

# Investigation of Different Stages of Aluminum Fluoride Crystal Growth

**Bayat, Mahmoud\*<sup>+</sup> and Taeb, Abbas**

Faculty of Chemical Engineering, Iran University of Science and Technology,  
P.O.Box 16765-163, Tehran, I.R.IRAN

**Rastegar, Saeed**

Faculty of Polymer Engineering, Amirkabir University of Technology, P.O.Box 15875-4413,  
Tehran, I.R.IRAN

**ABSTRACT:** Crystallization of Aluminum fluoride at atmospheric pressure has been considered. Structure, size and shape of crystals formed during the crystallization process have been investigated. By applying the direct analysis method for the existed aluminum in solution, the aluminum fluoride nucleation process has been detected as a concentration valley at the outset of crystallization process. The linear rate of growth of aluminum fluoride crystals has been measured by taking SEM micrographs from crystals during crystallization process. The rate of crystal growth in longitudinal direction is about  $10^{-9}$  m/s and nearly six times more than the rate of crystal growth in side direction. It is indicated that the aluminum fluoride nucleation process is repeated after completion of growth of initial crystals.

**KEY WORDS:** Aluminum fluoride, Crystallization, Nucleation, Crystal growth, Surface interaction.

## INTRODUCTION

Three well-defined kinds of hydrated crystals of aluminum fluoride have been recognized. The most stable form is three-hydrated one, which exist in  $\alpha$  and  $\beta$  forms. The solubility of the  $\alpha$  form in water is a bit more than  $\beta$  form. The  $\alpha$  form is obtained by treatment of aluminum with hydrogen fluoride at temperatures less than 25°C. It converts gradually and irreversibly to the  $\beta$  form in presence of humidity. The  $\beta$  form is obtained by crystallization of aqueous solution at 100°C. The  $\beta$

crystals have a tetragonal structure and the density of 2.09 g/cm<sup>3</sup>. While the solubility of aluminum fluoride in water is only about 16 g/l and nearly independent of temperature [1], but because of metastable nature of the aqueous solutions of aluminum fluoride, a solution of 200–250 g/l is stable in room temperature for hours without any crystallization. Agitation at high temperature causes crystallization in about four hours. At temperatures higher than 100°C and high pressure, hemihydrated, up to

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\* To whom correspondence should be addressed.

<sup>+</sup> E-mail: mmahmood\_in@yahoo.com

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mono-hydrated crystals are formed [2]. In aluminum fluoride crystallization, nucleation starts with delay. Victor [3] suggests addition of 130 g/l of fine tri-hydrated aluminum fluoride crystals ( $2-3\mu$ ) to reduce the crystallization time to half an hour. Ehret [4], pointed out that the  $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$  crystals units are in the form of  $[\text{AlF}_2 \cdot 4\text{H}_2\text{O}]^+$  and  $[\text{AlF}_4 \cdot 2\text{H}_2\text{O}]^-$  ions. So each aluminum fluoride trihydrate molecule, before entering the crystal structure should be converted into the above-mentioned ion complexes. Therefore crystallization of aluminum fluoride is limited by surface interaction process and volume diffusion doesn't affect the crystallization rate.

Nielsen and Altintas [5], believe that the  $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$  crystals contain  $\text{AlF}_3 (\text{H}_2\text{O})_2$  units and the third water molecule is not coordinated with aluminum ion but is placed between the chains, forming four hydrogen bonds with two hydrogen atoms and two fluoride ions belonging to four different polymeric strands of  $\text{AlF}_3 (\text{H}_2\text{O})_2$  units.

In contrast to previous works on crystallization of aluminum fluoride, which used concentrated solutions of pure aluminum fluoride as the precursor, in this work, aluminum fluoride solutions prepared by reaction of aluminum hydroxide and Fluosilicic acid. This method of preparing  $\text{AlF}_3$  solution is of much more industrial importance. On the other hand, in previous works, the measurement of the electrical conductivity of the crystallizing solution has been used to study the crystallization process but in this work the crystallization process has been followed by determination of the concentration of aluminum in the solution and also by electron microscopic investigations. Since the conductivity values can be influenced by different ionic species in the solution, the direct determination of the soluble aluminum is a more exact and reliable method.

