15], [16], [18]. Generally, for such a preparation method, the polymeric aluminum percentage in the PACl can be 80-90% [4]. In fact, for the industrial sector, the reaction of (2) was commonly used for PACl preparation, which was an acid dissolutions procedure. In this acidification procedure, solid aluminum oxide or amorphous aluminum hydroxide was acidified with HCl at high or normal temperature to prepare high concentration $\text{PACl}_{\text{acid}}$ coagulant. Because the aluminum concentration was high, the percentage of the polymeric aluminum usually dropped to 30%, which is significantly lower than the percentage found in the alkaline addition process (low concentration).



When the $\text{PACl}_{\text{base}}$ was prepared from adding alkali into the AlCl_3 solution, Bertsch and Parker [19], based on the kinetic theory, explained the reaction mechanism of Al_{13} formation. This reaction was shown by the direction of solid line in Fig. 1. The path I represented the reaction after adding all alkali solution immediately. The solution was partially supersaturated so that a large amount of aluminum hydroxide was formed. When time passed, the aluminum hydroxide precipitated, and some gibbsite formed. The path II and III indicated the production paths of Al_{13} . In path II, the Al_{13} formed while the

Wen Po Cheng is with the Department of Safety, Health and Environmental Engineering National United University, Miaoli, Taiwan 360 (phone: 886-37-382278; fax: 886-37-382281; e-mail: cwp@nuu.edu.tw).

Chia Yun Chung was with Department of Safety, Health and Environmental Engineering National United University, Miaoli, Taiwan 360 (phone: 886-37-382278; fax: 886-37-382281).

Ruey Fang Yu is with the Department of Safety, Health and Environmental Engineering National United University, Miaoli, Taiwan 360 (phone: 886-37-382279; fax: 886-37-382281).

hydrolysis process was slowly occurring. Through path II_a, the Al₁₃ was hydrolyzed to form an octahedral structure crystal with a singular nuclear of Al³⁺. Through path II_b, the anion bridging reaction caused the singular nuclear to polymerize and to form the aluminum polymer of [Al₁₃]_A whose A represented the bridged anion numbers of the Al₁₃. After bridging reaction lasting for a sufficient amount of time, the [Al₁₃]_A could group into [Al₁₃]_n. These [Al₁₃]_n could precipitate to form the floc of

amorphous aluminum hydroxide. Finally, the amorphous aluminum hydroxide was transformed into gibbsite after bridging reaction lasting for an aging period. In path III, the alkaline was rapidly added into the solution. Through the anion bridging reaction, Al₁₃ presented as the format of [Al₁₃]_n. Through the path II_c, Al₁₃ could precipitate and accumulate on [Al₁₃]_n which could be transformed into the floc of amorphous aluminum hydroxide. Finally, it also changed into the gibbsite.

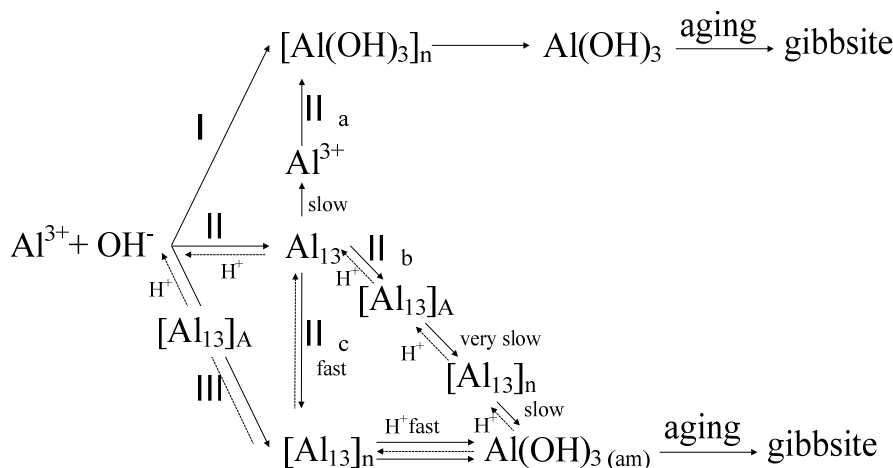


Fig. 1 A diagram of the kinetic mechanism for forming Al₁₃

In Fig. 1, Bertsch and Parker [19] found the formation mechanism of Al₁₃ was discussed as a one-way reaction (solid line) occurring between the singular nuclear Al and hydroxide ions. However, Stol et al. [20] acidified 5×10⁻² mol/L Al(NO₃)₃ solution until the pH reached to 2. Then, the solution was titrated with strong alkali solution until the B value equaled 3.0 so that the amorphous aluminum hydroxide was produced. After the alkalization process, the solution was slowly acidified again until the pH reached to 2. Stol et al. [20] used the pH value to plot against the B value of the solution to explain their relationship. The result indicated that before acidifying the solution pH to 2, the pH in alkalization process was higher than the pH value in acidification process at same B value. However, the trends of titration curves for both alkaline and acid titrations were very similar. Hence, Stol et al. [20] pointed out that these two titration processes could not be completely reversed. Similarly, Ye et al. [21] dissolved freshly formed aluminum hydroxide (amorphous Al(OH)₃) by adding acid and found that the natures and solubility of Al precipitation products could strongly affect the formation of the Al₁₃ in an acid addition process. However, the research of Ye et al. [21] did not focus on the study of Al₁₃ formation mechanism, the aluminum species composition and the effects of alkalization process. Therefore, whether these two titration processes were reversible or not is still unclear.

