Effect of Hydroxyl Aluminum Ratio on Preparation of PAC from Aluminum Ash

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Abstract: The oligomeric polymeric aluminum chloride prepared from secondary aluminum ash was used as raw material, and hydrolytic polymerization was carried out with different ratios of calcium oxide, and the structure and phase transformation process of the polymeric aluminum chloride produced by hydrolytic polymerization were characterized by XRD and infrared spectroscopy. The results showed that at the hydroxyl-aluminum ratio of 0.25, the phases of hydrolysis polymerization products were $Al(OH)_3$, AlOCl, $AlCl_3$-$6H_2O$, $Ca_3Al_2(OH)_{12}$; at the hydroxyl-aluminum ratio of 0.5, the main phases were $Al(OH)_3$, AlO(OH), $AlCl_3$-$6H_2O$, $Ca_3Al(OH)_7$-$3H_2O$, $Ca_3Al_2(O_4H_4)$, the main phase is $AlCl_3$-$6H_2O$, $((Al_{13}(OH)_{24}(H_2O)_{24}))Cl_{15}(H_2O)_{13}$ when the hydroxyl-aluminum ratio is 0.75, and the polymeric $((Al_{13}(OH)_{24}(H_2O)_{24}))Cl_{15}(H_2O)_{13}$ molecules account for 70.4%, When the hydroxy-aluminum ratio is 1, the main phase is indeterminate; A large amount of OH- appears in the prepared high polymer polyaluminum chloride molecule, and the peak height of the absorption peak of Al-OH-Al can also indicate that there are a large number of Al-OH-Al bonds in the sample, which proves that the polyaluminum chloride contains a large number of Al-OH-Al bonds. There are $((Al_{13}(OH)_{24}(H_2O)_{24}))Cl_{15}(H_2O)_{13}$ molecules.

1 INTRODUCTION

By the end of 2021, China produced 60.9 million tons of aluminum, depending on the raw material, each ton of aluminum produces raw material feeding amount ranging from 0.3% to 10% aluminum ash, and the disposal fee of 2000-4000 RMB/ton is required to be paid for the disposal of aluminum ash. The new environmental protection law in April 2014 requires that enterprises must dispose of hazardous waste generated from electrolytic aluminum according to the hazardous waste disposal requirements. China included aluminum ash in the National Hazardous Waste List in 2016. Nitrides and carbides in aluminum ash hydrolyze when exposed to moisture, emitting strong irritating gases, and fluoride pollutes soil and groundwater resources and causes fluorosis to human and animal bones.

China relies on imported bauxite resources, while the electrolytic aluminum industry consumes more than 100 million tons of bauxite resources annually. Secondary aluminum ash is a mixture of metallic aluminum, alumina, aluminum nitride and salt solvent with 50%-80% aluminum content, which is a high-quality secondary aluminum resource, so it is significant to realize the effective recycling of secondary resources of aluminum ash.

Polymeric aluminum chloride is a kind of water-soluble inorganic polymer with a wide range of applications. The preparation of polymeric aluminum chloride using aluminides in aluminum ash leached from hydrochloric acid is an effective way to realize the resource utilization of secondary aluminum ash from hazardous waste. Kefeng Du et al. experimentally studied the preparation of polymerized aluminum chloride from aluminum ash residue and waste hydrochloric acid. The degree of polymerization of aluminum chloride affects its physicochemical properties, application areas and use effects, and according to the degree of polymerization, aluminum chloride is divided into monomer (Al^{3+}, $Al(OH)^{2+}$), dimer ($Al_2(OH)_2{}^{4+}$), trimer ($Al_3(OH)_3(H_2O)_9{}^{6+}$), and hyperpolymer ($Al_{13}$, Al_{30}), etc. Al_{13} is considered the best among PACs because of its large charge and molecular weight, it is easy to bond and bridge in water and form flocs, thus Al_{13} is considered the best component in PAC, and the more Al_{13} content proves the higher quality of its PAC. Yuan Huizhou [11] et al. prepared polyaluminum solutions with different degrees of alkalinity by

