

# 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  $^{27}\text{Al}$  NMR analysis of those two PACl preparation procedures, the reaction rate constant ( $k$ ) values and  $\text{Al}_{13}$  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.

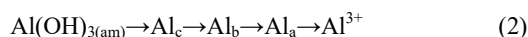
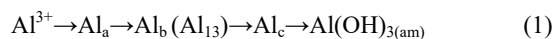
**Keywords**—Polyaluminum chloride,  $\text{Al}_{13}$ , amorphous aluminum hydroxide, Ferron test.

## 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.  $\text{Al}_{13}$  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  $\text{Al}_a$ ,  $\text{Al}_b$ , and  $\text{Al}_c$ , respectively. The previous discussed  $\text{Al}_{13}$  was identified as  $\text{Al}_b$ . 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 ( $\text{AlCl}_3$ ) solution so that  $\text{Al}^{3+}$  could react with  $\text{OH}^-$  to form high  $\text{Al}_{13}$  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  $\text{AlCl}_3$  solution, Bertsch and Parker [19], based on the kinetic theory, explained the reaction mechanism of  $\text{Al}_{13}$  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  $\text{Al}_{13}$ . In path II, the  $\text{Al}_{13}$  formed while the

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hydrolysis process was slowly occurring. Through path II<sub>a</sub>, the Al<sub>13</sub> was hydrolyzed to form an octahedral structure crystal with a singular nuclear of Al<sup>3+</sup>. Through path II<sub>b</sub>, the anion bridging reaction caused the singular nuclear to polymerize and to form the aluminum polymer of [Al<sub>13</sub>]<sub>A</sub> whose A represented the bridged anion numbers of the Al<sub>13</sub>. After bridging reaction lasting for a sufficient amount of time, the [Al<sub>13</sub>]<sub>A</sub> could group into [Al<sub>13</sub>]<sub>n</sub>. These [Al<sub>13</sub>]<sub>n</sub> 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, Al<sub>13</sub> presented as the format of [Al<sub>13</sub>]<sub>n</sub>. Through the path II<sub>c</sub>, Al<sub>13</sub> could precipitate and accumulate on [Al<sub>13</sub>]<sub>n</sub> which could be transformed into the floc of amorphous aluminum hydroxide. Finally, it also changed into the gibbsite.

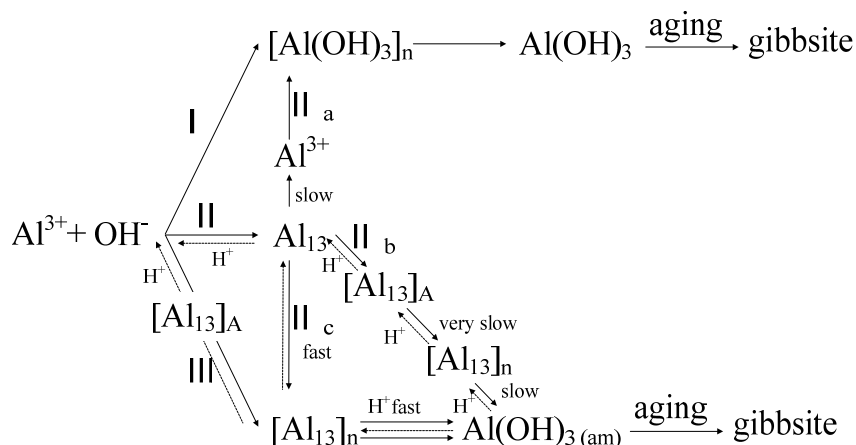


Fig. 1 A diagram of the kinetic mechanism for forming Al<sub>13</sub>

In Fig. 1, Bertsch and Parker [19] found the formation mechanism of Al<sub>13</sub> was discussed as a one-way reaction (solid line) occurring between the singular nuclear Al and hydroxide ions. However, Stol et al. [20] acidified  $5 \times 10^{-2}$  mol/L Al(NO<sub>3</sub>)<sub>3</sub> 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)<sub>3</sub>) by adding acid and found that the natures and solubility of Al precipitation products could strongly affect the formation of the Al<sub>13</sub> in an acid addition process. However, the research of Ye et al. [21] did not focus on the study of Al<sub>13</sub> 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<sub>b</sub> 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:

$$\log[\text{Al}_b]_{\text{um}} = \log[\text{Al}_b] - (k/2.303)t \quad (3)$$

where [Al<sub>b</sub>]<sub>um</sub> is the Al<sub>b</sub> concentration before reacting with the Ferron reagent. The final measured Al<sub>b</sub> concentration is shown as [Al<sub>b</sub>] [17]. The k and t represent the reaction rate constant and the reaction time. Because the Al<sub>b</sub> 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<sub>b</sub> 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, AlCl<sub>3</sub> and Al(OH)<sub>3</sub> were used as the raw materials to prepare the PACl coagulant. The AlCl<sub>3</sub> solution was conducted in alkalization and the Al(OH)<sub>3</sub> 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<sub>acid</sub> and PACl<sub>base</sub> coagulants were prepared. In addition, the structure of Al<sub>b</sub> preparing from acid and alkaline addition methods was analyzed by both Ferron test and <sup>27</sup>Al NMR so that the preparation method effect on the Al<sub>b</sub> format could be further discussed.

## II. EXPERIMENTAL METHODS

### A. Alkali Polymerization Method

The PACl<sub>base</sub> 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 AlCl<sub>3</sub> 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<sub>base</sub> solutions), they were kept at 30 °C for 3 days as the aging process.

#### B. Acidic Dissolution Method

In this study, PACl<sub>acid</sub> was prepared by slowly adding acid solutions in Al(OH)<sub>3</sub> solution to adjust various B values. At first, the 2.0 N NaOH solution was adding to various AlCl<sub>3</sub> solutions by using syringe at a droplet speed of 0.3 mL/min to adjust the pH to 7. These AlCl<sub>3</sub> solutions should be rapidly mixed with a stir so that the NaOH may quickly react with AlCl<sub>3</sub> to form amorphous Al(OH)<sub>3</sub>. 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)<sub>3</sub> in the acidic dissolution process. When the pH is at 7, the aluminum formats are almost presenting as Al(OH)<sub>3</sub> [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)<sub>3</sub> in this study, when the NaOH solution was used to adjust 0.1, 0.2, 1.0, and 2.0 M AlCl<sub>3</sub> solutions until their pH was 7, based on the alkaline addition amount, the B<sub>pH7</sub> values were calculated to be 2.8, 2.76, 2.75, and 2.72. Then, the freshly formed aluminum hydroxide (amorphous Al(OH)<sub>3</sub>) 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<sub>acid</sub> solution; B<sub>pH7</sub>: The sample's B value of the prepared Al solution at pH 7; [H<sup>+</sup>]: The added H<sup>+</sup> 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)<sub>3</sub> 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<sub>acid</sub> with various total aluminum concentrations and B values was prepared. Finally, these PACl<sub>acid</sub> 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<sub>a</sub>, Al<sub>b</sub>, and Al<sub>c</sub> 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<sup>-4</sup> - 4×10<sup>-4</sup> 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<sub>a</sub>, and 1 min to 2 h as Al<sub>b</sub>, then the concentration of Al<sub>c</sub>, was obtained from the remainder of Al<sub>T</sub>. According to (3), the reaction rate constant (k) was calculated (τ<sup>-1</sup>).

