

Kinetics of crystal growth on seeded precipitation of sodium aluminate solutions with new device^①

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Abstract: A new device was designed, which can effectively avoid the undesired nucleation and agglomeration of fine particles on the experimental results during the seeded precipitation of sodium aluminate solution, and moreover, the experimental conditions are nearly kept constant during the experiment. With the new device, it is proven that a good result can be obtained on the kinetics study of the crystal growth in seeded precipitation of sodium aluminate solution. Experiments were carried out with the concentration of Na₂O (N_k) 170 g/L, the mole ratio of Na₂O to Al₂O₃ (α_k) all between 1.52 to 2.01, at 65, 70, 75 °C, respectively. And the kinetics equation of crystal growth of gibbsite was deduced.

Key words: sodium aluminate solution; seeded precipitation; crystal growth; kinetics

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1 INTRODUCTION

The crystallization of gibbsite (γ -Al(OH)₃) from seeded precipitation of sodium aluminate solutions related to the inherently slow growth rate of crystal, is an important step for Bayer process. Considerable researchers have made a good few studies on the mechanisms and kinetics of gibbsite growth for the improvement of the product yield without sacrificing quality. Most of the previous studies^[1-9] have focused on the influence of the process parameters, such as temperature, supersaturation, caustic concentration, seed charge, and on the kinetics of crystal growth using batch crystallizer. As a matter of fact, because the undesired nucleation and agglomeration of fine particles often disturb the particle size distribution, many experimental results are unsatisfactory. Therefore, the aim of the present work is to investigate the kinetics of crystal growth on seeded precipitation of sodium aluminate solutions with a self-made new device, where the secondary nucleation and fine particle agglomeration could be effectively avoided, and the crystallization driving force could be kept nearly constant during experiment.

2 EXPERIMENTAL

2.1 Principle

It was well known that the seeded precipitation

of sodium aluminate solutions is a chemical crystallization process, in which the mechanism involves several main essential steps as follows: second nucleation, agglomeration of fine particle, seed or nuclei growth, and the breakage and attrition of crystal. In theory, if any other factors are negligible, the particle size distribution (PSD) of nucleation, agglomeration, and crystal growth can be shown as in Fig. 1. The reasons are as follows: 1) during the seeded precipitation of sodium aluminate solutions, the original particle size of second nucleation is about 1.42 μ m to 2 μ m; 2) it is easy to generate agglomeration for the particles less than 30 μ m but agglomeration for the particles exceeding 30 μ m is likely impossible; 3) according to the conclusion from Misra and White^[10], the crystal growth of gibbsite from sodium aluminate solutions is size independent, in other words, the ΔL law is suitable for the system of sodium aluminate solution.

2.2 Design of new precipitation device

In order to avoid the limitation of the batch reactor that is used to investigate the kinetics of crystal growth on seeded precipitation of sodium aluminate solution. The new precipitation device is designed in our experiment as shown in Fig. 2. The device mainly consists of three well-sealed tanks of cylindrical double jacketted stainless steel vessels (crystallizer: 0.5 L; cycle solution reservoir: 5 L; fine particle redissolve tank: 0.5 L, respectively.); two triple valves,