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controlling the amount of alkali addition to explore the effect of pH on polyaluminum morphology. Lv Jianxiao et al. explored the effect of total aluminum concentration on the distribution of Al morphology in polymerized aluminum chloride, and high aluminum concentration is more likely to form products with high polymerization, but too high aluminum concentration will produce aluminum hydroxide precipitation, which affects the coalescence effect. Liu, Liang et al. explored the effects of total aluminum concentration, alkalinity, reaction temperature and alkalinity rate on the content of the generated Al_{13}.Yaneth Cardona et al. studied the formation pattern of Al_{13} molecules and Al_{30} molecules。

Regarding the structure and phase transformation process of polymeric aluminum chloride generated by the hydrolysis and polymerization of calcium oxide and oligomeric PAC, there are few relevant studies in China. This paper adopts the method of CaO regulation of oligomeric PAC hydroxyaluminum ratio (-OH to Al ratio) to study the structure and phase transition law of polymerized aluminum chloride generated by hydrolysis polymerization. It provides technical support to explore the comprehensive utilization of high value of high purity aluminum ash residue.

2 EXPERIMENTS AND MATERIALS

Xinjiang Zhonghe Co., Ltd. with particle size less than 425 μm, deionized water, 35% hydrochloric acid (analytically pure) and CaO (analytically pure) were used as raw materials, and the aluminum ash was washed and dried in acid solution. Take 150 g of the dried acid solution powder, add 875 ml of deionized water to a constant temperature water bath at 80℃, and under the effect of mechanical stirring, add CaO according to the hydroxy-aluminum ratio of 0, 0.25, 0.5, 0.75, 1.0, respectively, and wait for the reaction for 4h, then cool to room temperature and leave for 24h, followed by drying the polymeric aluminum chloride solution using an electric thermostatic drying oven at 75℃, and wait for the appearance of a large number of The solid-liquid separation was carried out when a large number of crystals appeared; the physical phase changes and molecular structure of the prepared polymeric aluminum chloride were analyzed by X-ray diffraction (XRD) and infrared spectroscopy.

3 EXPERIMENTAL RESULTS AND ANALYSIS

3.1 Preparation of Low Hydroxyl Ratio Oligomeric Aluminum Chloride by Acid Leaching Method

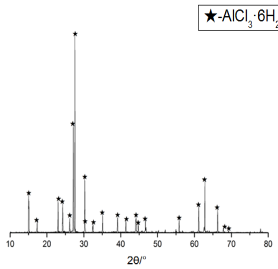

Figure 1: XRD analysis of polymeric aluminum chloride prepared by acid leaching method

As shown in Figure 1, the XRD pattern of polymeric aluminum chloride prepared by acid leaching method. From Fig. 1, it can be seen that the material phase obtained after acid dissolution of high purity aluminum ash is relatively single with less impurities. The aluminum ash can be obtained as relatively pure $AlCl_3$-$6H_2O$ after acid washing. the polymerization degree of $AlCl_3$-$6H_2O$ prepared directly by acid leaching method is low, and the water purification effect of this low hydroxyl ratio low polymerization degree aluminum chloride is poor. High polymerization contains a large number of hydroxyl groups, and the hydroxyl groups, because they can form hydrogen bonds in water, prompt the polymerization of aluminum chloride molecules and adsorption of impurities in water, so improving the polymerization degree of polymerized aluminum chloride can improve the water purification effect of polymerized aluminum chloride.

In order to improve the polymerization degree of polymerized aluminum chloride and strengthen the water purification effect, the polymerized aluminum chloride prepared directly by acid leaching method is adjusted by adding CaO.