## EXPERIMENTAL

### Materials

Aqueous solution of aluminum fluoride was prepared by reaction of aluminum hydroxide and Fluosilicic acid. In order to make the process as similar as possible to the industrial process, excess amounts of Fluosilicic acid (0.5-1 wt% excess) was used. The prepared solution after completion of the reaction had pH 3. Technical grade aluminum hydroxide with a purity of 99% and average particle size of  $25\mu$  was used. Fluosilicic acid with a concentration of 20 wt% was prepared by adding

analytical grade silica gel (Merck) to technical grade hydrofluoric acid. After reaction, aqueous solution of aluminum fluoride immediately was separated from silica precipitates in a notch filter and was used for crystallization experiments.

## EQUIPMENT AND PROCEDURE

A one-liter glass beaker was used as crystallization vessel, heated by a hot oil bath and equipped with a digital differential speed stirrer. The diameter of the Teflon propeller was 65 millimeters. A notch filter with a diameter of 100 millimeters was used to separate crystals out of mother liquor.

Scanning Electron Microscopy, Topcon SR50, was used for determination of shape and size of crystals.

X-ray diffraction, Philips PW1800, with radiation  $\text{CuK}\alpha 1$  ( $\lambda=1.5404$ ) was used for determination of crystal structures.

To investigate the aluminum fluoride crystallization by direct analysis method, about 10 ml of slurry was taken out of beaker and filtered. The filtrate was analyzed for determination of soluble aluminum concentration and the cake was analyzed using Scanning Electron Microscopy for determination of the shape and size of the crystals. Also some crystals were analyzed by XRD for determination of crystal structure.

Aluminum fluoride is a strongly stable complex, so that none of the classical methods for determination of  $\text{Al}^{3+}$  cations - specially complexometric titration - can be applied for determining aluminum ion concentration in presence of fluorine. Therefore, for direct determination of aluminum concentration it is necessary to decompose aluminum fluoride through alkali-fusion. To measure aluminum fluoride concentration in filtrate, 2ml of filtrate was slowly evaporated and dried in platinum pot and then fused with anhydrous sodium carbonate. Then fused salts was dissolved in 10 wt% aqueous solution of hydrogen chloride. Aluminum concentration was then determined by EDTA method using Eriochrome blue indicator [6].

Each experiment was started with 500ml of aluminum fluoride aqueous solution and evaporated water during experiment has been made up to avoid errors in aluminum concentration determination.

Experiments were performed at  $85^\circ\text{C}$  &  $95^\circ\text{C}$ , stirrer speed of 260 rpm, initial aluminum fluoride concentrations

of 140g/l, 170g/l & 280g/l and seeding with 20g/l, 50g/l, 100g/l, 150g/l and 200 g/l aluminum fluoride trihydrate (AFT) crystals. The crystallization process was stopped after five hours.

## RESULTS AND DISCUSSION

Fig.1 shows variation of aluminum fluoride concentration with time of crystallization for a 170 g/L aqueous solution without seeding. As shown in Fig. 1, concentration of the soluble aluminum fluoride in the solution decreases as the crystallization proceed. At early stages of the crystallization, a sharp decrease followed by a rapid increase in concentration of the soluble aluminum fluoride was detected. After this period, the change in concentration of the soluble aluminum fluoride is almost linear. The inset in Fig. 1, shows the linearly decreasing concentration of the soluble aluminum fluoride during the crystallization process. From the fit equation, the time of completion of crystallization is calculated to be 380 minutes.

Fig. 2 shows the dependence of the soluble aluminum fluoride concentration during crystallization as a function of crystallization temperatures and initial concentration. The *concentration valley*, like in Fig. 1 is observed in Fig. 2 as well. Fig. 2 shows that the depth and the width of the *concentration valley* depend on initial concentration and is almost independent of crystallization temperature.

In order to find the origin of the *concentration valley*, the crystallization process and different possible crystal structures of aluminum fluoride should be considered.

During initial stages of crystallization, the concentration of the soluble aluminum fluoride decreases and then increases. It seems that some of the soluble aluminum fluoride molecules are being converted to the small particles, (which, can be separated by a filter paper) after a certain time these particles dissolve in the solution again. If the process of disappearing and reappearing of the soluble aluminum fluoride is a kind of crystallization and re-dissolution, the crystal structure should differ from the AFT itself. Since the solubility of the AFT crystals in water is very low.