In the Al-Ferron test, the reaction of Al_b and Ferron reagent followed a first order reaction. According to (3), when absorption and reaction time were measured, the slope of the linear equation (3) was the rate constant of the reaction:

$$\log[A_{b,um}] = \log[A_b] - (k/2.303)t \quad (3)$$

where [A_{b,um}] is the Al_b concentration before reacting with the Ferron reagent. The final measured Al_b concentration is shown as [A_b] [17]. The k and t represent the reaction rate constant and the reaction time. Because the Al_b represents the polymeric aluminum, slightly polymerized aluminum species may rapidly react with the Ferron reagent. In contrast, the reaction to form the highly polymerized Al_b is relatively slow. Hence, when the component percentage of the highly polymerized aluminum is increased in PACl, the reaction rate of the polymeric aluminum reacting with Ferron reagent becomes relatively slow. The reaction rate constant (k) becomes relatively small [17], [22]. In this study, AlCl₃ and Al(OH)₃ were used as the raw materials to prepare the PACl coagulant. The AlCl₃ solution was conducted in alkalization and the Al(OH)₃ was conducted in acidification. Through changing the aluminum concentration, B value, pH of the acid and the way of alkaline addition. Then, the differences of aluminum format and composition of the PACl were studied while both PACl_{acid} and PACl_{base} coagulants were prepared. In addition, the structure of Al_b preparing from acid and alkaline addition methods was analyzed by both Ferron test and ²⁷Al NMR so that the preparation method effect on the Al_b format could be further discussed.

II. EXPERIMENTAL METHODS

A. Alkali Polymerization Method

The PACl_{base} was prepared from slowly adding NaOH solution at the speed of 0.2 mL/min. Some variable parameters such as total aluminum concentration and B value were compared. In this study, four levels of AlCl₃ were prepared as the solution concentrations of 0.1, 0.2, 1.0, and 2.0 M. The

volume of these solutions was set to be 50 mL. The B value is the ratio of hydroxide and total aluminum concentration. Therefore, the B value can be adjusted by adjusting the adding amount of the sodium hydroxide (NaOH). Hence, 50 mL of various NaOH solutions were used to adjust B values to be 1.0, 1.5, 2.0, 2.3, and 2.5 so that the total aluminum concentrations became 0.05, 0.1, 0.5, and 1.0 M. For these solutions (PACl_{base} solutions), they were kept at 30 °C for 3 days as the aging process.

B. Acidic Dissolution Method

In this study, PACl_{acid} was prepared by slowly adding acid solutions in Al(OH)₃ solution to adjust various B values. At first, the 2.0 N NaOH solution was adding to various AlCl₃ solutions by using syringe at a droplet speed of 0.3 mL/min to adjust the pH to 7. These AlCl₃ solutions should be rapidly mixed with a stir so that the NaOH may quickly react with AlCl₃ to form amorphous Al(OH)₃. The solution volume is adjusted to 50 mL, and the aluminum concentrations were adjusted to 0.1, 0.2, 1.0, and 2.0 M. These solutions were used as the source of Al(OH)₃ in the acidic dissolution process. When the pH is at 7, the aluminum formats are almost presenting as Al(OH)₃ [23] and no extra hydroxide ion may react with the added acid. Therefore, the added acid amount can be accurately calculated under various B value conditions. According to the experimental result of preparing Al(OH)₃ in this study, when the NaOH solution was used to adjust 0.1, 0.2, 1.0, and 2.0 M AlCl₃ solutions until their pH was 7, based on the alkaline addition amount, the B_{pH7} values were calculated to be 2.8, 2.76, 2.75, and 2.72. Then, the freshly formed aluminum hydroxide (amorphous Al(OH)₃) was acidified by 50 mL various concentrations HCl solution. After the acid addition, the B value can be calculated as:

$$B = B_{pH7} - ([H^+]/[Al]) \quad (4)$$

where B: The sample's basicity value of the prepared PACl_{acid} solution; B_{pH7}: The sample's B value of the prepared Al solution at pH 7; [H⁺]: The added H⁺ concentration; [Al]: Total aluminum concentration. Hence, 50 mL of various concentrations of HCl solutions was slowly and separately added into 50 mL of 0.1, 0.2, 1.0, and 2.0 M Al(OH)₃ solutions. After the acid addition, the B values became 1.0, 1.5, 2.0, 2.3, and 2.5, and the final aluminum concentration becomes 0.05, 0.1, 0.5, and 1.0 M. Therefore, PACl_{acid} with various total aluminum concentrations and B values was prepared. Finally, these PACl_{acid} solutions were kept at 30 °C for 3 days aging period.

C. Ferron Test

The reactions between the Al species and Ferron reagent have kinetic difference, the Al species can be divided into Al_a, Al_b, and Al_c parts, respectively [24]. The prepared solution was diluted so that the aluminum concentration was adjusted to the detectable range of this Ferron test method (2×10⁻⁴ - 4×10⁻⁴ M). Then, 0.75 mL Ferron reagent was added into the mixture of 0.5 mL sample and 1.45 mL de-ionized water. Then, the sample

was placed in a spectrophotometer (Thermo, Genesys 10S) to measure the absorption data at the wavelength of 366 nm. The absorption data were recorded every 30 seconds for 2 hours. 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. According to (3), the reaction rate constant (k) was calculated (t⁻¹).

D. ²⁷Al NMR Analysis

The analysis steps presented by Lin et al. [25] were adapted in this study. At first, to prepare 0.1 M AlCl₃ solution, 12.0715 mg AlCl₃ · 6H₂O was weighted and added into 0.5 mL 40% NaOD (Aldrich, 99%) solution with small amount of D₂O (Aldrich, 99%). After the solid completely dissolving, the solution was diluted with D₂O to the volume of 2 mL. Then, the inner standard of 0.1 M Al(OD)₄⁻ solution was prepared. The aluminum measured by ²⁷Al-NMR was 80 ppm. The inner standard of Al(OD)₄⁻ solution was added in a 5-mm sample tube (Wilmad 517). Then, the 0.1 M PACl solution prepared from acid addition or alkaline addition method was added into 10 mm sample tube (Wilmad 513-7). Finally, the previously described 5-mm sample tube (containing Al(OD)₄⁻ solution) was inserted into this 10-mm sample tube, and the ²⁷Al-NMR measuring procedure was carried out. In this study, spectra were recorded with a Unity Inova-500 MHz Spectrometer (Varian, USA). The analytical conditions were set to be 130.246 MHz, pulse length 10μsec at π/2, recycle delay 300 ms, temperature 298 K, transients 1600 times. The ²⁷Al-NMR may be used for the analysis of four compounds, mononuclear Al (Al_m), dimeric Al (Al₂), Al₁₃(AlO₄Al₁₂(OH)₂₄(H₂O)₁₂)⁷⁺ and the inner standard (Al(OD)₄⁻). Their concentrations were 0, 3-4, 62.5, and 80 ppm, respectively.