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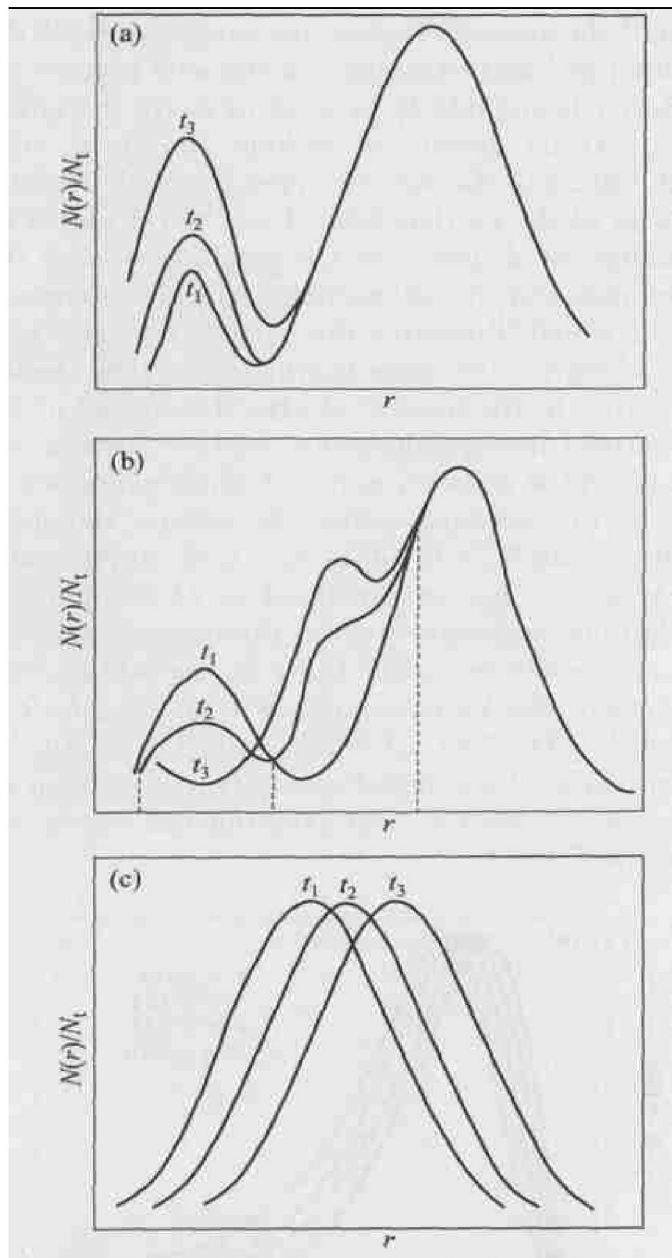


Fig. 1 Essential process for precipitation of sodium aluminate solution

(a) —Nucleation; (b) —Agglomeration; (c) —Growth
(t is time; N_r is number of particles;
 N_t is total number of particles)

a pump and stir device. All the parts that contact with sodium aluminate solutions are well alkalifast. The redissolve tank, which is used to precipitate and redissolve the fine particles generated by secondary nucleation and breakage of seed, could ensure experimental result not effected by the secondary nucleation. The cycle solution reservoir is used to supply the sodium aluminate solution for the crystallizer. The crystallizer is a key part of the precipitation device where the seeded precipitation of sodium aluminate solutions was performed. It is equipped with three wall baffles to prevent the solution from rotating around the crystallizer and a three-bladed stainless steel stirrer; it also has a sealed cover slab with a hole which can be sealed by a cork to allow seed injection

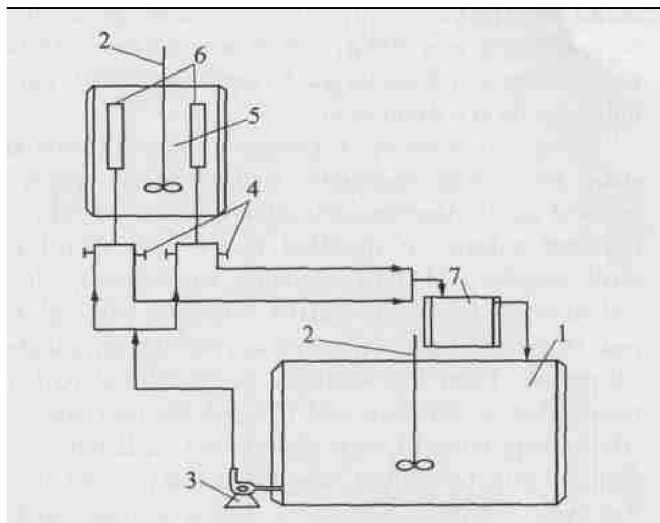


Fig. 2 Sketch map of precipitation device
1—Cycle solution reservoir; 2—Stirrer; 3—Pump for cycle;
4—Triple valves; 5—Crystallizer; 6—Filter devices;
7—Fine particle redissolve tank

