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# Synthesis of aluminum ammonium sulfate from waste aluminum processing solution by crystallization

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## Abstract

Experimental tests were conducted in the present study to investigate synthesis of aluminum ammonium sulfate (aluminum alum) by crystallization from the waste acid solution of aluminum surface finishing industry. Effects of various operating conditions including the molar ratio of ammonia and aluminum ion, temperature, mixer speed, seed alum dosage, initial sulfuric acid and aluminum ion concentrations on the aluminum alum formation, crystal size distribution, acid remaining and aluminum ion removal were examined. The crystallization process was found to be quite effective in recovering resource materials (sulfuric acid and aluminum) in the form of aluminum alum from the waste acid solution. Based on the test results, optimum operating conditions were recommended for efficient operation of the crystallization process. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Synthesis; Aluminum ammonium sulfate; Crystallization

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## 1. Introduction

Aluminum surface finishing has been a rapidly growing industry in many countries around the world for many decades [1]. The primary products of this industry include aluminum cables and wires, various types of structural materials, electric capacitors, etc. The aluminum surface finishing industry invariably produces a significant quantity of waste acid solution. Depending on specific type of aluminum surface finishing, the waste acid solution may contain sulfuric acid, hydrochloric acid, phosphoric acid,

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additives along with appreciable amount of dissolved aluminum. A typical waste acid solution is that generated in the etching of aluminum foil used for high-power electric capacitors. Hundreds of thousand tons of such waste acid solution have been produced annually in Taiwan alone [1]. Conventional treatment method of the waste acid solution is by neutralization for direct discharge. The neutralization process, however, generates over twice the amount of aluminum sludge more than the original waste acid solution which causes ensuing disposal problem. Furthermore, in the neutralization process, resource materials (sulfuric acid, aluminum, etc.) are lost, which otherwise can be possibly recovered [1,2].

In the past, very little work has been done in regard with recovery of the resource materials from the waste acid solution. Kobuchi et al. [2] investigated the recovery of nitric acid and hydrofluoric acid by diffusion dialysis from waste acid solution generated in the steel, metal-refining and electroplating industries. Sridhar and Subramaniam [4] examined the sulfuric acid recovery from sulfates of calcium, magnesium, sodium and potassium present in the cation exchange regeneration waste by diffusion dialysis. Liaw et al. [1] employed crystallization method in producing 4A zeolites from the waste etching acid solution of an aluminum structural material plant, containing significant amounts of sodium hydroxide, sodium aluminate, sulfuric acid and aluminum sulfate. In a recent work, Lin and Lo [3] utilized diffusion dialysis to treat the waste acid solution. That work [3] focused on recovering sulfuric acid from the waste solution for reuse in the process. The aluminum ion remained largely in the dialysate which needed to be further treated.

The objective of this study is to employ crystallization method in producing aluminum ammonium sulfate (ammonium alum) from the waste acid solution generated in the etching of aluminum foil for high-power electric capacitors. The reason for employing the present method is twofold. First, the waste acid solution contains ample amounts of aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) for ammonium alum synthesis. The extra chemical that needs to be added is ammonia ( $\text{NH}_3$ ). Second, ammonium alum is an important chemical widely used as coagulant for water purification and as additive in food processing, paper-making, dyestuff manufacturing, etc., and is also used in gemstone synthesis. Experimental investigations were conducted in the present study to examine the effects of various operating variables on the performances of the crystallization process with an aim of deriving the optimum operating conditions for such a process.

## 2. Materials and methods

The present crystallization study was carried out a simple jar test device, as shown in Fig. 1. The device had six 1-l glass beakers, each of them being provided with a variable stirrer. An external cooling system consisting of 50% ethylene glycol and 50% deionized water was employed for temperature control during the crystallization test runs.

