Factors Affecting Aluminum Dissolve from Acidified Water Purification Sludge

Wen Po Cheng, Chi Hua Fu, Ping Hung Chen, Ruey Fang Yu

***Abstract*—**Recovering resources from water purification sludge (WPS) have been gradually stipulated in environmental protection laws and regulations in many nations. Hence, reusing the WPS is becoming an important topic, and recovering alum from WPS is one of the many practical alternatives. Most previous research efforts have been conducted on studying the amphoteric characteristic of aluminum hydroxide for investigating the optimum pH range to dissolve the Al(III) species from WPS, but it has been lack of reaction kinetics or mechanisms related discussion. Therefore, in this investigation, water purification sludge (WPS) solution was broken by ultrasound to make particle size of reactants smaller, specific surface area larger. According to the reaction kinetics, these phenomena let the dissolved aluminum salt quantity increased and the reaction rate go faster.

***Keywords*—**Aluminum, Acidification, Sludge, Recovery.

I. Introduction

In drinking water and wastewater treatment processes, a coagulant, such as aluminum sulfate or poly aluminum chloride may react with colloids/particles in raw water forming settled flocs. After settling the flocs, the resultant chemical sludge is dewatering to produce a sludge cake. In Taiwan, around 120,000 tons of water purification sludge (WPS) is generated from water treatment plants annually, and about 30% of this sludge is alum salt [1], [2]. Alum sludge is composed of the aluminum coagulant and mineral clay in raw water. Water purification sludge contains less heavy metal and organic contamination than wastewater treatment sludge, because the raw water that is used to purify water is relatively clean and the coagulant that is used for treatment is of relatively high quality. Therefore, it is still an issue to choose a disposal method for the water purification sludge (WPS) that would be reasonable in terms of technology and economy. There are laboratory and full scale attempts at using WPS as a component in the manufacture of concrete; as geotechnical works materials; as a potential for use in agriculture; as a primary source of aluminum and iron based coagulants through several recovery process; and for phosphorus reduction during wastewater treatment [3]-[6]. Therefore, recovering aluminum salt from such the large amount of produced water purification sludge is worthwhile.

According to past research, the main approaches for recovering alum from WPS include acidification, basification, membrane separation, and ion exchange [7]-[14]. Since aluminum hydroxide, $Al(OH)_3$, is an amphoteric compound, it can be dissolved in acid or alkaline solutions. It also reacts with acid to form soluble aluminum ions, and forms soluble $Al(OH)_4^-$ ions in alkali. According to [15], if the pH of alum sludge is reduced by adding H_2SO_4 to between 1 and 3, then an aluminum recovery rate of approximately 70 to 90% can be achieved. If NaOH or $Ca(OH)_2$ is used to extract and recover the aluminum, then the aluminum recovery rate is highest at a pH between 11.2 and 11.8. These acidification or basification methods are relatively simple. Therefore, they are commonly used for aluminum recovery and in studies of the regeneration of coagulant. For example, the pH that has recently been found to maximize aluminum dissolution efficiency (in terms of moles of aluminum dissolved per mole of H^+ or OH^- ion) in Taiwan is 2 and 12 in acidification and basification treatments, respectively [16], [17]. However, in the basification process, the humic acid in the alum sludge may easily dissolve in a strong alkaline solution, inhibiting the recovery of the aluminum. Accordingly, the acidification process is generally more convenient and more efficient than the basification process for recovering aluminum from sludge. Additionally, the size of the sludge particles and the dissolution temperature are important factors that influence the dissolution of metal ions. When the sludge particles are small, the ability to form complex bonds between the sludge particles and the metal ions is poor. Such weak bonds may promote the dissolution of the sludge. Therefore, the metal is easily dissolved (pH<2.5). Additionally, a higher dissolution temperature provides sufficient energy to break the amorphous chemical bonds of the sludge and increase the metal dissolution rate [18], [19]. Accordingly, during the acidification process, increasing the solution temperature may increase the quantity of aluminum dissolved.

II. Experimental

A. Sludge Preparation

Sludge was obtained from the sludge drying bed of Ming-Der water treatment plant at Miao-Li, Taiwan. After the sludge was dried at 60°C and well mixed, a sludge sample was prepared. This water treatment plant uses traditional coagulation and flocculation processes to treat roughly 35,000 tons of water/day. Polyaluminum chloride (basicity, 47.6%; Al_2O_3, 10.57%; Chung Hwa Chemical Industrial Works, Ltd., Taiwan) is added to the rapid-mixing tank. After mixing, the treated water flows into three flocculation tanks that are connected in series. Flocculation mixing was *via* a mechanical paddle. Following flocculation, the