and sample suspension. Two filter devices, which are connected with two triple valves, were set into the crystallizer. According to the needs of experiments, the sieves of filter can be replaced freely. With the filter device, sodium aluminate solution can be easily passed into and out of the crystallizer but crystal seeds can always stay in the crystallizer. By controlling the two triple valves, the direction of the input solution would be changed in order to avoid the filter clogged by fine particles during the experiments. The characteristic of the device is that it can ensure the experimental conditions nearly kept constant, including the supersaturation degree of suspension and the temperature of solution. In other words, the crystallization driving force can nearly be kept constant during experiment, and moreover, the effect of unwanted nucleation and agglomeration of fine particles on the experimental results can be effectively avoided. With the new device, it is proven that a good result on the study of the crystal growth kinetics can be obtained on seeded precipitation of sodium aluminate solution.

2.3 Procedure

According to the conditions of nucleation and agglomeration of fine particles, there is almost no nucleation when the temperature of solution is above 65 °C and it is difficult for fine particles to agglomerate when the particle size exceeds 30 μm. In order to avoid the nucleation and agglomeration of fine particles, runs were carried out with caustic concentration of Na_2O (N_k) 170 g/L, the initial α_k from 1.52 to 2.01, where α_k is the mole ratio of Na_2O to Al_2O_3 , at

65, 70, 75 °C, respectively. Seed addition was 100 g, which was obtained from wet sieving and dried at 50 °C constantly with particle size larger than 30 μm.

The solutions were prepared from industrial sheet alkali and aluminum hydroxide. A known mass of sheet alkali was dissolved in one-half of the required volume of distilled water in a stainless steel vessel, Al(OH)₃ crystals were slowly dissolved in the heated up caustic solutions with agitation to get the high concentration sodium aluminate solutions. Then the solutions were diluted to the required concentration and filtered for two times. At the beginning of each experiment, 5 L pure sodium aluminate solution was filled and preheated at the cycle solution reservoir; 100 g crystal seeds were filled and preheated at crystallizer, where the temperature was controlled (precision ±0.5 °C) by extrinsic cycle style water bath produced by Shanghai Optics Instrument Company. When the controlled temperature was reached, the cycle pump and the stir device were started up. The stir device with a speed of 250–300 r/min was used by a JJ-1 style of precision electromotion puffer, which is produced by the Instrumental Plant of Shenzhen Guohua in China, it can ensure the coherence of suspensions. The samples were periodically removed for crystalline product characterization and solution concentration analysis during each run. Every sample was separated with a centrifugal machine. The concentrations of alumina and caustic of clear solution were measured with standard analysis method. The solid of sample was washed for three times in hot distilled water for the PSD determination by the style of Malvern Mastersizer2000, England.

3 RESULTS AND ANALYSIS

The kinetic study of crystal growth is achieved by gathering the messages of particle size distribution (PSD) during the seeded precipitation. Fig. 3 shows the PSD curves for seeded precipitation with $N_k = 170$ g/L, α_k of 1.62 and 1.93 at 65 °C, respectively. The PSD curves under other conditions are similar with those shown in Fig. 3, from which it can be seen that the PSD curves just have a parallel movement without other changes. The result is in agreement with the PSD pattern predicted in Fig. 1(c). From Fig. 3 the following conclusions can be made: 1) with the self-made new device, the results of PSD curve indicate that without nucleation and agglomeration only the crystal growth process can be found during the experiments; 2) the rate of crystal growth is independent of the size of the particles and can be ex-