XRD analysis revealed that these initial species have the same structure as final crystals, i.e.  $\beta\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ . The XRD results for samples 2 and 13 (Fig. 1) have been

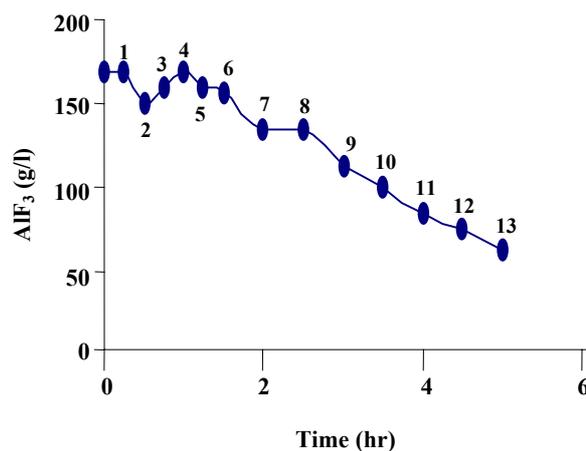


Fig. 1: Variation of aluminum fluoride concentration versus time. Temp. = 95°C, Stirrer speed = 260 rpm.

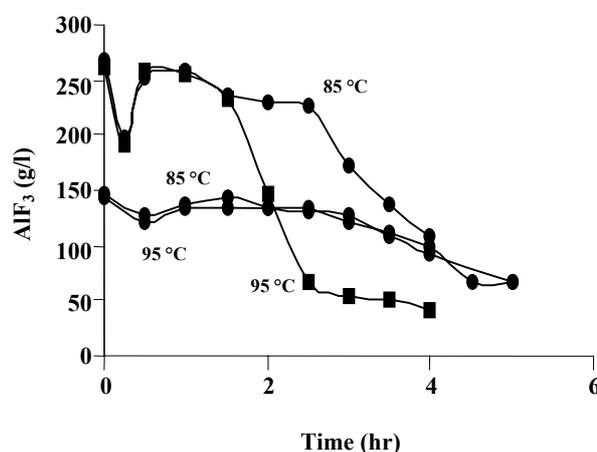


Fig. 2: Variation of aluminum fluoride concentration versus time.

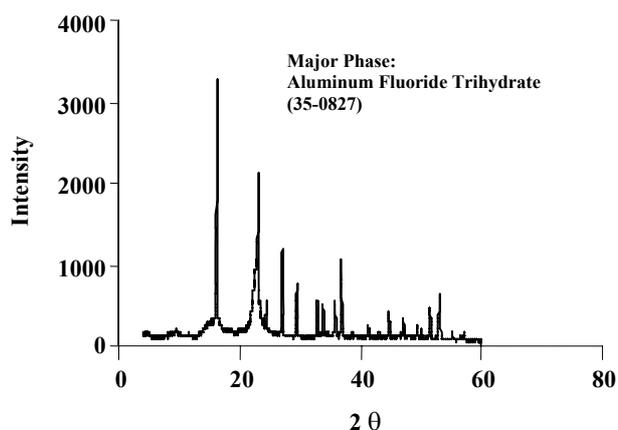


Fig. 3: XRD analysis from crystals of sample 2.

shown in Figs. 3,4. The crystals of sample 2 were so fine that the separation from filter paper was not possible and they were analyzed by XRD in place, Fig. 3 shows background of the filter paper XRD. XRD analysis data of 2 and 13 samples have been analyzed by APD software package and the crystal structure of aluminum fluoride tri-hydrated was recognized.

So, the concentration valley can not be the result of a crystallization and re-dissolution process. Another possibility is that the initial concentration drop is due to a nucleation and aggregation of the small nuclei and the following increase in soluble aluminum concentration is due to break down of the aggregates.

The aggregated nuclei are of such a big size that can be retained by the filter paper but the nuclei themselves can pass the filter paper easily. According to Blaszcak et. al. [7] the  $\text{SiF}_6^{2-}$  species are able to be adsorbed on the surface of AFT particles caused by their opposite surface charge. Since the initial nuclei are extremely small, the adsorbed fluosilicic acid anion can act as very fine interaction points between nuclei. This will cause the formation of large aggregates, which, can be separated by filter paper. As the crystallization proceeds, the aggregates start to convert into fine monomeric particles. This conversion might be due to one of the following reasons:

- The monomeric particles are unstable nuclei, which can re-dissolve in the aqueous phase [8].
- The  $\text{SiF}_6^{2-}$  adhesives are incorporated into the crystal structure of the nuclei [7].
- As the nuclei grow, they get such a big size that the bonding power of the  $\text{SiF}_6^{2-}$  adhesives does not suffice for holding the monomeric particles together and the aggregates re-arrange to form more compact aggregates or break down into their monomeric units.

Any of the above processes can be reseen for solubility of aluminum fluoride in the filtrate (point 4 in Fig. 1).