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water is treated consecutively by sedimentation, filtration, and chlorination to meet drinking water standards. The sludge samples were dried at 105°C. An Energy Dispersive Spectrometer (EDS) (Fig. 1) was used to analyze the elemental composition of the sludge. Analysis showed that Si, Al, and Fe were the dominant elements. The sludge sample was also analyzed by X-ray diffraction (XRD) to identify its crystal structure. The sludge is primarily composed of SiO_2 and Al_2O_3 (Fig. 2). Additionally, the sludge may have also contained some Fe_2O_3, $KAl_3Si_3O_{10}(OH)_2$ (Muscovite), and $(Ca,Na)(Si,Al)_4O_8$ (Labradorite). The EDS and XRD results indicate that aluminum is a major metal in the sludge sample. The total amount of aluminum that can leach out in the acidification process was determined using the standard method by Taiwan's Environmental Protection Administration (NIEA R353.00C; dissolved in nitric acid (1:1)). The quantity of aluminum was 40.03 mg Al/1 g sludge.

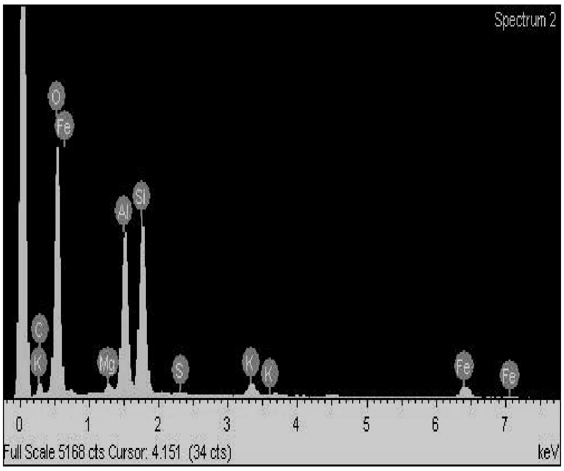

Fig. 1 Element analysis by Energy Dispersive Spectroscopy (EDS)

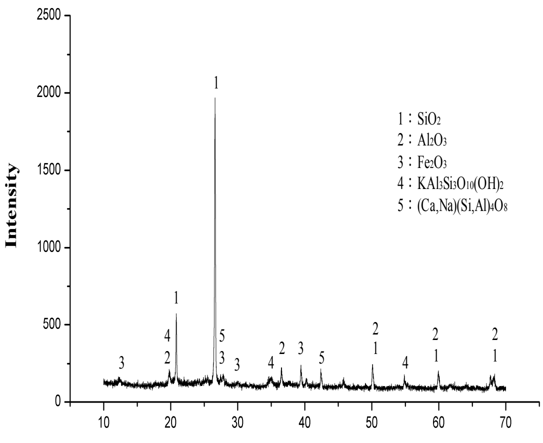

Fig. 2 Crystal structure analysis of the sludge by X-ray diffraction (XRD)

B. Determination of Acid Dosage

Thirty grams of the sludge sample were added to a beaker with 1000 mL distilled water to prepare 3% (W/W) sludge solution. Two of these sludge solutions were separately titrated with HCl and H_2SO_4. In each titration process, 30 mL of acid was added to the test sludge solution. The pH and added volumes of acids (HCl and H_2SO_4) were recorded. If the pH of sludge solution after mixing exceeded two, then another 30 mL acid was added to the solution with mixing until the pH dropped below two, and the total acid dosages were again determined.

C. Sludge Acidification Experiment

Dried sludge was added to a beaker to prepare 3% (W/W) sludge solution. Then, to two of these sludge solutions was separately added the previously determined volume of H_2SO_4. One solution was placement and the other solution mixing with a magnetic stirrer. The effects of acid and reaction time on aluminum recovery were studied. The same 3% (W/W) solution was also treated with ultrasonic waves for one hour. The sample of these ultrasonically treated solutions were added equal volumes of H_2SO_4. The solutions with mixing were tested at 25°C, respectively. This experiment demonstrated that the sludge size and reaction temperature influences the dissolution of aluminum. During the reaction, a series of solution samples were filtrated and analyzed by atomic absorption spectrometry (Z-5000 Hitachi Co. Japan) to obtain aluminum concentration.

III. Results and Discussion

A. Determination of Acid Dosage

In this investigation, two acids, H_2SO_4 and HCl, were used to recover aluminum ions from sludge, and to regenerate aluminum sulfate or aluminum chloride solutions. At 25°C, the different dosages H_2SO_4 were separately added to each sample of sludge solution.