pressed as $G(L) = dL/dt$. Therefore, the rate of crystal growth maintains the same if the supersaturation and temperature of the solution are kept constant. So the new precipitation device is suitable to be used to study the kinetics of crystal growth of sodium aluminate solutions. Because the rate of crystal growth is independent of the particle size, it can be calculated by changing the diameter of the single crystal or the mean diameter of all particles, median diameter (d_{50}), which illustrates the particle diameter corresponding to 50% mass cumulated particles below the sieve. In the present study, the change of d_{50} for particle size distribution is used to illustrate the rate of crystal growth, namely $G(L)$ is expressed as $\Delta d_{50}/t$. For example, when the sodium aluminate solution with $N_k = 170$ g/L, $\alpha_k = 1.52$, is precipitated at 65 °C, d_{50} was analyzed as 74.238 μm and 84.486 μm respectively from the beginning to the end of precipitation after 12 h. So the rate of crystal growth can be calculated as $G(L) = \Delta d_{50}/t = (84.486 - 74.238)/12 = 0.854 \mu\text{m} \cdot \text{h}^{-1}$. In our experiments, the original d_{50} of crystal seeds for all runs was 74.238 μm. All experimental results are listed in Table 1.

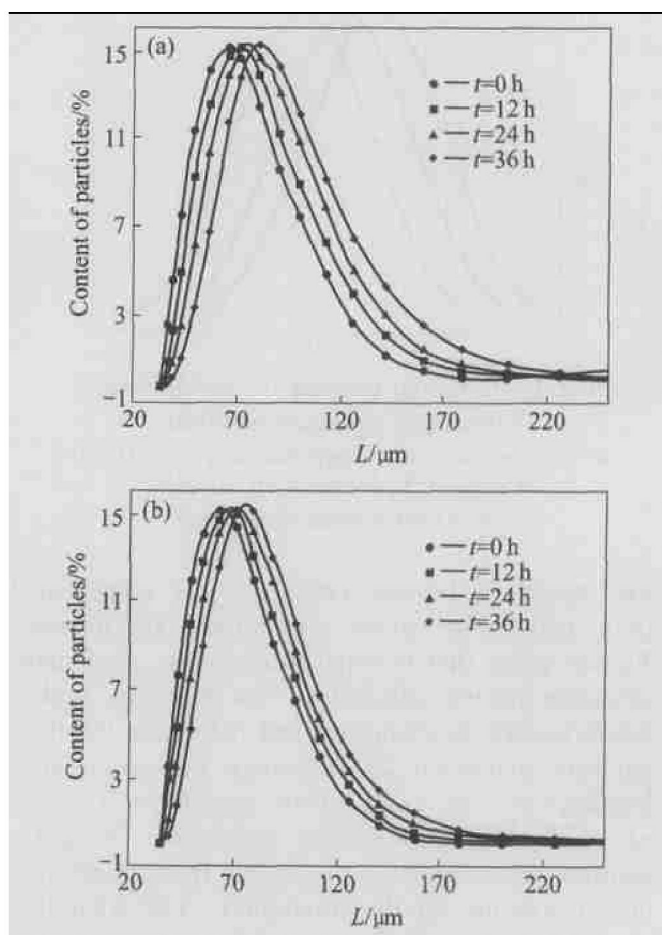


Fig. 3 PSD of solid on sodium aluminate solution with different α_k at different times (N_k 170 g/L, 65 °C, seed charge 100 g)
(a) — $\alpha_k = 1.62$; (b) — $\alpha_k = 1.93$

Table 1 Rate of crystal growth ($G(L)$) under different conditions ($\mu\text{m/h}$)

$\theta/^\circ\text{C}$	α_k					
	1.52	1.62	1.71	1.81	1.93	2.01
65	0.854	0.66	0.486	0.389	0.214	0.207
70	1.006	0.753	0.529	0.383	0.253	0.188
75	1.118	0.698	0.526	0.419	0.207	0.138