3.2 Analysis of the Effect of Different Hydroxy-Aluminum Ratio Adjustment on the Physical Phase of PAC

From Fig. 2(a), the XRD spectrum of hydroxyaluminum ratio of 0 shows that there is no significant change in the structure of the PAC prepared without the addition of CaO hydrolysis polymerization product (PAC) and acid leaching, indicating that the aluminum chloride polymerization reaction is not obvious. From Fig. 2(b), the XRD spectrum of hydroxyaluminum ratio of 0.25 shows that the composition of the physical phase is $Al(OH)_3$, AlOCl, $AlCl_3$-$6H_2O$, $Ca_3Al_2(OH)_{12}$, and the appearance of $Ca_3Al_2(OH)_{12}$ indicates that the PAC polymerization increases when the hydroxyaluminum ratio is 0.25. From Fig. 2(c), which shows the XRD spectrum of the hydroxyaluminum ratio of 0.5, it can be seen that the composition of the phases are $Al(OH)_3$, AlO(OH), $AlCl_3$-$6H_2O$, $Ca_3Al(OH)_7$-$3H_2O$, $Ca_3Al_2(O_4H_4)$, from which it can be seen that the diffraction peak of $AlCl_3$-$6H_2O$ is weakened and the appearance of the dimeric phase with higher polymerization $Ca_3Al_2(O_4H_4)$, indicating that the degree of PAC polymerization continued to increase when the hydroxyl-aluminum ratio was 0.5, but the pH remained low due to the addition of less CaO, less $Ca(OH)_2$ was generated, and thus no polymers appeared in the physical phase. Fig. 2(d) shows the spectrum of hydroxyl-aluminum ratio of 0.75, and the XRD results show that the composition of the physical phase is $AlCl_3$-$6H_2O$, $((Al_{13}(OH)_{24}(H_2O)_{24}))Cl_{15}(H_2O)_{13}$, and it can be seen from the figure that the polymeric phase $((Al_{13}(OH)_{24}(H_2O)_{24}))Cl_{15}(H_2O)_{13}$ appears in the physical phase, and the PAC polymerization further increased. Fig. 2(e) shows the XRD spectrum of hydroxyaluminum ratio of 1. The XRD results indicate an indefinite phase. In summary, the polymerization degree of PAC increased with the increase of the hydroxyaluminum ratio from 0 to 0.75, and the indefinite phase was formed when the hydroxyaluminum ratio was 1. This indicates that the increase of CaO is too large, which will make the polymeric phase $((Al_{13}(OH)_{24}(H_2O)_{24}))Cl_{15}(H_2O)_{13}$ hydrolyze and polymerize to form the indefinite aluminum phase, but the phase will directly polymerize to form the indefinite phase in the later The reaction will directly polymerize to form indefinite $Al(OH)_3$, which will affect the water purification effect of PAC.

Due to the high degree of polymerization of the generated PAC in Fig. 2(d), cell refinement and quantitative analysis were performed using JADE software, and the results showed that $((Al_{13}(OH)_{24}(H_2O)_{24}))Cl_{15}(H_2O)_{13}$ in the prepared polymeric aluminum chloride accounted for 70.4% of the total amount and the structure was highly polymeric aluminum chloride cluster structure, and the cell parameters of the generated Al13 molecules were a = 13.9859, b = 23.4673, c = 22.3724, $\alpha = 90°$, $\beta = 91.05°$, $\gamma = 90°$, and the molecular radius is 1.08 nm.

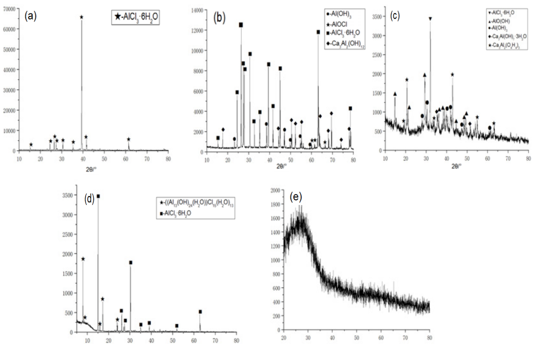

Figure 2: Analysis of the influence of CaO content on phase.