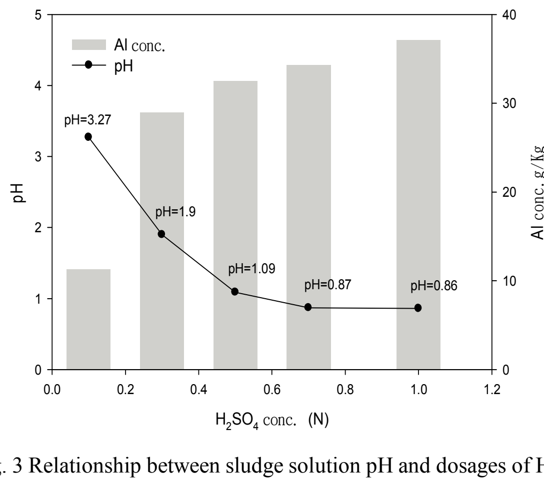

Fig. 3 Relationship between sludge solution pH and dosages of H_2SO_4

The pH was recorded as the acid was added with mixing. No more acid was added when the pH stabilized at less than two. According to Fig. 3, in the initial stage of the addition of acid, the acid reacted with the alkaline carbonate, rapidly reducing the pH. When pH the dropped below three, then the acid initiated the dissolution mechanisms reacting with aluminum and other metal hydroxide compounds in the sludge. In this stage, the pH dropped slowly. When the pH was close to two, the acid dosage was close to the optimal dosage at which aluminum dissolution efficiency was maximal. The added acid was consumed as it destroyed the amorphous chemical bonds and released the alum ions. Therefore, even increasing the acid dosage did not significantly reduce the pH values. Since the drop in pH is strongly affected by the contents of the sludge, including the percentages of $CaCO_3$, metal hydroxide compounds and aluminum, determining acid dosages by simple calculation based on chemical reaction equations is difficult. When 0.3N H_2SO_4 were added, the pHs of the acidified sludge solutions dropped to close to but less than two. Therefore, the solution pH was determined to be about 2.

B. Acid Species Affects Quantity of Dissolved Aluminum

When the reaction temperature was 25°C, 30 g sludge was added to 1 L distilled water. To two of the test sludge solutions were separately added HCl and H_2SO_4 to control the solution pH at 2. Then the test solutions were then mixed suing magnetic stirrers for 120 minutes. During the mixing, water samples were extracted every 30 minutes for aluminum concentration analysis. According to the data in Fig. 4, for a particular acid dosage, the dissolved aluminum concentration in the solution that was acidified using H_2SO_4 clearly exceeded that in the solution that was acidified using HCl. When the solution was mixed for ten minutes, the aluminum concentration in the H_2SO_4-acidified solution was 206.4 mg/L. This concentration was 68.7% higher than that the aluminum concentration found in the HCl-acidified solution, which was 122.38 mg/L.

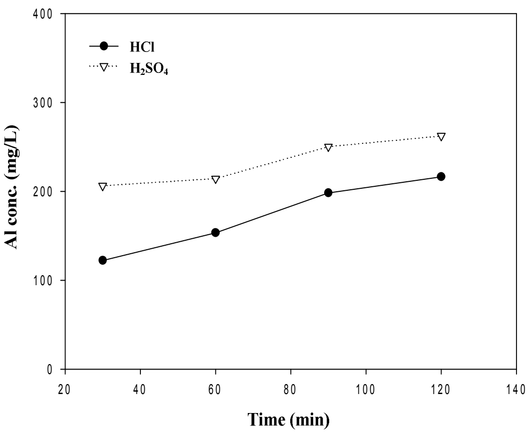

Fig. 4 Relationship between dissolved aluminum concentration and reaction time

When the experiment was terminated at 120 minutes, the aluminum concentration in H_2SO_4-acidified solution was 262.4 mg/L, which was 21.3% higher than the concentration of 216.35 mg/L in the HCl-acidified solution. These results indicate that adding H_2SO_4 is more efficient in dissolving aluminum than adding HCl. The main reason is that the chemical affinity between SO_4^{2-} and the aluminum ion exceeds that between Cl^- and the aluminum ion, and aluminum sulfate complexes are therefore significantly stronger than aluminum chloride complexes [20], [21]. Accordingly, H_2SO_4 relatively easily dissolves the aluminum ions into the solution. Hence, H_2SO_4 is traditionally used to recover aluminum from sludge.