III. RESULTS AND DISCUSSIONS

A. Aluminum Formats in Various Al Concentration Solutions

To compare the aluminum formats affected by acid or alkaline addition, the acid or alkaline was slowly added into the Al solution to prepare the PACl under the conditions of various Al concentrations and different B values. The distribution pattern of aluminum format obtained from Ferron test result was shown in Fig. 2 for alkalization method and Fig. 3 for the acidification method.

The data of Fig. 2 show that Al_a concentration is not affected by the aluminum concentration. However, the component percentage of the Al_b is inversely proportional to the aluminum concentration. When the aluminum concentration is 0.05 M and the B value is 2.3, the percentage of Al_b reaches to the highest value. The percentage of Al_c is proportional to the Al concentration. When the aluminum concentration is 1.0 M, the Al_c is the major aluminum format. The reason for causing such a result is mainly because when the aluminum concentration in the solution is low, the hydroxide ion of the added alkaline could react with Al³⁺ to polymerize the aluminum ion to form the intermediate compound of Al_b. The percentage of Al_b is proportional to the added alkaline dose. In contrast, the percentage of Al_a is inversely proportional to the added

alkaline dose. However, due to the low aluminum concentration, it is not easy to form a highly polymerized aluminum compound of Al_c at these B values range. When the aluminum concentration is increased, the Al_b percentage is decreased. The main reason causing such a result is that when the Al concentration is high, the alkaline addition may cause complex hydrolysis and violent polymerization reaction in the Al solution. If the hydrolysis and polymerization reaction can be continuously progressing, the chances to form a large molecular polymer are relatively increased [25]. The aluminum format could be the aluminum floc or could be similar to the structure of Al₁₃ whose molecular weight is relatively high. However, one thing should be pointed out that the Ferron test cannot react with such a high molecular weight aluminum polymer. Hence, it causes that the Al_c percentage is proportional to the aluminum concentration when the B value is the same. Besides, when the total aluminum concentration is increased, pH value is decreased so that the precursor Al(OH)₄⁻ to form the Al₁₃ is limited. Hence, the percentage of Al₁₃ is reduced so that the Al_b percentage is inversely proportional to the aluminum concentration. In the other words, when the

aluminum concentration is the same but the B value is different, the result shows that the Al_a is inversely proportional to the B value but the Al_b is proportional to the B value. However, the Al_b is decreased when the B value is 2.5. Because the B value is defined as $B = [\text{OH}^-]/[\text{Al}^{3+}]$, if the Al concentration is the same and the B value is small, the pH of the solution is relatively low. Therefore, the Al_a becomes the primary format of the aluminum. If the B value is increased, the solution's pH is increased so that the Al_b is also increased. However, if the B value is too high, part of the Al_b might transform to the Al_c. This transformation phenomenon is especially obvious when the B value is increased [26]. According to the experimental result, when the B value is 2.3, there was a significant portion of the Al_b existing in the PACl_{base}. However, when the B value was 2.5, there was a tendency that the Al_b was decreased and the portion of the Al_c was increased. The reason for this result is that when B value is increased, the opportunity to form various hydroxide compounds or form gibbsite is increased. Hence, when the B value is increased to 2.5, the Al_b is decreased and the Al_c is increased [27].

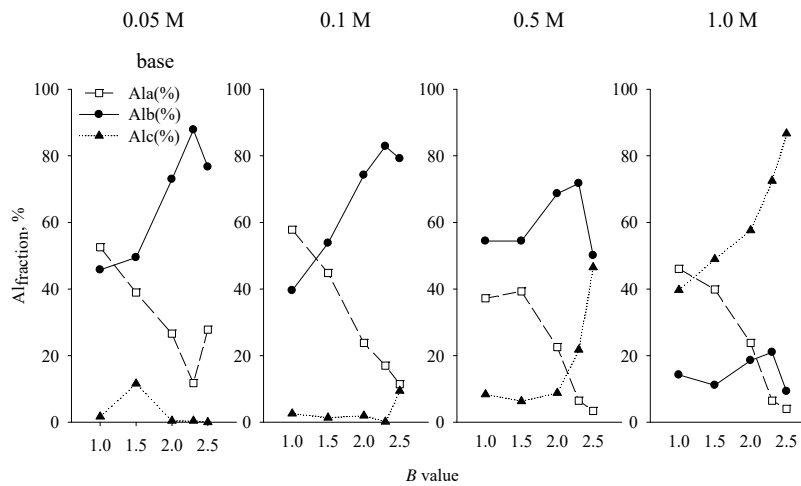


Fig. 2 The aluminum format in PACl_{base} prepared from alkalization method at different aluminum concentrations

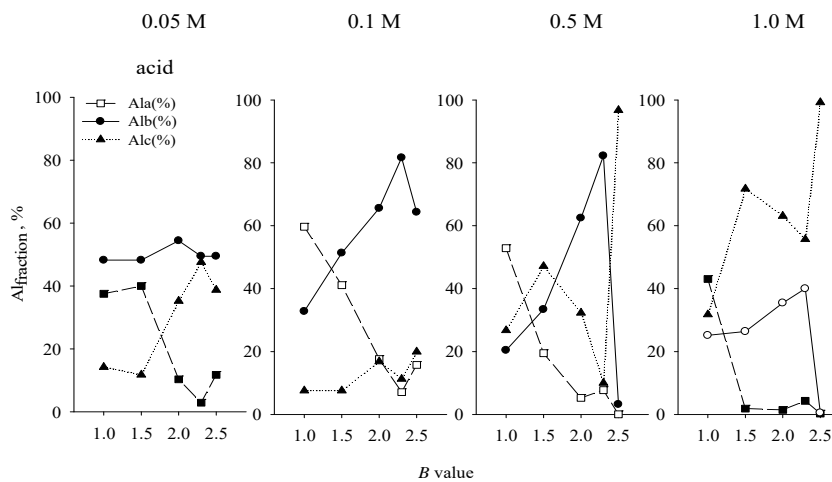


Fig. 3 The aluminum format in PACl_{acid} prepared from acidification method at different aluminum concentration