According to the formula from Misra^[11], $A^* = N_k \exp(6.2106 - 2486.7/\theta + 1.08753N_k/T)$, α_k and α_k^* of solution expressed as $\alpha_k = 1.645N_k/A$, $\alpha_k^* = 1.645N_k/A^*$, the supersaturation of solution can be expressed as $\sigma = A - A^*$ or $\beta = (1/\alpha_k - 1/\alpha_k^*)$, respectively, where A^* is the equilibrium solubility for the sodium aluminate solution at given temperature and caustic concentration. Because of the caustic soda concentration is changeless during experiment, so β is used to express the solution supersaturation in this research. According to the data of the rate of crystal growth $G(L)$ shown in Table 1, $G(L)$ is plotted as a function of supersaturation square β^2 as shown in Fig. 4. It illustrates a good linear relationship for β^2 and $G(L)$. The kinetic constant k_G at different temperatures is obtained from Fig. 4.

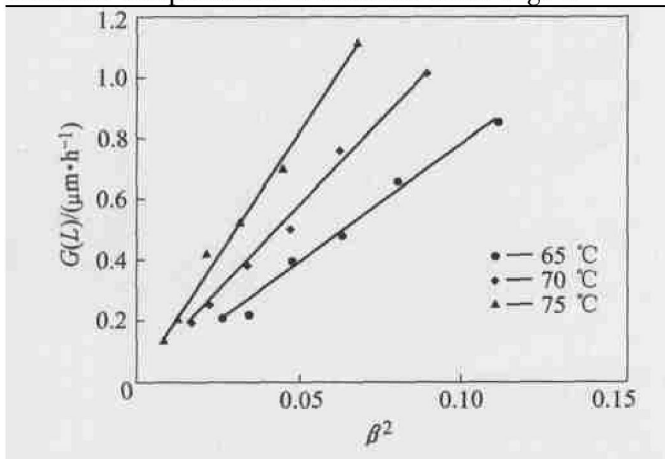


Fig. 4 Curves of growth rate of crystal vs supersaturation squared

Many studies have shown that the effect of temperature on the rate of crystal growth follows the Arrhenius relationship. Fig. 5 shows the Arrhenius plot, where k_G from Fig. 4 is plotted against $1/T$. The straight line shown in Fig. 5 corresponding to an activation energy E_a of 67.301 kJ/mol and the pre-exponential k_0 of $2.058 \times 10^{11} \mu\text{m/h}$, and the kinetics of crystal growth of sodium aluminate solution can be obtained as

$$G(L) = 2.058 \times 10^{11} \beta^2 \exp(-67.301/RT)$$

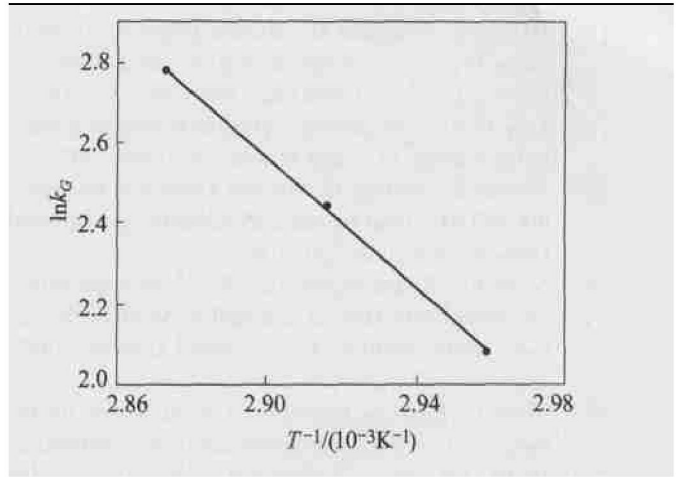


Fig. 5 Arrhenius plot for growth rate data

Table 2 Activation energies for crystal growth of $\text{Al}(\text{OH})_3$ by different researchers