The waste acid solution was simulated by dissolving 10 g aluminum powder in 1 l of deionized water containing 200 g sulfuric acid. This sulfuric acid concentration, which is equivalent to 2.025 M  $\text{H}_2\text{SO}_4$ , is approximately equal to that found in the waste acid

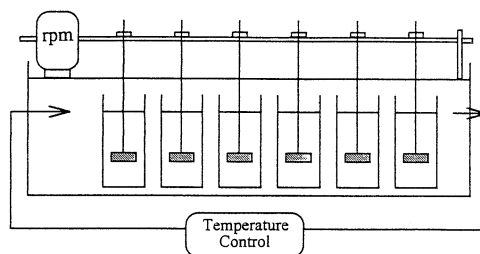


Fig. 1. Experimental setup.

solution exiting from an aluminum foil etching process. It is noted that the initial sulfuric acid concentration in a fresh batch of surface finishing acid solution is approximately equal to 2.1 M.

For each test run, 500 ml of the prepared stock acid solution were put in each beaker and the desired temperature was properly maintained by the water bath. After the steady state temperature was reached, appropriate amounts of ammonia and seed alum crystals were added to each beaker. Mixing at the desired speed was set immediately to start the test run. The ammonia (as represented by ammonium hydroxide of molar basis) was of industrial grade, as obtained from Fu Chang Chemical, Taiwan. The ammonium alum used for seeding was obtained E Merck (GR grade, E Merck, Darmstadt, Germany) which was ground to less than 0.05 mm in particle size. It should be noted that ammonium alum seeds of known amount were added in all test runs except for the cases noted. After a test run was started, small samples were then taken from the beakers once every 30 min or 1 h for determination of the sulfuric acid and aluminum ion concentrations. The sulfuric acid and aluminum ion concentration were measured by the method of Mohler [5] using a Metrohm autoburette (Model 716 Titrino, Metrohm, Switzerland). The total acid concentration was defined as the total sulfate including  $\text{H}_2\text{SO}_4$  plus  $\text{Al}_2(\text{SO}_4)_3$  expressed as  $\text{H}_2\text{SO}_4$  [5]. Accordingly, the percent acid remaining (AR) and aluminum ion removal (AIR) were, respectively, defined as follows:

$$\text{AR}(\%) = \frac{\text{Final total acid conc.} \times \text{Final volume of solution}}{\text{Initial total acid conc.} \times \text{Initial volume of solution}} \times 100 \quad (1)$$

$$\text{AIR}(\%) = \frac{\text{Initial aluminum ion conc.} - \text{Final aluminum ion conc.}}{\text{Initial aluminum ion conc.}} \times 100 \quad (2)$$

The two parameters and more importantly the amount of ammonium alum crystals obtained for each test run were employed to assess the performance of the crystallization process.

After a solution sample was taken from the glass beaker, the ammonium alum crystals formed in that beaker were separated from the residual solution by filtration through a piece of filter cloth. Those ammonium alum crystals were thoroughly washed with ethanol and were dried at 45°C in an electric oven for an hour. The dried ammonium alum crystals were put in a desiccator and their total weight determined. To find any compositional difference between the commercial and synthetic aluminum

alums, the X-ray deflection spectrophotos of the two alums were taken using a Philip XRD spectrophotometers (Model PW1700, Philips Electronic, Netherlands).

### 3. Results and discussion

Fig. 2 compares the XRD spectrophotos of the commercial (top) and the synthetic (bottom) aluminum alum crystals. It is apparent that the relative deflection angles and intensities were essentially the same for both spectrophotos, implying very little difference in composition for the two crystal samples, as anticipated. Fig. 3 shows the SEM images of the two alum crystals. The top image for the commercial alum) is more uniform in size while the bottom image (the synthetic one) has a wide range of different sizes. Both crystals were in rounded cubic shape and visually there is not much basic difference in appearance. Using a GBC ICP-AES (GBC Scientific Equipment, Victoria, Australia), both the commercial and synthetic alums were found to contain over 5 wt.% of Al and less than 0.01 wt.% of various metal ions (i.e. Ti, Ni, Sn, P, Na, Si, Fe, Cu, Cr, Mn, and Zn), implying that both aluminum alum have over 99% purity.