#### D. <sup>27</sup>Al NMR Analysis

The analysis steps presented by Lin et al. [25] were adapted in this study. At first, to prepare 0.1 M AlCl<sub>3</sub> solution, 12.0715 mg AlCl<sub>3</sub>·6H<sub>2</sub>O was weighted and added into 0.5 mL 40% NaOD (Aldrich, 99%) solution with small amount of D<sub>2</sub>O (Aldrich, 99%). After the solid completely dissolving, the solution was diluted with D<sub>2</sub>O to the volume of 2 mL. Then, the inner standard of 0.1 M Al(OD)<sub>4</sub><sup>-</sup> solution was prepared. The aluminum measured by <sup>27</sup>Al-NMR was 80 ppm. The inner standard of Al(OD)<sub>4</sub><sup>-</sup> 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)<sub>4</sub><sup>-</sup> solution) was inserted into this 10-mm sample tube, and the <sup>27</sup>Al-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 <sup>27</sup>Al-NMR may be used for the analysis of four compounds, mononuclear Al (Al<sub>m</sub>), dimeric Al (Al<sub>2</sub>), Al<sub>13</sub>(AlO<sub>4</sub>Al<sub>12</sub>(OH)<sub>24</sub>(H<sub>2</sub>O)<sub>12</sub>)<sup>7+</sup> and the inner standard (Al(OD)<sub>4</sub><sup>-</sup>). 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<sub>a</sub> concentration is not affected by the aluminum concentration. However, the component percentage of the Al<sub>b</sub> 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<sub>b</sub> reaches to the highest value. The percentage of Al<sub>c</sub> is proportional to the Al concentration. When the aluminum concentration is 1.0 M, the Al<sub>c</sub> 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 Al<sup>3+</sup> to polymerize the aluminum ion to form the intermediate compound of Al<sub>b</sub>. The percentage of Al<sub>b</sub> is proportional to the added alkaline dose. In contrast, the percentage of Al<sub>a</sub> 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  $Al_{13}$  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  $Al_{13}$  is limited. Hence, the percentage of  $Al_{13}$  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  $B = [OH]/[AlT]$ , 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].

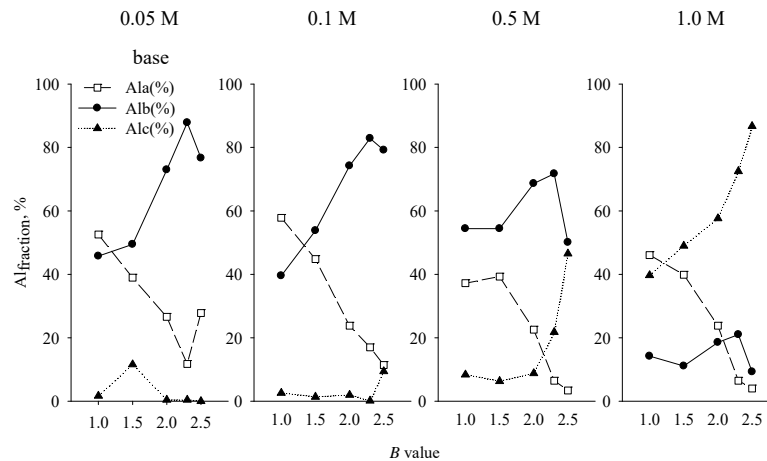


Fig. 2 The aluminum format in  $PACl_{base}$  prepared from alkalization method at different aluminum concentrations

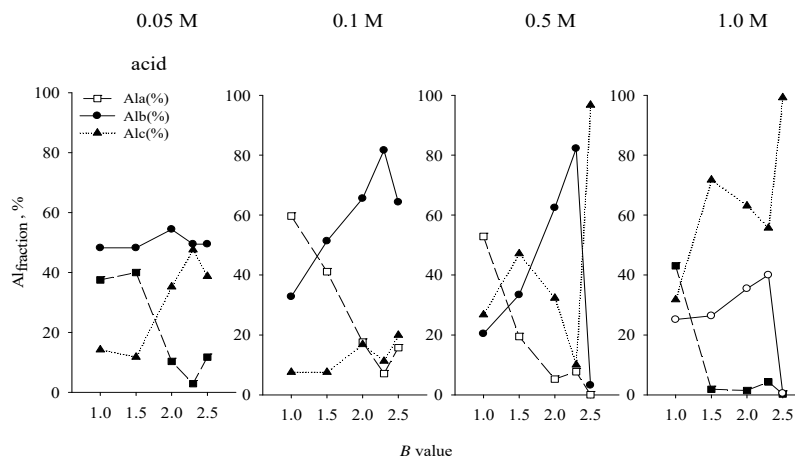


Fig. 3 The aluminum format in  $PACl_{acid}$  prepared from acidification method at different aluminum concentration