Resercher(s)	$E_a / (\text{kJ} \cdot \text{mol}^{-1})$
Misra and White ^[11]	59.832
King ^[4]	53.184
Low ^[12]	62.325
Oberley and Scott ^[13]	83.100
Mordini and Cristol ^[14]	78.945
Bateman ^[15]	70.635
Present study	67.301

4 CONCLUSIONS

The previous kinetic studies of crystal growth of sodium aluminate solution were often disturbed by unwanted secondary nucleation, agglomeration, breakdown of crystal. With the self-made new device, the effects of secondary nucleation, agglomeration, crystal breakdown can be neglected in the present study. Experiments were carried out with concentration of $\text{Na}_2\text{O} (N_k)$ 170 g/L, the mole ratio of Na_2O to $\text{Al}_2\text{O}_3 (\alpha_k)$ are all between 1.52 to 2.01, at 65, 70, 75 °C, respectively. The kinetics equation of crystal growth on sodium aluminate solution was deduced. The activation energy 67.301 kJ/mol and the pre-exponential $2.058 \times 10^{11} \mu\text{m/h}$ are obtained.

REFERENCES

[1] White E T, Bateman S H. Effect of caustic concentration on the growth rate of $\text{Al}(\text{OH})_3$ particles[J]. Light Metals, 1988: 157 - 165.
 [2] Brown N. Crystal growth and nucleation of aluminium trihydroxide from seeded caustic aluminate solutions[J].

- J Crystal Growth, 1972, 12: 39 - 50.
- [3] Halfon A, Kaliaguine C. Alumina trihydrate crystallization Part I : secondary nucleation and growth rate kinetics[J]. Can J Chem Eng, 1974, 54: 160 - 167.
- [4] King W R. Some studies in alumina trihydrate precipitation kinetics[J]. Light Metals, 1973: 551 - 563.
- [5] Veessler S, Boistelle R. Growth kinetics of hydrargillite $Al(OH)_3$ from caustic soda solutions [J]. J Crystal Growth, 1994, 142: 177 - 183.
- [6] Veessler S, Rource S, Boistelle R. About supersaturation and growth rates of hydragillite $Al(OH)_3$ in alumina caustic solution[J]. J Crystal Growth, 1993, 130: 411 - 420.
- [7] Muhr H, Pierre J, Plasari E. A rapid method for the determination of growth kinetic constants: Application to the precipitation of aluminum trihydroxide[J]. Ind Eng chem Res, 1997, 36: 675 - 681.
- [8] Seyssieq I, Veessler S. A non-immersed induction conductivity system for controlling supersaturation in corrosive media: the case of gibbsite crystals agglomeration in Bayer liquors[J]. J Crystal Growth, 1996, 169: 124 - 128.
- [9] Ilievski D. Development and application of a constant supersaturation, semi - batch crystalliser for investigating gibbsite agglomeration[J]. J Crystal Growth, 2001, 233: 846 - 862.
- [10] Misra C, White E T. Kinetics of crystallization of aluminium trihydroxide from seeds caustic aluminate solutions[J]. Chem Eng Progr Sympos Ser, 1970, 110: 53 - 61.
- [11] Misra C. Solubility of aluminium trihydroxide (hydrargillite) in sodium hydroxide solution[J]. Chem Eng, 1970, 20: 619 - 628.
- [12] Low G. Agglomeration Effects in Aluminium Trihydroxide Precipitation [D]. Queensland: University of Queensland, 1975.
- [13] Overbey T L, Scott C E. Characterization of Bayer plant liquors and seeds—Utilizing a mathematical model for precipitation[J]. Light Metals, 1978: 163 - 168.
- [14] Mordi J, Cristol B. Mathematical model of alumina trihydrate precipitation from Bayer aluminate liquors[A]. Proceedings of 4th Yugoslav International Symposium on Aluminium Titograd[C], 1982.
- [15] Bateman S H. Effect of Caustic Concentration on the Growth Rate of Aluminium Trihydroxide Particles[D]. Queensland: University of Queensland, 1984.

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