The ammonium alum is formed according to the following equation:



By the above equation, the molar ratio of ammonia ( $\text{NH}_3$ ) and aluminum ion would exert certain influence on the ammonium alum crystal formation. Fig. 4 displays the acid

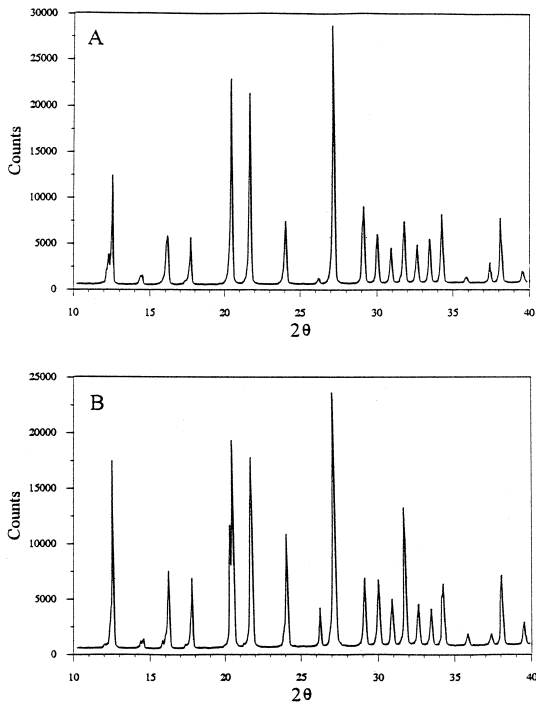


Fig. 2. The XRD spectrophotos of the commercial and synthetic aluminum alum crystals.

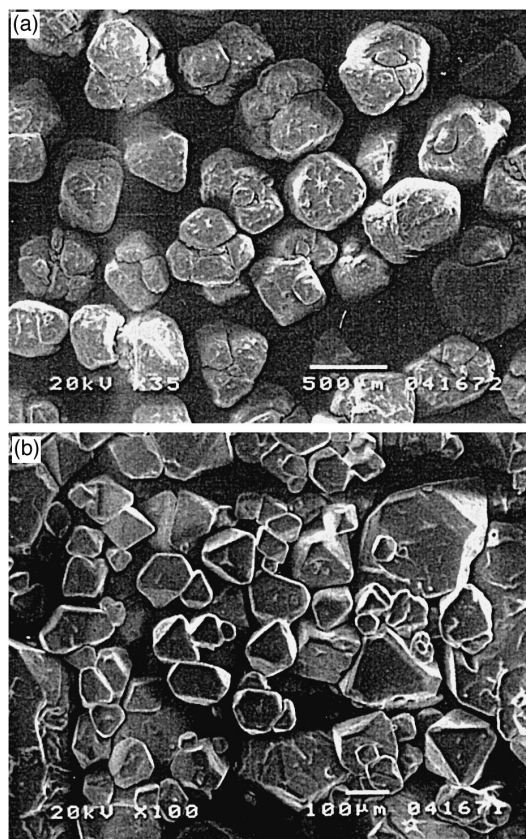


Fig. 3. SEM images of the commercial (top) and the synthetic (bottom) aluminum alums.

remaining, aluminum ion removal and the amount of ammonium alum crystal formed as a function of the molar ratio of ammonia and aluminum ion. The amount of ammonium alum crystal formed increases steadily with an increase in the molar ratio. The amount of ammonium alum crystal formed tends to level off after the molar ratio reaches 1.2 which is close the theoretical molar ratio of 1, as revealed by the above equation. The increase in the ammonium alum production leads to a decrease in the acid remaining and an increase in the aluminum ion removal due to simultaneous removal of sulfuric acid and aluminum ion during the crystallization process.