3.3 High Polymeric Aluminum Chloride Molecular Infrared Spectrum Analysis

Fig. 3 shows the results of infrared spectrum analysis of the prepared PAC when the hydroxyl-aluminum ratio is 0.75. From Fig. 3, it can be seen that the prepared PAC has a strong and wide absorption band at 3058.427 cm^{-1}, and the absorption band is located at 3600-2800 cm^{-1}, where the absorption peak is generated by the stretching vibration of the -OH group in the PAC connected with the aluminum ion and the -OH group in the adsorbed water molecule, indicating the presence of a large number of -OH groups in polymeric aluminum chloride. A sharp peak at 1632.877 cm^{-1}, which is an absorption peak generated by the bending vibration of H-O-H of bound water in the Al_{13} molecule, indicating that the prepared polymeric aluminum chloride contains a large amount of bound water. The absorption peaks appearing at 1138.840 cm^{-1}, 837.896 cm^{-1} are in-plane bending vibration absorption peaks produced by Al-OH-Al, the intensity of which can indicate the number of bonds, and the reaction aluminum chloride polymerizes between Al atoms during hydrolysis by Al-OH-Al bond bridging to form polymeric aluminum chloride. The two sharper absorption peaks at 596.463 cm^{-1} and 538.643 cm^{-1} are the bending vibration peaks of Al-OH, and there are components of the polymerization state in the reaction PAC; the peak at 2413.293 cm^{-1} is the peak caused by atmospheric CO_2.

From the infrared spectrogram, it can be seen that a large number of -OH groups appear in the PAC prepared with a hydroxyl aluminum ratio of 0.75, and the peak height of the absorption peak of Al-OH-Al can also indicate the presence of a large number of Al-OH-Al bonds in the prepared PAC, which can indicate that $((Al_{13}(OH)_{24}(H_2O)_{24}))Cl_{15}(H_2O)_{13}$ is indeed present and the content very high.

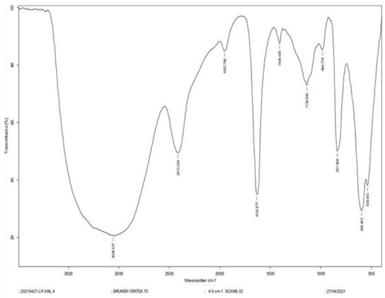

Figure 3: Infrared spectrum analysis of polyaluminum chloride molecule with high ratio

4 DISCUSSION

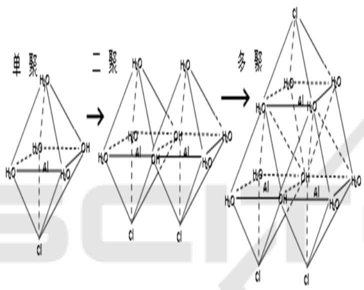

Figure 4: The phase transformation law of polyaluminum chloride molecules

CaO adjusts the PAC hydroxy-aluminum ratio, and its phase change pattern is shown in Fig. 4. Aluminum chloride molecules ionize Al^{3+} in water, Al^{3+} will spontaneously carry out hydrolysis reaction with H_2O molecules to form octahedral $Al(OH)_2^+$ with Al^{3+} as the core, octahedral Al(OH)2+ will hydrolyze with OH- in solution again to $Al(OH)_4^-$, $Al(OH)_4^-$ is the precursor for the formation of polymer molecules.