According to Fig. 3, the result of preparing  $\text{PACl}_{\text{acid}}$  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  $\text{Al}_a$  and  $\text{Al}_b$  are inversely proportional to the total aluminum concentration, but the  $\text{Al}_c$  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  $\text{Al}(\text{OH})_3$  solution, the  $[\text{Al}(\text{OH})_3]_n$  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  $[\text{Al}(\text{OH})_3]_n$  so that the  $\text{Al}_b$  percentage is relatively low and the  $\text{Al}_b$  structure is relatively complex. Hence, the acid cannot significantly dissolve the  $\text{Al}_c$  to increase the  $\text{Al}_a$  or  $\text{Al}_b$  percentage. Similarly, when the aluminum conditions are the same but B value is different, Fig. 3 shows that the  $\text{Al}_a$  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  $[\text{Al}(\text{OH})_3]_n$  into  $\text{Al}_a$  or  $\text{Al}_b$ . Hence, when the B value is low ( $B=1$ ), the primary format of the aluminum is  $\text{Al}_a$ . The  $\text{Al}_b$  is increased with the B value is increased. However, the percentage of  $\text{Al}_b$  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  $[\text{Al}(\text{OH})_3]_n$ . When the aluminum at high level (0.5 M and 1 M), the  $\text{Al}_b$  can almost not be in  $\text{PACl}_{\text{acid}}$ . The main reason is that the high Al concentration may form a larger polymer of  $[\text{Al}(\text{OH})_3]_n$  than the polymer formed in the low Al concentration solution. Hence, it is not easy to dissolve the polymer into  $\text{Al}_a$  or  $\text{Al}_b$ .

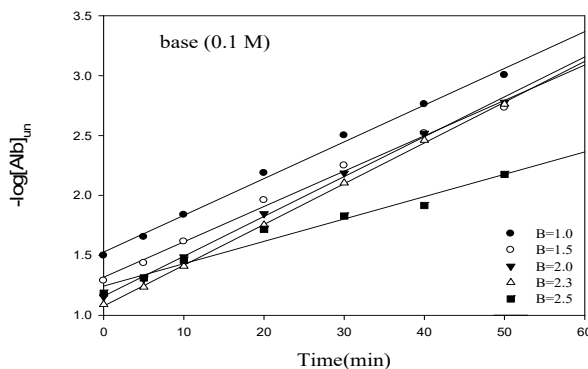


Fig. 4 The reaction kinetic data of the Ferron test to prepare the  $\text{PACl}_{\text{base}}$  by using the alkali polymerization method

#### B. The Reaction Rate Constant $k$ of Ferron Test

According to the above discussed results, the aluminum formats in both  $\text{PACl}_{\text{acid}}$  and  $\text{PACl}_{\text{base}}$  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  $[\text{Al}_b]_{\text{un}}$  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  $\text{Al}_b$  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.

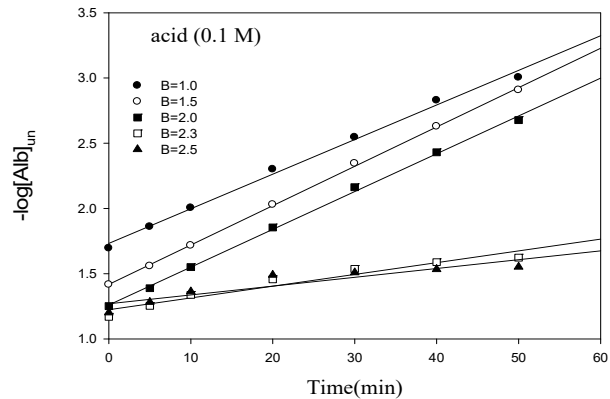


Fig. 5 The reaction kinetic data obtained from preparing the  $\text{PACl}_{\text{acid}}$  by using the acidic dissolution method