According to Fig. 3, the result of preparing $PACl_{acid}$ from acid addition method indicates that when the Al concentrations are 0.1 M, 0.5 M and 1.0 M, the percentages of both Al_a and Al_b are inversely proportional to the total aluminum concentration, but the Al_c percentage is proportional to the aluminum concentration. This result is similar to the result of the alkaline addition method which is shown in Fig. 2. When the proton ion is added into the $Al(OH)_3$ solution, the $[Al(OH)_3]_n$ is dissolved and its molecular size is reduced [20]. Hence, when the Al concentration is high, the aluminum is highly polymerized to form a large $[Al(OH)_3]_n$ so that the Al_b percentage is relatively low and the Al_b structure is relatively complex. Hence, the acid cannot significantly dissolve the Al_c to increase the Al_a or Al_b percentage. Similarly, when the aluminum conditions are the same but B value is different, Fig. 3 shows that the Al_a is inversely proportional to the B value. When the adding acid dose is high, which represents that the B value is low, the added proton ion may dissolve the large polymer of $[Al(OH)_3]_n$ into Al_a or Al_b . Hence, when the B value is low ($B=1$), the primary format of the aluminum is Al_a . The Al_b is increased with the B value is increased. However, the percentage of Al_b found at $B=2.5$ is less than the percentage found at $B=2.3$. This result obtained from acidification method is similar to the result from the alkalization method. The main reason is because low amount of proton ion addition cannot dissolve the large polymer of $[Al(OH)_3]_n$. When the aluminum at high level (0.5 M and 1 M), the Al_b can almost not be in $PACl_{acid}$. The main reason is that the high Al concentration may form a larger polymer of $[Al(OH)_3]_n$ than the polymer formed in the low Al concentration solution. Hence, it is not easy to dissolve the polymer into Al_a or Al_b .

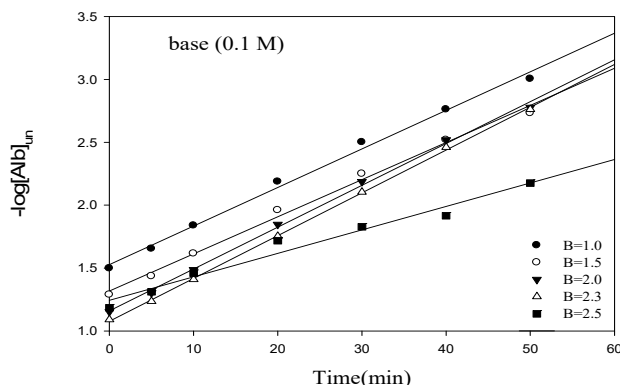


Fig. 4 The reaction kinetic data of the Ferron test to prepare the $PACl_{base}$ by using the alkali polymerization method

B. The Reaction Rate Constant k of Ferron Test

According to the above discussed results, the aluminum formats in both $PACl_{acid}$ and $PACl_{base}$ are very similar in the cases of preparing PACl at various conditions. For example, when the Al concentration was 0.1 M, the aluminum format obtained from both methods was the same. However, when 0.1 M PACl reacted with Ferron reagent at different reaction time, the $[Al_b]_{um}$ concentration was obtained from calculating the converted absorption data. The calculation follows the reaction rate equation, which is shown in (1). According to Figs. 4 and 5,

when the Al_b in PACl prepared from both methods reacted with the Ferron reagent, the slopes of the lines in both figures represent the reaction rate constants. The k values are significantly different at the conditions of high B values. Based on the experimental results, the data of k value, pH and the aluminum formats are listed in Table I.

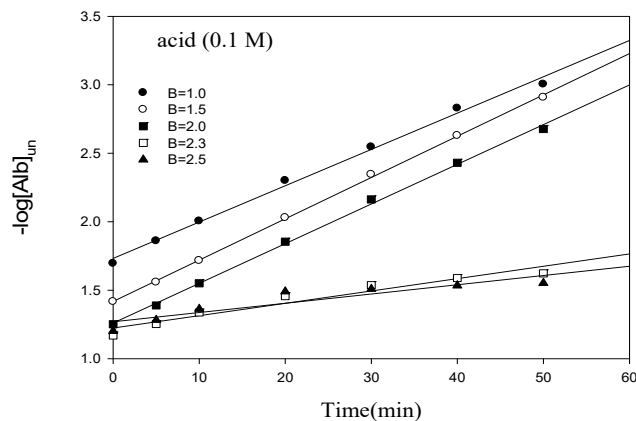


Fig. 5 The reaction kinetic data obtained from preparing the $PACl_{acid}$ by using the acidic dissolution method

TABLE I
 THE REACTION KINETIC DATA OF THE FERRON TEST TO PREPARE PACl BY USING ALKALI POLYMERIZATION OR ACIDIC DISSOLUTION METHODS

	B	pH	Al_T (M)	Al_a (%)	Al_b (%)	Al_c (%)	k (t^{-1})	R^2
Base	1.0	3.64	0.1	57.82	39.58	2.60	0.069	0.995
	1.5	3.74	0.1	44.83	53.80	1.37	0.067	0.994
	2.0	3.88	0.1	23.81	74.21	1.99	0.076	0.997
	2.3	4.01	0.1	17.01	82.86	0.13	0.078	0.999
	2.5	4.99	0.1	11.44	79.15	9.41	0.041	0.971
Acid	1.0	3.36	0.1	59.67	32.77	7.55	0.060	0.996
	1.5	3.72	0.1	41.12	51.33	7.55	0.069	0.999
	2.0	3.98	0.1	17.62	65.55	16.83	0.062	0.940
	2.3	4.13	0.1	7.11	81.63	11.26	0.016	0.915
	2.5	4.30	0.1	15.77	64.31	19.92	0.012	0.823