Like those of other inorganic salts [6], the solubility of ammonium alum in water is well known to be highly temperature dependent. Fig. 5 shows the relation between the solubility and the operating temperature. The saturation curve divides the whole region into the oversaturation region to the upper left and the undersaturation region to the lower right. As seen here, an initial point in the undersaturation region can be brought horizontally to saturation simply by lowering the operating temperature. Hence, a lower operating temperature will greatly facilitate crystallization. For the present study, the

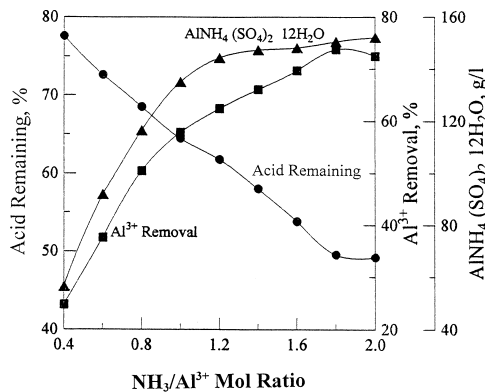


Fig. 4. Effect of  $\text{NH}_3/\text{Al}^{3+}$  molar ratio on the acid remaining, aluminum ion removal and aluminum alum crystal formed with 2.025 M initial sulfuric acid concentration, 1.03 M initial aluminum ion concentration, 3 g seed alum dosage, 10 rpm mixer speed and 5°C.

temperature was chosen to be between 2 and 10°C. Fig. 6 demonstrates the acid remaining, aluminum ion removal and the amount of ammonium alum crystal formed as a function of temperature. As the operating temperature was reduced from 10 to 2.5°C, the amount of ammonium alum crystals formed was more than doubled from 73.5 g/l to 154.3 g/l. The operating temperature was seen to have relatively little effect on the acid remaining and aluminum ion removal. Hence, for maximum aluminum alum formation, a low operating temperature at or below 7°C is definitely beneficial. Although low crystallization temperature can be achieved in industrial applications by a refrigeration system, an excessively low one may not necessarily be advantageous because of high energy consumption and other practical difficulties associated with operation at such a low temperature.

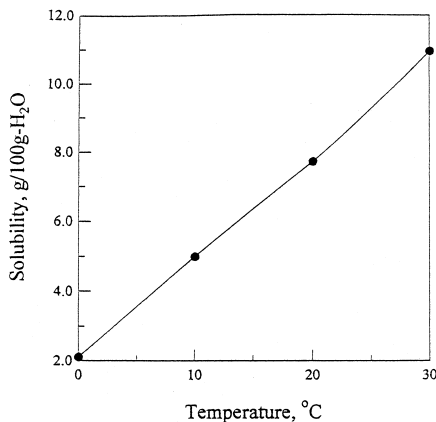


Fig. 5. Solubility of aluminum alum as a function of temperature.

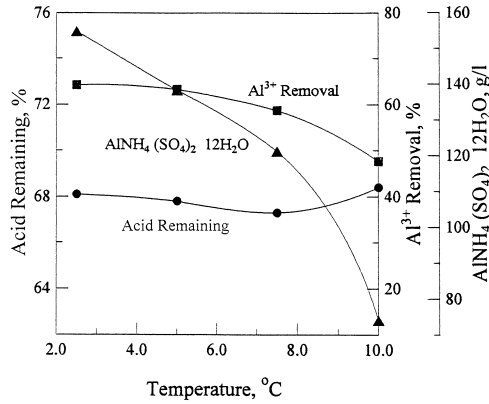


Fig. 6. Effect of temperature on the acid remaining, aluminum ion removal and aluminum alum crystal formed with 2.025 M initial sulfuric acid concentration, 1.03 M initial aluminum ion concentration, 3 g seed alum dosage, 10 rpm mixer speed and 1.2  $\text{NH}_3/\text{Al}^{3+}$  molar ratio.