All above-mentioned hypotheses indicate a relationship between concentration valley and nucleation process. For proving this claim, some experiments have been conducted by seeding to eliminate nucleation process. Bulk particles of AFT with size of 3-20  $\mu$  were used for seeding. According to Fig. 5 with sufficient seeding (more than 100g/l) and subsequent elimination of nucleation process, the concentration valley was also disappeared. Consequently the dependence of concentration valley to nucleation process is evident and one can relate the depth of concentration valley to nucleation.

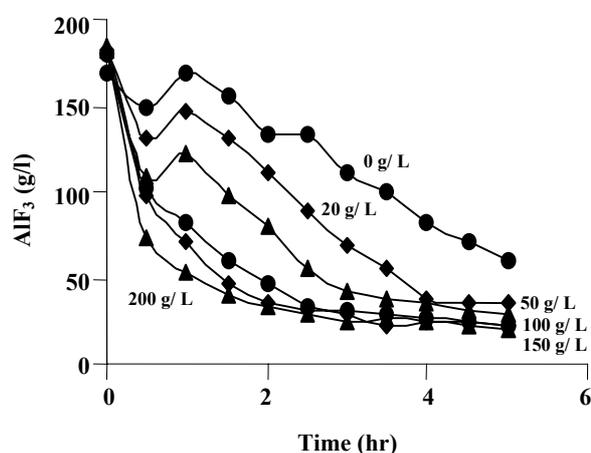
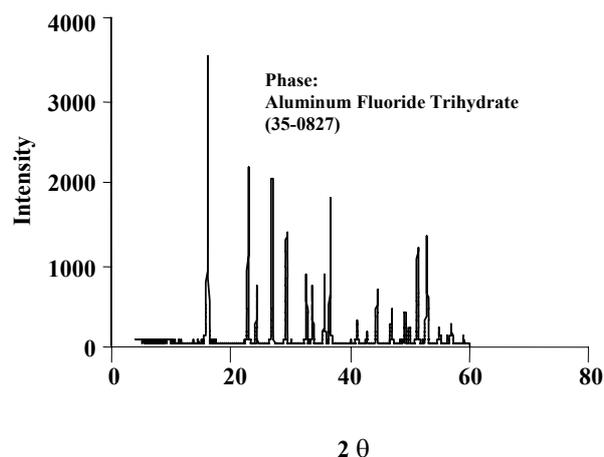


Fig. 5: Seeding effect on the crystallization process of aluminum fluoride.

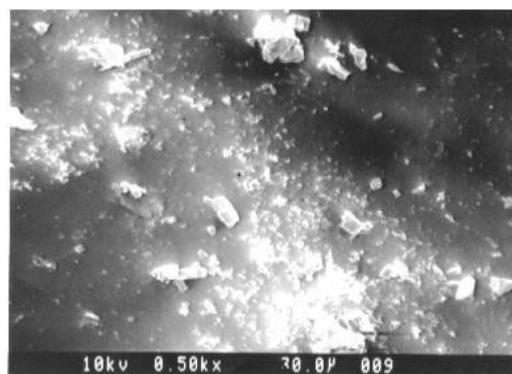


Fig. 6: Aluminum fluoride crystals after 45 minutes of crystallization.

After achieving the concentration valley, the stable nuclei start to grow into larger crystals. To investigate the crystallization process, SEM micrographs were taken at different crystallization times. The growth process of aluminum fluoride crystals can be described based on these images as follow.

The numbering of the following samples are based on different points in Fig. 1.

**Sample 3 (45 minutes after onset of crystallization)**

Some aggregated particles from sample (2), which, has not been broken down can be seen in Fig. 6. The crystals are very fine ( smaller than  $2\ \mu$  ) and of granular shape.

**Sample 5 (75 minutes after the onset of crystallization)**

As shown in Fig. 7, crystals are of tetragonal shape. Some of them are aggregated during the drying process. Their average size is  $3\ \mu \times 12\ \mu$ . As can be seen 60 minutes after the onset of the crystallization, the main phase of crystal growth has been started and longitudinal growth of crystals has been faster than side growth, the globular particles in sample (3) have been converted to the tetragonal ones.

**Sample 8 (150 minutes after the onset of crystallization)**

As shown in Fig. 8, crystals have grown up to  $17\ \mu$  in length while their side have only grown to  $6\ \mu$ .

**Sample 10 (210 minutes after the onset of crystallization)**

As shown in Fig. 9, length growth of crystals has been stopped but in side directions they have grown to reach  $8\ \mu$ . The stop of growth in the length direction will cause the rate of crystal growth to reduce and it lets formation of new nuclei so some new needle crystals of  $1\ \mu \times 4\ \mu$  appear.