When the Ferron test is used for the aluminum format analysis, there are at least two Al nuclear in the Al_b polymer. Hence, in the beginning of the reaction, the Ferron reagent prefers to react with low polymerized aluminum compound. When the Al is highly polymerized, it needs a relatively long time for aluminum polymer to react with Ferron reagent. Generally, this type of the reaction can be described by a first order reaction [16]. The data regression of a first order reaction may be presented as a linear equation whose slope represents the reaction rate constant (k). In the process of Ferron reagent reacting with the Al_b , the k value is strongly affected by the aluminum format in PACl. High k value indicates that the average molecular size of the aluminum polymer in Al_b is relatively small (the primary aluminum species is Al_{13}). Low k value indicates that the average molecular size of the aluminum polymer in Al_b is large. Therefore, the reaction of Al_b and Ferron reagent is slow. According to the past documents, when the alkalization method is used for preparing $PACl_{base}$ at B value < 2.5 , the k value does not obviously change (the primary

species is Al_{13} in Al_b) because the Al_b percentage in $PACl_{base}$ is very close to the percentage of Keggin- Al_{13} which is analyzed by the NMR method [17]. However, the k value found at $B = 2.5$ condition is smaller than that found at $B < 2.5$ condition. When the NMR is used to measure the Keggin- Al_{13} in $PACl_{base}$, the Keggin- Al_{13} percentage is less than the percentage determined from the Ferron test. The above results suggest that, at $B = 2.5$ condition, the polymeric aluminum (Al_b) is not only containing the Al_{13} but also containing some polymer whose molecular size is larger than the size of the Al_{13} [17].

According to the result of alkaline addition method in Table I, when the B value is in the range of 1.0-2.3, the k value does not obviously change. However, when the B value is 2.5, the k value significantly drops. These results agree with the result presented by Feng et al. [17]. In contrast, in Table I, when the

acid addition method is used and the B value is greater than 2.0, the k value obviously drops. At $B = 1.0-2.0$, when the k values obtained from both methods are compared, there are no significant differences between the k values. When B value is greater than 2.0, the differences between the k values are very significant. For example, when the B value is 2.3, the Al_b percentages for both methods are very close to 82%. But, the k value difference is very significant. The k value found in alkaline addition method is 0.078, but the one which is found in acid addition method is 0.016. Hence, part of the Al_b should be the high molecular size polymer whose molecular size is greater than the size of Al_{13} because the above cases show that the Al_b percentages are similar but the k values are very different.

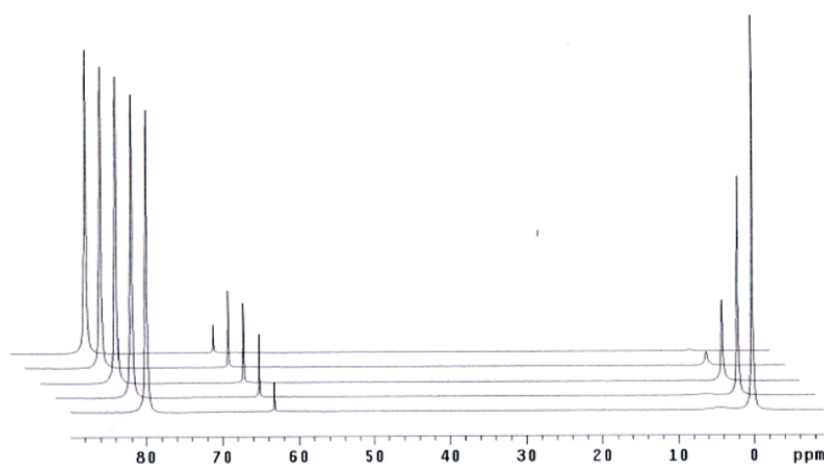


Fig. 6 The ^{27}Al NMR analysis for the $PACl_{base}$ prepared from alkali polymerization method

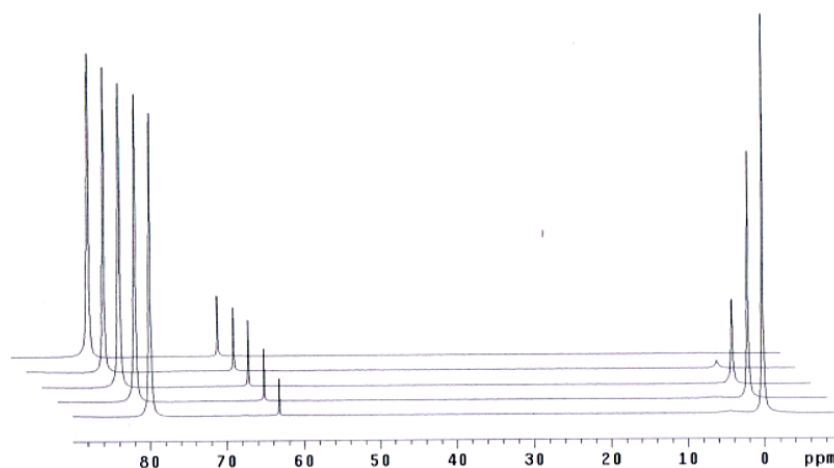


Fig. 7 The ^{27}Al NMR analysis for the $PACl_{acid}$ prepared from acidic dissolution method

C. The Result of $PACl$ Analyzed by ^{27}Al NMR

According to the experimental result of the Ferron test, when the Al concentration is 0.1 M, the aluminum formats in $PACl$ preparing from both methods do not change very much. However, when the Ferron test is used to measure the reaction rate, although the aluminum formats do not change very much, the Al_b formation mechanisms are not the same. For example,

when B value is 2.3, the molecular size of the Al_b produced from the alkali polymerization method is small but the average size found from acidic dissolution method is large. In this study, the ^{27}Al NMR was used to analyze the differences between two methods. Figs. 6 and 7 show that the ^{27}Al NMR analytical results of the $PACl$ prepared from acid and alkaline addition in the conditions of 0.1 M Al concentration at 25 °C.

Figs. 8 and 9 show the percentage of Al_{13} produced from alkali polymerization method and the percentage of Al_b in PACI prepared from acidic dissolution method.