Another important factor influencing crystallization is the mixer speed. The effect of mixer speed on crystallization is quite complex because of many conflicting factors affecting crystallization [6,7]. A high mixer speed provides a more uniform aqueous environment and better contact among aluminum sulfate, sulfuric acid and ammonia which is beneficial. However, at high mixer speed, the solubility of ammonium alum increases also. Crystals need a certain amount of time to nucleate and form on the seed surface and hence, high speed might not allow all chemicals sufficient time for crystal nucleation and formation. Besides, high mixer speed could break up the nascent crystals also. To demonstrate the effect of mixer speed, test runs were performed with a mixer speed between 10 and 100 rpm. Fig. 7 displays the test results. The ammonium alum formation is seen to decrease steadily with increasing mixer speed, implying that the

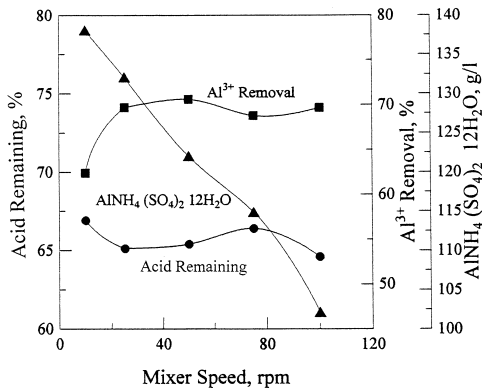


Fig. 7. Effect of mixer speed on the acid remaining, aluminum ion removal and aluminum alum crystal formed with 2.025 M initial sulfuric acid concentration, 1.03 M initial aluminum ion concentration, 3 g seed alum dosage, 1.2  $\text{NH}_3/\text{Al}^{3+}$  molar ratio and 5°C.

negative aspects at high mixer speed outweighs the advantageous ones. Therefore, a low mixer speed at or below 20 rpm appears to be necessary for effective crystallization. It is also noted here that the mixer speed at or above 20 rpm has relatively little influence on the acid remaining and aluminum ion removal.

Pertaining to Fig. 7, the mixer speed had significant impact on the sizes and size distributions of the ammonium alum crystals. Fig. 8 demonstrates the weight percent of crystal vs. the crystal size at various mixer speeds. It is apparent that for mixer speed at or less than 50 rpm, a larger portion of the ammonium alum crystals formed had a size greater than 1.68 mm with broad size distribution. As the mixer speed was increased to 100 rpm, only a few crystals had a size larger than 1.68 mm and a great majority of them were small sizes between 0.59 and 0.71 mm. From the test results shown here and Fig. 7, it can be concluded that an increase in the mixer speed not only reduces the total ammonium alum formation, but also the crystal size. In terms of these two aspects, a low mixer speed at or below 20 rpm is recommended.

The alum crystal seeds used in the present experimental tests were obtained by grinding the commercial ammonium alum to particle sizes smaller than 0.05 mm in diameter. In the previous figures (Figs. 4–8), 3 g/l of seed dosage were used. It would be of interest to explore what influence the amount of seed crystals will have on crystallization. Fig. 9 shows the test results using various amounts of seed crystal. As noted in this figure, the effect of the amount of seed crystal on the acid remaining and aluminum ion removal is marginal. However, its effect on the ammonium alum formation is quite strong. An increase in the alum seed dosage will provide more surface for nucleation and size growth of crystal and is theoretically beneficial to the present crystallization. Yet an optimum seed dosage of 2 g/l is apparent in this figure. The reason is not exactly known. It might be due to the fact that alum crystal seeds require certain amount of aluminum sulfate to sustain their appropriate growth. In the present

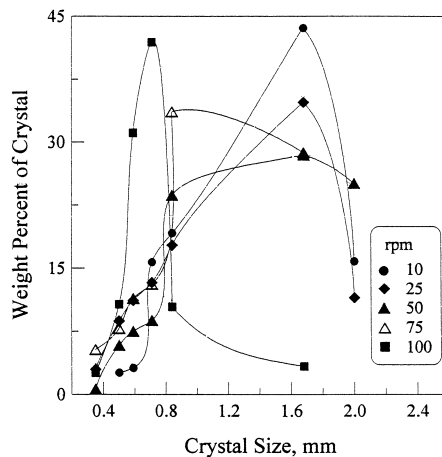


Fig. 8. Weight percent of alum crystal vs. the crystal size at various mixer speeds with 4.05 N initial sulfuric acid concentration, 1.03 M initial aluminum ion concentration, 3 g seed alum dosage, 1.2  $\text{NH}_3/\text{Al}^{3+}$  molar ratio and 5°C.