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

	B	pH	$\text{Al}_T$ (M)	$\text{Al}_a$ (%)	$\text{Al}_b$ (%)	$\text{Al}_c$ (%)	$k$ ( $\text{r}^{-1}$ )	$R^2$
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  $\text{Al}_b$  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  $\text{Al}_b$ , 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  $\text{Al}_b$  is relatively small (the primary aluminum species is  $\text{Al}_{13}$ ). Low  $k$  value indicates that the average molecular size of the aluminum polymer in  $\text{Al}_b$  is large. Therefore, the reaction of  $\text{Al}_b$  and Ferron reagent is slow. According to the past documents, when the alkalization method is used for preparing  $\text{PACl}_{\text{base}}$  at  $B$  value  $< 2.5$ , the  $k$  value does not obviously change (the primary

species is  $\text{Al}_{13}$  in  $\text{Al}_b$ ) because the  $\text{Al}_b$  percentage in  $\text{PACl}_{\text{base}}$  is very close to the percentage of Keggin- $\text{Al}_{13}$  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- $\text{Al}_{13}$  in  $\text{PACl}_{\text{base}}$ , the Keggin- $\text{Al}_{13}$  percentage is less than the percentage determined from the Ferron test. The above results suggest that, at  $B = 2.5$  condition, the polymeric aluminum ( $\text{Al}_b$ ) is not only containing the  $\text{Al}_{13}$  but also containing some polymer whose molecular size is larger than the size of the  $\text{Al}_{13}$  [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  $\text{Al}_b$  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  $\text{Al}_b$  should be the high molecular size polymer whose molecular size is greater than the size of  $\text{Al}_{13}$  because the above cases show that the  $\text{Al}_b$  percentages are similar but the  $k$  values are very different.

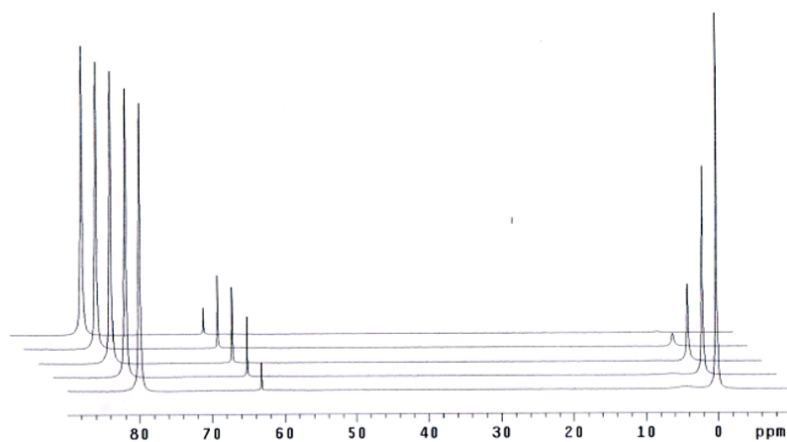


Fig. 6 The  $^{27}\text{Al}$  NMR analysis for the  $\text{PACl}_{\text{base}}$  prepared from alkali polymerization method

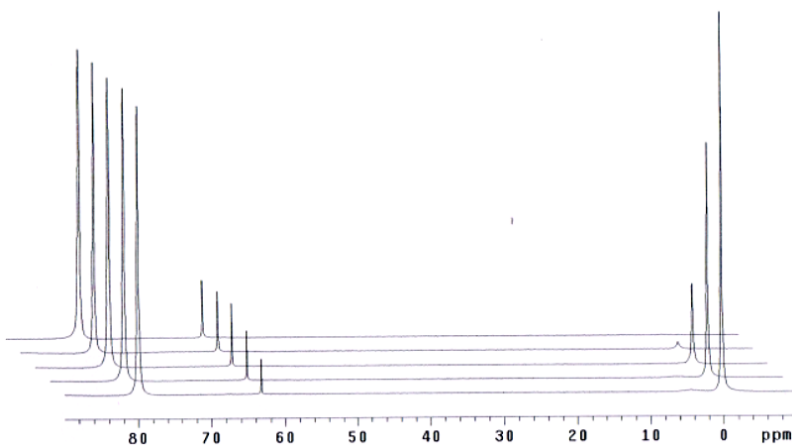


Fig. 7 The  $^{27}\text{Al}$  NMR analysis for the  $\text{PACl}_{\text{acid}}$  prepared from acidic dissolution method