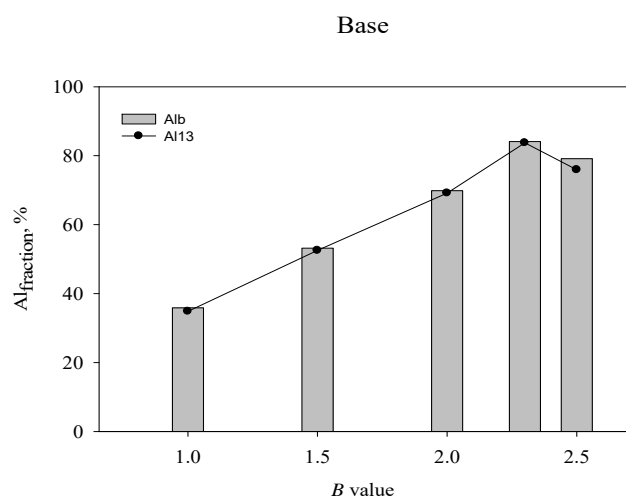


Fig. 8 The aluminum format patterns of Al_{13} and Al_b prepared from alkaline addition methods

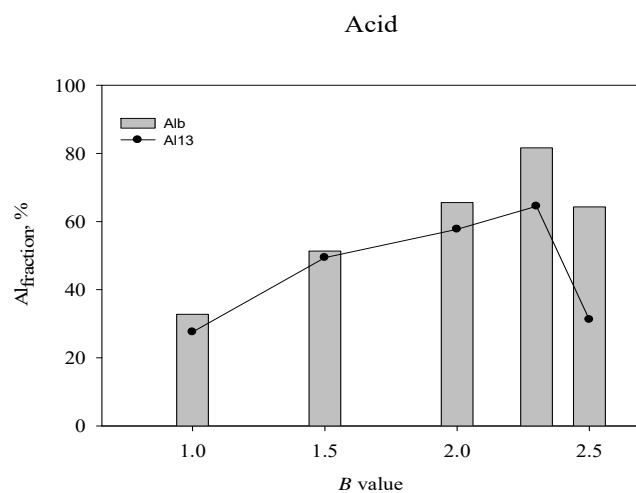


Fig. 9 The aluminum format patterns of Al_{13} and Al_b prepared from acid addition methods

According to Fig. 8, the percentages of both Al_b and Al_{13} in $PACI_{base}$ prepared from alkali polymerization method are very similar. When B value is 2.3, the Al_b percentage analyzed by Ferron test is 82.86%. The Al_{13} percentage analyzed by ^{27}Al NMR is 83.72%, which is very close to the percentage obtained from Ferron test analysis. Therefore, the Al_b in $PACI_{base}$ prepared from alkali polymerization method is likely to be the Al_{13} . This result agrees with the conclusions presented in many documents [17], [28]-[30]. However, in Fig. 9, the percentages of Al_b and Al_{13} in $PACI_{acid}$ prepared from acidic dissolution method are significantly different when the B value is high. When the B values are 2.3 and 2.5, the Al_b percentages analyzed by Ferron test are 81.63% and 64.31%, respectively. When the ^{27}Al NMR is used for the Al_{13} percentages analysis under the B values of 2.3 and 2.5, the percentages of Al_{13} are

64.48% and 31.20%. According to these results, when the B value is high (B = 2.3 and 2.5), the percentages of Al_b in $PACI_{acid}$ is different from the percentage of the Al_{13} in $PACI_{base}$. Similarly, according to the result of the Ferron test kinetic mechanism, when the B value is high, the $PACI_{acid}$ still contains some of the Al_{13} and some of the Al_b whose molecular size is larger than the size of the Al_{13} . These results confirm that the Al_b formats in PACI prepared from either acidic or alkali method are different. The polymeric aluminum (Al_b) prepared from alkali method is Keggin structure, which is known as Al_{13} . Although the reaction of acidic method may be reversed to form the Keggin structure Al_{13} , it is an incomplete reverse reaction. When the B value is high (B=2.3 or 2.5), the forming polymeric aluminum is not only containing Al_{13} , but also containing the large molecular polymerized compound which can react with the Ferron reagent.

When the $Al(OH)_3$ is dissolving at acid condition, the dissolution is the primary mechanism [20]. The large molecular aluminum polymer is dissolving into the small molecular polymer. Some of the researchers pointed out that the structure of the $Al(OH)_3$ can be described as a Core-links model [31]. In an acidic dissolution process, the highly polymerized $Al(OH)_3$ in a structure of 6-membered ring format may be dissolved to form a slightly polymerized 6-membered ring structure Al_b compound. If the dissolution- polymerization reaction does occur, it is impossible to form the Al_{13} compound. However, according to the experimental result of this study, when the fresh $Al(OH)_3$ was formed in an alkali polymerization process, the $Al(OH)_3$ was immediately adding the acid to prepare the $PACI_{acid}$ which still contained the Al_{13} . Therefore, when the alkali solution is titrating against the $AlCl_3$ solution to make the pH value equal to 7, the solution's B value is about 2.8. Under such conditions, the freshly amorphous $Al(OH)_3$ may be formed by the Al_{13} and its molecular structure is presenting as a multiple Keggin structure which is bounded with the OH bound. Therefore, when acid is added in the solution, the OH bound is broken and the polymer returns to the single Keggin- Al_{13} compound. When a small amount of acid is added (i.e. B value is high, B=2.3 and 2.5), the added acid cannot completely dissolve the highly polymerized Keggin- Al_{13} compound so that the produced polymer's molecular size is larger than the size of Al_{13} compound.

D. The Formation Mechanism of Al_{13} in $PACI_{acid}$ Prepared from Acid Addition Method

According to the experimental results in this study, it is confirmed that the Al_{13} presents in the acidification process of the amorphous aluminum hydroxide dissolution. It also indicated that the reaction mechanism might be the same as the direction of dashed line in Fig. 1. That means the Al_{13} formation mechanism in acid addition process and the mechanism presented by Bertsch and Parker [19] (i.e. the solid line path in Fig. 1) might be the reversible reaction mechanisms.