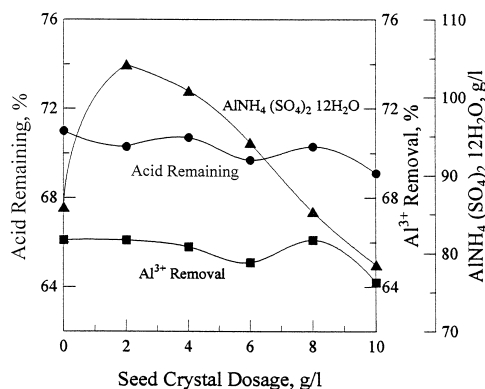


Fig. 9. Effect of seed crystal dosage on the acid remaining, aluminum ion removal and aluminum alum crystal formed with 2.025 M initial sulfuric acid concentration, 1.03 M initial aluminum ion concentration, 10 rpm mixer speed, 1.2  $\text{NH}_3/\text{Al}^{3+}$  molar ratio and 5°C.

system, the amount of aluminum sulfate available in the original waste solution was limited and was not sufficient to maintain proper crystal growth when there were too many alum seed crystals exceed 2 g/l dosage. It is also noted here that at or above 8 g/l seed dosage, the amount of ammonium alum formed is even worse than that without seeding. Therefore, for maximum benefit, a seed dosage of no more than 2 g/l would be appropriate for the present crystallization process.

Another aspect of practical importance to examine is the effects of initial sulfuric acid and aluminum ion concentration on crystallization. The waste aluminum solution from a surface processing production line is expected to have sulfuric acid and aluminum ion concentrations significantly less than 3 M and 0.8 M, respectively. Both concentrations were considered to be the upper limits for the test runs displayed in Figs. 10 and 11. It is noted in Fig. 10(a) that an increase in the initial sulfuric acid concentration up to 2.55 M of the initial waste acid solution considerably improves the ammonium alum formation, acid recovery and aluminum ion removal. After that, the ammonium alum formation starts to reverse. Hence, an optimum initial sulfuric acid concentration occurs in the close neighbourhood of 2.55 M. The initial sulfuric acid concentration not only affects the ammonium alum formation, but also the alum crystal size distribution, as revealed by Fig. 10(b). For initial sulfuric acid concentration lower than 2.06 M, a major portion of alum crystals formed were larger than 1.68 mm and the size distribution was relatively narrower than those above 2.06 M. But as the initial sulfuric acid concentration is increased beyond 2.55 M, the higher percentage alum crystal size formed apparently starts to shift to smaller ones.

The effect of initial aluminum ion concentration on crystallization is demonstrated in Fig. 11. The figure shows that both the aluminum ion removal and the ammonium alum crystal formation increases rapidly with an increase in the initial aluminum ion concentration, but the acid remaining decreases steadily. The ammonium alum crystal formation reaches a peak at 1.27 M which represents the optimum initial aluminum ion concentration for crystallization.

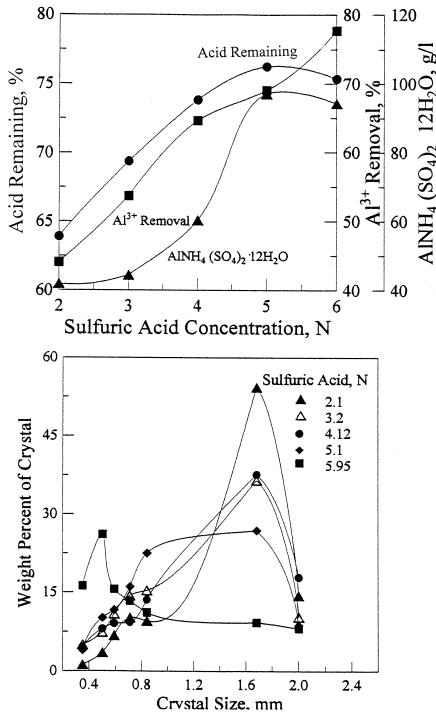


Fig. 10. Effect of initial sulfuric acid concentration on the acid remaining, aluminum ion removal and aluminum alum crystal formed (top) and the crystal size distribution (bottom) with 1.03 M initial aluminum ion concentration, 3 g seed alum dosage, 10 rpm mixer speed, 1.2 NH<sub>3</sub>/Al<sup>3+</sup> molar ratio and 5°C.