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} \quad (1)$$

$$Al(OH)^{2+} + OH^- \rightarrow Al(OH)_4{}^- \quad (2)$$

When CaO is added to the PAC solution, CaO will first react with H_2O to form $Ca(OH)_2$. The presence of $Ca(OH)_2$ will cause the pH of the solution to rise, which will further accelerate the hydrolysis reaction of Al^{3+} and increase the amount of octahedral $Al(OH)_2^+$, and the octahedral $Al(OH)_2^+$ with Al^{3+} as the core will polymerize through the Al-OH-Al bond to form dimer $Al_2(OH)_2^{4+}$, but due to the strong acidity of the solution, the amount of OH- is low, forming monomeric $Al(OH)_4^-$, $Al(OH)_2$+ and dimeric $Al_2(OH)_2^{4+}$ in smaller amounts, preventing the formation of polymeric molecules.

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (3)$$

$$Al(OH)^{2+} + H_2O \rightarrow Al_2(OH)^{2+} \quad (4)$$

As CaO increases and the pH continues to rise, forced hydrolysis of Al^{3+} occurs, resulting in an increase in $Al(OH)_4^-$ molecules. $Al(OH)_4^-$ will use ion bridging to aggregate octahedral $Al(OH)_2^+$ monomers and dimeric $Al_2(OH)_2^{4+}$ to form Al_{13} molecules with $Al(OH)_4^-$ as the core, and Al_{13} can decompose to Al^{3+}, again or form $[Al_{13}]n$ by physical aggregation and ion bridging.

$$Al(OH)_4{}^- + Al_2(OH)^{2+} + Al(OH)^{2+} + OH^- \rightarrow Al_{13}(OH)_{24}{}^{15+} \quad (5)$$

With further increase of CaO, the amount of $Ca(OH)_2$ formed by reaction with H_2O is also increasing, and the pH of the sample is increasing, the content of Al_{13} will also increase, and subsequently, Al_{13} will be transformed into $[Al_{13}]n$, and then Al_{13} will be bonded with the transformed $[Al_{13}]n$ under the effect of ion bridging. The strong electrostatic adsorption ability of $[Al_{13}]n$ allows a large amount of Al_{13} to be deposited on the $[Al_{13}]n$ molecule, forming a gel-like indefinite solid phase. When an excessive amount of CaO is added, these indefinite solid phases are transformed into amorphous $Al(OH)_3$, which makes the purification effect of PAC poor.

$$Al_{13}(OH)_{24}{}^{15+} + OH^- + H_2O \rightarrow Al(OH)_3 (6)$$

5 CONCLUSION

(1) The degree of polymerization of aluminum chloride can be adjusted by adding a certain amount of CaO, but the addition of excessive CaO will form an indefinite form of $Al(OH)_3$.

(2) When the hydroxyl-aluminum ratio is 0.25, the phases of hydrolysis polymerization products are $Al(OH)_3$, AlOCl, $AlCl_3$-$6H_2O$, $Ca_3Al_2(OH)_{12}$; when the hydroxyl-aluminum ratio is 0.5, the main phases are $Al(OH_3$, AlO(OH), $AlCl_3$-$6H_2O$, $Ca_3Al(OH)_7$-$3H_2O$, $Ca_3Al_2(O_4H_4)$. At the hydroxyl aluminum ratio of 0.75, the main phases were $AlCl_3$-$6H_2O$, $((Al_{13}(OH)_{24}(H_2O)_{24}))Cl_{15}(H_2O)_{13}$, and the polymeric $((Al_{13}(OH)_{24}(H_2O)_{24}))Cl_{15}(H_2O)_{13}$ molecules accounted for 70.4%, and at the hydroxyl aluminum ratio of 1, the main phases were indefinite phases

(3) The presence of a large amount of OH- in the prepared polymerized aluminum chloride molecules in the polymerized state and the peak height of the absorption peak of Al-OH-Al can also indicate the presence of a large amount of Al-OH-Al bonds in the

sample, which proves the presence of $((Al_{13}(OH)_{24}(H_2O)_{24}))Cl_{15}(H_2O)_{13}$ molecules in the polymerized aluminum chloride.

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