Fig. 10 shows the titration curve of 0.1 M aluminum chloride solution. The solution was titrated by alkaline at first and then titrated by acid. According to Fig. 10, the solution is titrated with NaOH until B=3 and then titrated with HCl until B=0. The

shapes of these two titration curves are very similar. However, the reactions directions of both titrations are opposite. This result agrees with the result presented by Stol et al. [20] who used aluminum nitrate as the solution. In Fig. 10, when B value is zero, the pH values in both acidic and alkali processes are very similar. It means that the acid equivalent amount may neutralize the added alkaline amount so that the neutralization is confirmed to be a reversible reaction. However, when the B value is not 0, the pH values obtained from both titrations are different (i.e. an irreversible reaction). That is why Stol et al. [20] did not suggest that the reactions of both acidic and alkali addition processes were reversible reactions. However, the alkali addition process is a homogeneous reaction so that the reaction path of solid line in Fig. 1 can be manipulated by controlling titration speed and B value. In this way, the percentage of the formed Al_{13} can be controlled. In contrast, the acidic addition reaction is a heterogeneous reaction. Hence, the dashed line direction in Fig. 1 is not easy to be controlled. When the B value of the solution is titrated from 3 to 0, the path of acid titration is different from the path of alkaline addition procedure. The experimental result is listed in Table I. In Table I, when B value is the same, the percentage of Al_c in $PACl_{acid}$ is significantly higher than that in the $PACl_{base}$. It indicated that part of the added acid is not consumed by the Al_c . Hence, when the B value is the same, the pH in an acid addition process is different from the pH in an alkaline addition process.

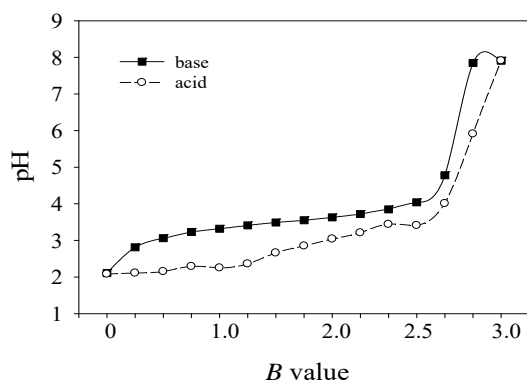


Fig. 10 The titration curve of acidic and alkali titration

When the acid concentration is high ($B=1.0-2.0$), most of the aluminum format is transformed into Al_{13} and Al^{3+} through the path of II_b or II_c as shown in Fig. 1. This suspected conclusion can be confirmed by Ferron test and NMR analyses. Because the polymeric aluminum (Al_b) measured by Ferron test includes both Al_{13} and $[Al_{13}]_A$, but the test cannot measure the $[Al_{13}]_n$. However, the NMR method can only measure the Al_{13} . Hence, according to the experimental result described in the previous paragraphs, when the B value is about 1.0-2.0, the Al_b measured from Ferron test and the Al_{13} measured from NMR analysis has similar percentage in $PACl_{acid}$. When B value is in the range of 2.3-2.5, the Al_b percentage in $PACl_{acid}$ measured from Ferron test is very different from the percentage of Al_{13} in $PACl_{acid}$ measured from NMR analysis. The reason is that because the acid amount is small, most of the aluminum

formats take the path II_b to convert aluminum format back to the format of $[Al_{13}]_A$ or Al_{13} . When the B value is increased, the percentage of $[Al_{13}]_A$ is also increased. According the result of this study, in an acid addition process, the direction of dashed line in Fig. 1 points out the formation mechanism of Al_{13} . This mechanism indicated that the acid and alkaline addition reactions are reversible. However, the percentage of dissolved Al_{13} in $PACl_{acid}$ is affected by the added amount of the acid. For example, when the $PACl_{acid}$ is prepared from 0.1 M aluminum solution with the B value of 2.3 at 25°C, the percentage of the Al_b is 81.63%. But, the percentage of the Al_{13} is only 64.48%. Hence, it shows that only 70% of aluminum transferred back to the format of Al_{13} . The remaining aluminum may be present in the format of $[Al_{13}]_A$ or $[Al_{13}]_n$. Therefore, according to Fig. 10, when acid and alkaline addition processes are carried out at the same B value condition, the acid addition method presents a relatively low pH.

IV. CONCLUSION

When alkaline was added into the aluminum solution, the aluminum in the solution was polymerized and form $PACl_{base}$ coagulant. At the basicity (B) value is 2.3, the produced $PACl_{base}$ has the best character of coagulating performance. Simultaneously, the results of this study also indicate that, when the acid addition method at B value of 2.3, the Al_b percentage in the $PACl_{acid}$ is similarly high. However, according to the results of Ferron test and ^{27}Al NMR analysis, although the Al_b can be produced in both acid and alkaline addition method, the polymeric species of Al_b are not similar. The molecular size of the Al_b produced from alkaline addition method is relatively small and it is known as the Keggin- Al_{13} species. Relatively, the average molecular size that is produced from acid addition method is large. Hence, the result of this study suggested that the aluminum formats produced from acid and alkaline addition methods are not the same.