**Sample 12 (270 minutes after the onset of crystallization)**

As shown in Fig. 10, growth of old crystals is completely stopped. The new crystals grow gradually and the ratio of length growth to side growth is more than the old crystals. Their length reaches  $8\text{-}10\ \mu$  while their width is only  $1.5\text{-}2\ \mu$ .

Based on the above observations the longitudinal growth rate of the aluminium fluoride crystals is of the order of  $10^{-9}$  m/sec. Nielsen and Altintas[5] have determined the crystallisation rate of aluminium fluoride

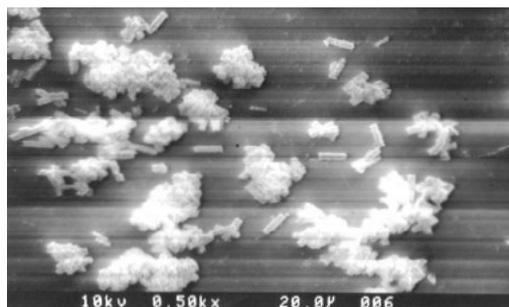


Fig. 7: Aluminum fluoride crystals after 75 minutes of crystallization.

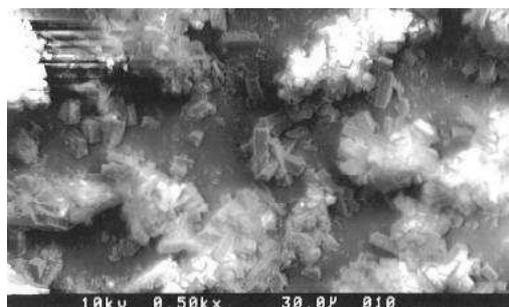


Fig. 8: Aluminum fluoride crystals after 150 minutes of crystallization.

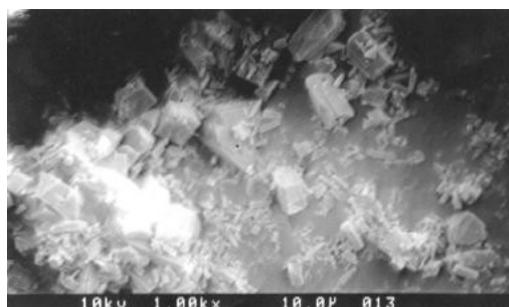


Fig. 9: Aluminium fluoride crystals after 210 minutes of crystallization.

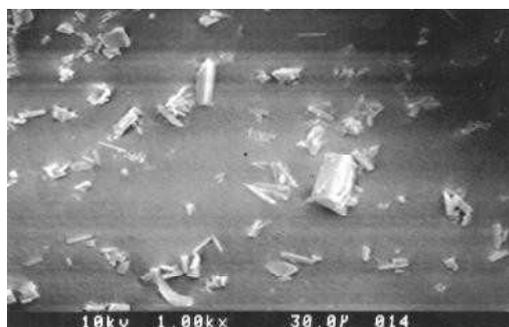


Fig. 10: Aluminum fluoride crystals after 270 minutes of crystallization.

from a concentrated aqueous solution as  $10^{-13}$  m/sec at 75 °C. This value is based on calculation and is the overall growth rate of crystals. According to this, the growth rate in longitudinal direction is much more than growth rates in other directions.

## CONCLUSION

The crystallization of the aluminum fluoride from aqueous solutions prepared from the reaction of aluminum hydroxide and excess amounts of fluosilicic acid has been investigated. Investigation of the crystallization process by direct analysis of the existed aluminum in the solution has been caused to detect the nucleation process of aluminum fluoride. Concentration valley represents the nucleation process has been occurred. Concentration valley consists of the initial formation of very small nuclei aggregates and then break-down of the aggregates into the small monomeric nuclei. The time scale of the concentration valley depends strongly on the initial concentration of the aluminum fluoride solution. The SEM micrographs of the growing crystals facilitated the measurement of linear rate of aluminum fluoride crystal growth. The longitudinal growth rate of the crystals is about  $1.0 \times 10^{-9}$  m/sec and approximately 6 times of the side growth rate in onset of crystal growth process. In the absence of additives, the growth of aluminum fluoride crystals is limited to about  $7 \times 20$  micrometers. Additionally if supersaturating condition has been remained yet, the nucleation process would have been occurred again but the newly-formed crystals have a longer needle-like structure than the initial ones. Investigation of the crystallization process by direct analysis provides the chance of separation of nuclei aggregates or unstable nuclei on the filter paper, hence the possibility of detecting the nucleation process is provided.

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