A test crystallization run was performed by utilizing the waste acid solution obtained from an aluminum anode-oxidizing plant in northern Taiwan. The original waste acid solution had some suspended solids and was first filtered using a fine glass fiber filter.

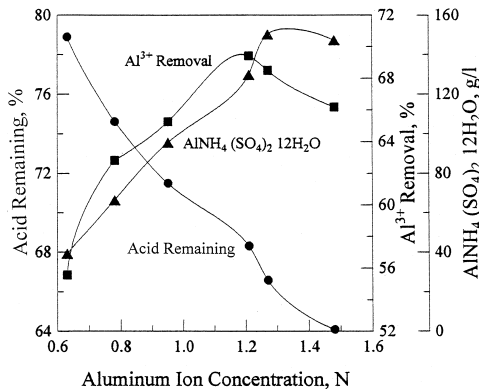


Fig. 11. Effect of initial aluminum ion concentration on the acid remaining, aluminum ion removal and aluminum alum crystal formed with 2.025 M initial sulfuric acid concentration, 3 g seed alum dosage, 10 rpm mixer speed, 1.2 NH<sub>3</sub>/Al<sup>3+</sup> molar ratio and 5°C.

After filtration, the waste acid solution was found to have 1.97 M sulfuric acid and 1.05 M aluminum ion concentrations. Crystallization test was performed at 5°C and under operating conditions similar to those shown in Fig. 6. In 5 h, 129.2 g/l of aluminum alum crystal were obtained. A case closest to this test run was that with 1.93 M sulfuric acid and 1.09 M aluminum ion concentrations shown in Fig. 6. For the latter case, the total amount of aluminum alum obtained was 137.8 g/l which was 6.7% higher than the former one. The result of the test run using the plant waste acid solution was deemed rather satisfactory considering that the plant waste acid solution could have some minor impurities.

As a final note, adoption of the crystallization method investigated in the present study to practical industrial applications represents a natural extension of this technology. In their previous study, Liaw et al. [1] had succeeded in scaling up the laboratory crystallizer to the pilot plant size and those investigators did not encounter much difficulty in the scale-up process other than the general design procedure involved [7]. However, due to certain similarity between the present system and that of Liaw et al. [1], not much complications are anticipated either in the scale-up of the present process.

#### 4. Conclusions

Experimental investigations were conducted to examine the synthesis of aluminum alum from the waste acid solution of an aluminum surface finishing industry by crystallization. Emphasis was placed on recovering sulfuric acid and aluminum ion from waste acid solution to form useful product (aluminum alum). Results from the test runs have indicated that the crystallization process is very efficient for this purpose. From those results, the following conclusions can be drawn: (1) The XRD spectroscopies and SEM images of both commercial and synthetic aluminum alum crystals reveal that the two alums had essentially the same composition and appearance. (2) An optimum  $\text{NH}_3/\text{Al}^{3+}$  molar ratio was experimentally observed to be 1.2 which was close to the theoretical value of the chemical reaction for aluminum alum formation. (3) An operating temperature less than 7°C and a mixer speed at or less than 20 rpm were found to be appropriate for efficient crystallization in terms of the amount of aluminum alum formed and the crystal size. (4) An optimum seed alum dosage around 2 g/l existed for the present crystallization process. (5) For best performance of crystallization, the initial sulfuric acid and aluminum ion concentrations around 2.55 M and 1.27 M, respectively, were found to be optimum.

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