ACKNOWLEDGMENT

We thank Mr. Chih-Hsiang Chen for assistance with laboratory work. The authors also acknowledge the financial support of Ministry of Science and Technology, Taiwan, R. O. C. for this work (NSC 102-2221-E-239 -001 -MY2)

REFERENCES

- [1] Yan MY, Wang DS, Ni JR, Qu JH, Chow CWK, Liu HL (2008) Mechanism of natural organic matter removal by polyaluminum chloride: effect of coagulant particle size and hydrolysis kinetics. *Water Res* 42:3361-3370.
- [2] Gao BY, Yue QY, Wang BJ (2004) Coagulation efficiency and residual aluminum content of polyaluminum silicate chloride in water treatment. *Acta Hydroch Hydrob* 32:125-130.
- [3] Sinha S, Yoon Y, Amy G, Yoon J (2004) Determining the effectiveness of conventional and alternative coagulants through effective characterization schemes. *Chemosphere* 57:1115-1122.
- [4] Cheng WP, Li CC, Yu RF (2007) Study of the coagulation property of polyaluminum silicate chloride coagulants prepared whit ultrasonic-assisted NaOH dosing. *Separation science and technology. Separation science and technology* 42:3217-3228.
- [5] Zouboulis AI, Tzoupanos N (2010) Alternative cost-effective preparation method of polyaluminium chloride (PAC) coagulant agent: Characterization and comparative application for water/wastewater

- treatment. *Desalination* 250: 339-344.
- [6] Bi Z, Feng CH, Wang DS, Ge XP, Tang HX (2013) Transformation of planar Mogel Al₁₃ coagulant during the dilution and aging process. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 416:73-79.
- [7] Lindahl G (1985) Stable solutions of basic aluminium sulphate containing polynucleate aluminium hydroxide sulphate complexes. United States Patent 4536384.
- [8] Kudermann G, Blaufuss KH (1993) Method for increasing the molar ratio of aluminum to chlorine in polyaluminum chloride solutions. United States Patent 5254224.
- [9] Kerven GL, Larsen PL, Blamey FPC (1995) Detrimental effects of sulfate on the formation of the Al₁₃ tridecameric polycation in synthetic soil solutions. *Soil Science Society of America* 59: 765-771.
- [10] Dufour, P., Process for the preparation of basic polyaluminum chlorosulphates and applications thereof, 1999, United States Patent 5879651.
- [11] Haake G, Geiler G, Haupt F (2001) Process for preparing sulfate-containing basic solutions of polyaluminumchloride. United States Patent 6241958.
- [12] Liu HJ, Qu JH, Hu CZ, Zhang SJ (2003) Characteristics of nanosized polyaluminum chloride coagulant prepared by electrolysis process. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 216:139-147.
- [13] Hu CZ, Liu HJ, Qua JH (2005) Preparation and characterization of polyaluminum chloride containing high content of Al₁₃ and active chlorine. *Colloids and surfaces. A, Physicochemical and engineering aspects* 260: 109-117.
- [14] Janaína AMP, Marcio S, Enrico D, José CP, José LF (2009) Cristiane A. Henriques The kinetics of gibbsite dissolution in NaOH. *Hydrometallurgy* 96:6-13.
- [15] Zhou W, Gao B, Liu L, Wang Y (2006) Al-ferron kinetics and quantitative calculation of Al(III) species in polyaluminum coagulants. *Colloids and surfaces A* 278:235-240.
- [16] Cheng WP, Li CC, Yu RF (2008) Preparing polyaluminum chloride coagulants using ultrasonic-assisted NaOH dosing. *Environ. Eng. Sci.* 25:451-459.
- [17] Feng CH, Tang HX, Wang DS (2007) Differentiation of hydroxyl-aluminum species at lower OH/Al ratios by combination of ²⁷Al NMR and Ferron assay improved with kinetic resolution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 305:76-82.
- [18] Cheng WP, Li CC, Yu RF (2007) A study on the removal of organic substances from low turbidity and low-alkalinity water with metal-polysilicate coagulants. *Colloids and surfaces A* 312:238-244.
- [19] Bertsch PM, Parker DR (1996) In: Sposito G (ed) *The environmental chemistry of aluminum*, 2nd edition. CRC Press, Boca Raton, Florida.
- [20] Stol RJ, Van Helden AK, De Bruyn PL (1976) Hydrolysis-precipitation studies of aluminum (III) solutions. 2. A kinetic study and model. *J. of Colloid and Interface Sci* 57:115-131.
- [21] Ye CQ, Wang DS, Shi BY, Ge XP, Qu JH (2007) Formation and transformation of Al₁₃ from freshly formed precipitate in partially neutralized Al(III) solution. *Journal of Sol-Gel Science and Technology* 41:257-265.
- [22] Shen YH, Brian A (1998) Dempsey, Synthesis and speciation of polyaluminum chloride for water treatment. *Environment International* 24:899-910.
- [23] Lydersen E, Salbu B, Poleo A B S, Muniz I P (1991) Formation and dissolution kinetics of Al(OH)_{3(s)} in synthetic freshwater solutions. *Water Resources Research* 27:351-357.
- [24] Wang D S, Tang H X, Gregory J. (2002) Relative importance of charge neutralization and precipitation on coagulation of Kaolin with PACl: Effect of sulfate ion. *Environmental Science and Technology* 36:1815-1820.
- [25] Lin JL, Huang CP, Chin CJ, Pan JR (2009) The origin of Al(OH)₃-rich and Al₁₃-aggregate flocs composition in PACl coagulation. *Water Research* 43:4285-4295.
- [26] Bertsch PM, Thomas GW, Bamhisel RI (1986) Characterization of hydroxy-aluminum solutions by aluminum-27 nuclear magnetic resonance spectroscopy. *Soil Science Society of America Journal* 50:825-830.
- [27] Bi S, Wang C, Cao Q, Zhang C (2004) Studies on the mechanism of hydrolysis and polymerization of aluminum salts in aqueous solution: correlations between the "Core-links" model and "Cage-like" Keggin-Al₁₃ model. *Coordination Chemistry Reviews* 248:441-455.
- [28] Huang L, Tang HX, Wang DS, Wang SF, Deng ZJ (2006) Al(III) speciation distribution and transformation in high concentration PACl solutions. 18:872-879.
- [29] Wu X, Wang D, Ge X, Tang H (2008) Coagulants of silica microspheres with hydrolyzed Al(III)-significance of Al₁₃ and Al₁₃ aggregates. *Colloids and surfaces A* 330:72-79.
- [30] Klopogge JT, Don S, Geus JW, Jansen JBH (1993) The effects of concentration and hydrolysis on the oligomerization and polymerization of Al(III) as evident from the Al NMR chemical shifts and line widths. *Journal of Non-Crystalline Solids* 160:144-151.
- [31] Hsu PH, Bates TF (1964) Formation of X-ray amorphous and crystalline aluminum hydroxide. *Miner. Mag.* 33:749-768.