C. Effect of Size of Sludge Particles on Aluminum Dissolution

Three sets of test sludge solutions, formed by adding 30 g sludge to 1 L distilled water, were prepared. These test solutions were treated with placement, stirring and 166 W ultrasonic for two hour. H_2SO_4 were separately added to control the solution pH at 2. Then, the solutions of stirring and 166 W ultrasonic pretreatment were mixed using stirrers for 120 minutes at mixing rate 80 rpm. According to Fig. 5, the aluminum concentrations in the ultrasonically treated H_2SO_4-acidified exceed those in the untreated solutions. Additionally the aluminum concentrations in stirring H_2SO_4-acidified solutions exceeded those in the placement-acidified solutions. The aluminum concentration rose rapidly to 345 mg/L for 40 minutes after H_2SO_4 was added to the solution (with ultrasonic pretreatment). The dissolution rate increase with increasing reaction time. These results indicate that the dissolution rate can be increased by ultrasonic pretreatment of the acidified solution. The results also indicate that after H_2SO_4 was added for 120 minutes, the aluminum concentration in the ultrasonically treated solution was 514 mg/L, which was 1.88 times the concentration (274 mg/L) in the untreated solution. Additionally, if the solution only placement for 120 minutes, the aluminum concentrations in the ultrasonically treated solutions was only 194 mg/L, which was 0.38 times the concentration in the solution of ultrasonic pretreatment. These results indicate that both ultrasonic pretreatment and H_2SO_4 acidification can increase the quantity of dissolved aluminum in the test solutions.

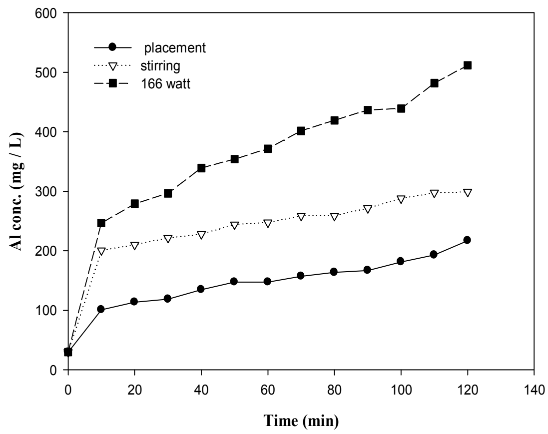

Fig. 5 Effect of ultrasonic pre-treatment on concentrations of dissolved aluminum

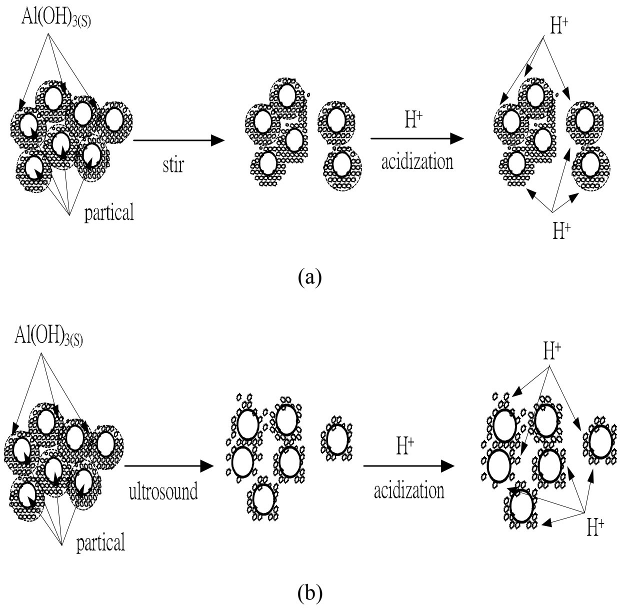

Fig. 6 Alum sludge acidification. (a) Effect of stir mixing on acidified sludge (b) Effect of stir mixing on acidified sludge

During the acidification process, the H^+ ions can react only at the surface of $Al(OH)_3$ and cannot acidify the interior the $Al(OH)_3$ particles in the sludge (Fig. 6 (a)). The ultrasonic vibration energy may create erosion points on the surfaces of the particles. Sludge particles vibrated and collided with each other, causing them to break up. Hence, by the capillary effect, H^+ ions may react with the surface and the interior of the $Al(OH)_3$ during the acidification process (Fig. 6 (b)). Therefore, the H^+ ions in the ultrasonically treated solution have more opportunities to react with the $Al(OH)_3$ than do those in the untreated solution and more aluminum ions can be dissolved in sludge.

IV. Conclusion

The acidification method was used in this investigation to recover alum salts from the sludge of a water treatment plant. The effects of acid species and sludge size on aluminum recovery were discussed. Experimental results revealed that ultrasonic treatment could break up the sludge particles and increase the quantity of aluminum dissolved. The aluminum dissolving efficiency in H_2SO_4-acidified solution exceeded that in HCl-acidified solution.

Acknowledgment

The authors would like to thank Mr. Tun-Jen Tien, Yu-Wei Huang and Ms. Ying-Ju Hsieh for their assistance with the laboratory work. The authors also appreciate the financial support of the National Science Council, Taiwan, R. O. C., (NSC-102-2221-E-239 -001 -MY2).

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