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

According to the experimental result of the Ferron test, when the  $\text{Al}$  concentration is 0.1 M, the aluminum formats in  $\text{PACl}$  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  $\text{Al}_b$  formation mechanisms are not the same. For example,

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

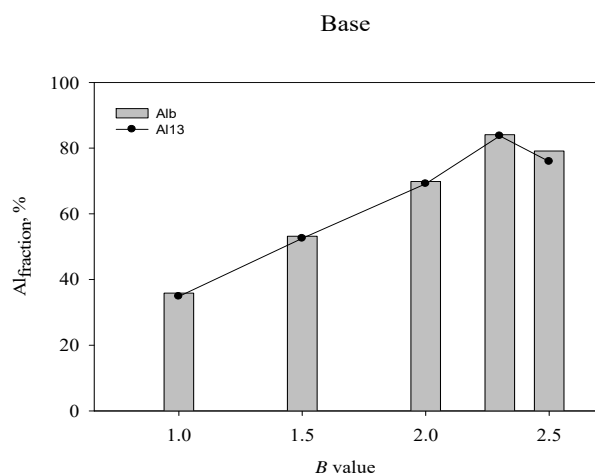


Fig. 8 The aluminum format patterns of  $Al_{13}$  and  $Al_b$  prepared from alkaline addition methods

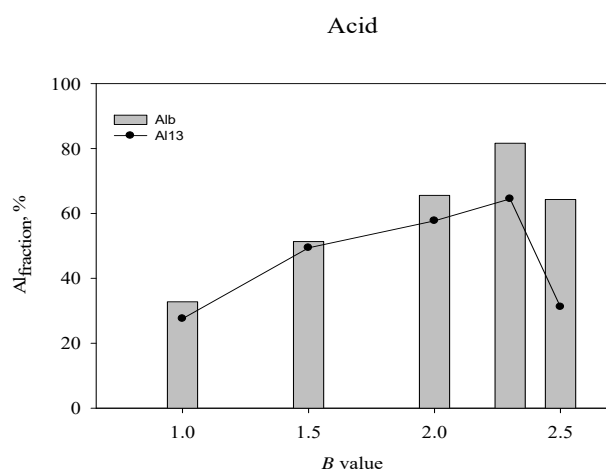


Fig. 9 The aluminum format patterns of  $Al_{13}$  and  $Al_b$  prepared from acid addition methods

According to Fig. 8, the percentages of both  $Al_b$  and  $Al_{13}$  in  $PACl_{base}$  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  $PACl_{base}$  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  $PACl_{acid}$  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  $PACl_{acid}$  is different from the percentage of the  $Al_{13}$  in  $PACl_{base}$ . Similarly, according to the result of the Ferron test kinetic mechanism, when the B value is high, the  $PACl_{acid}$  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 PACl 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  $PACl_{acid}$  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 $PACl_{acid}$ 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.

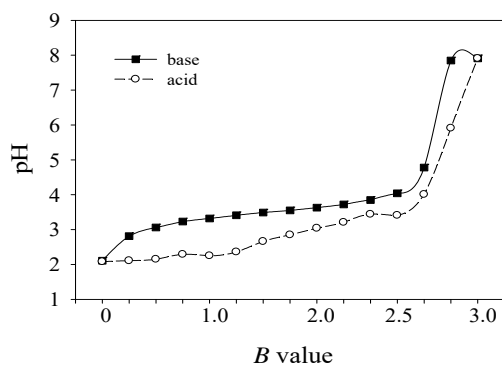


Fig. 10 The titration curve of acidic and alkali titration

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.

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