Effect of Ultrasound Frequency on the Precipitation Process of Supersaturated Sodium Aluminate Solution

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Abstract：The effects of frequency of ultrasound on the precipitation process of prepared supersaturated sodium aluminate solutions of practical concentration were studied experimentally under seeded, isothermal, batch crystallization conditions at various temperatures and initial α_k(mole ratio of Na_2O/Al_2O_3). The decomposition and the particle number percentage for size below 2 μm at time of 15 h were compared, particle size distribution and SEM photos of the product aluminum hydroxide were also analyzed. The results indicate that the ultrasonic treatment at 16 kHz can enhance the decomposition rate of sodium aluminate solutions, and also has effects on particle morphology and particle size distribution of aluminum hydroxide precipitated.

Key words：ultrasound; sodium aluminate solution; particle size distribution; nucleation

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1 INTRODUCTION

One of the important steps in the production of aluminum oxide by the Bayer process is crystallization of alumina trihydrate. This step is also called precipitation, in which seeded supersaturated sodium aluminate solution is cooled and decomposes to yield alumina trihydrate. It has a large effect on performance of Bayer process plants (e.g. plant capacity, energy consumption, final product quality). Considerable research focused on precipitation has been carried out for improving product yield without sacrificing product quality[1–4].

A satisfactory description of the Bayer precipitation includes four individual crystallization mechanisms which operate simultaneously during the formation of solid phase hydrate in seeded precipitation, i.e., nucleation, growth, agglomeration and breakage including attrition. A realistic model of the Bayer precipitation can be constructed by combining kinetic relations for these mechanisms with material, energy and population balances[1,5].

Nucleation is the formation of new crystals (nuclei) of very small sizes within the solution. These can form spontaneously due to the presence of seed crystals. The latter type is commonly known as “breeding” or “secondary” nucleation. Secondary nucleation is a major source of nuclei in many industrial precipitation processes, and it is an important mechanism which influences the quality and yield of products[1,5].

Sonochemistry is involved with using ultrasound to chemical reaction and has many

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applications in crystallization and precipitation. It has been reported that high-power ultrasound can enhance or alter reactions[6–10]. It is known that the decomposition fraction of precipitation process of diluted sodium aluminate solution can be enhanced by ultrasonic treatment[7,8]. However, the solution treated by ultrasound in the previous works was much diluted than that in practical processes, the ultrasound effect on particle size distribution and particle morphology were not studied, and the influence of parameters on ultrasound enhancement were not very clear. Hence, the present paper is mainly concerned with the effects of ultrasound frequency on precipitation under the conditions similar to those in industry.

2 EXPERIMENTAL

2.1 Experimental Conditions

The temperature, initial α_k, concentration and seeding levels investigated in the present work are all referred to the parameters of an industrial process in Changcheng Aluminium Co. Ltd. Initial α_k and precipitation temperature were considered as the most significant parameters which influenced the precipitation process[5], so these two parameters and the ultrasound frequency were chosen as the factors of an orthogonal experiment. Four levels were designated to each parameter as listed in a $L_{16}(4^5)$ design in Table 1.

Table 1 Experimental conditions defined by the orthogonal experiment by $L_{16}(4^5)$

No.	Factors/levels			No.	Factors/levels		
	Frequency of ultrasound (A)	Temp. (^{o}C) (B)	Initial α_k (C)		Frequency of ultrasound (A)	Temp. (^{o}C) (B)	Initial α_k (C)
1	16 kHz	50	1.55	9	33 kHz	50	2.00
2	16 kHz	55	1.80	10	33 kHz	55	2.20
3	16 kHz	60	2.00	11	33 kHz	60	1.55
4	16 kHz	65	2.20	12	33 kHz	65	1.80
5	No ultrasound	50	1.80	13	50 kHz	50	2.20
6	No ultrasound	55	1.55	14	50 kHz	55	2.00
7	No ultrasound	60	2.20	15	50 kHz	60	1.88
8	No ultrasound	65	2.00	16	50 kHz	65	1.55

2.2 Experimental Procedures

The Concentrated caustic aluminate solutions were prepared by dissolving calculated amount of industrial aluminium trihydroxide (from Changcheng Aluminium Co. Ltd., Zhengzhou) in NaOH solutions (AR) with suitable heating. After completely dissolved, the solutions were carefully filtered so that they were optically clear (no solid nuclei present).

Ultrasound treatment was performed with different ultrasonic converters made by Dahang Ultrasonic Equipment Co. Ltd. (Shanghai). The input power of each ultrasound converter was controlled at (200±20) W, and the time of the treatment was 10 min.

The concentrated sodium aluminate solutions of different initial α_k were diluted to (155±5) g/L. 1 L of solution was put into a 3.5 L reaction tank(ϕ10 cm), keeping a constant agitation rate and temperature. There was a central, 3-blade, 45^o-pitch, 7 cm-diameter stainless propeller in each tank. The propeller was 1.5 cm above the bottom. There was no baffle within the tanks, the agitation rate

was 300 r/min. The same amount of seeds (600 g) was added in each experimental run, and the mean diameter of seeds was 45.8 μm.

12 slurry samples (about 10 L each) were removed at a fixed time interval, from the reaction tank during the run. Each sample was centrifuged, and the particle size distribution of some of the solid phase was determined by a Marlvern Mastersizer 2000 and their SEM photographs obtained by a JSM–5600LV scanning electronic microscope (JEOL, Japan). The α_k of the liquid phase was analyzed by the titration method, the decomposition ratio η was calculated by:

$$\eta = \frac{\alpha_k - \alpha_{k,0}}{\alpha_k}, \tag{1}$$

where $\alpha_{k,0}$ is the initial mole ratio of Na_2O/Al_2O_3, and α_k is the mole ratio of Na_2O/Al_2O_3 of a sample.

3 RESULTS

In order to determine the ultrasound effect on the precipitation process, the decomposition fraction (η) of the solution and particle number percentage with size below 2 μm at the time of 15 h were chosen as the characteristic indexes, the size below 2 μm was commonly considered as the particle size range of nuclei[5] and 15 h was the time when the largest quantity of nuclei created. Results and analysis were shown in Table 2.

Table 2 Results and analysis of the orthogonal experiments

	Experiment No.	A	B	C	η (%)	Particle number percentage (%)
	1	1	1	1	35.8	23.0
	2	1	2	2	32.0	20.3
	3	1	3	3	31.2	15.4
	4	1	4	4	28.1	11.5
	5	2	1	2	32.8	15.6
	6	2	2	1	31.4	14.1
	7	2	3	4	28.1	9.1
	8	2	4	3	27.4	7.7
	9	3	1	3	30.4	12.8
	10	3	2	4	28.1	9.2
	11	3	3	1	31.1	12.3
	12	3	4	2	30.4	8.1
	13	4	1	4	29.0	11.7
	14	4	2	3	30.5	11.0
	15	4	3	2	28.0	7.6
	16	4	4	1	29.6	8.9
η (%)	Average of the first level	31.8	32.0	32.0		
	Average of the second level	29.9	30.5	30.8		
	Average of the third level	30.0	29.6	29.9		
	Average of the fourth level	29.3	28.9	28.3		
Particle number percentage (%)	Average of the first level	17.6	15.8	14.6		
	Average of the second level	11.6	13.7	12.9		
	Average of the third level	10.6	11.1	11.7		
	Average of the fourth level	9.8	9.1	10.4		

The above results show that the decomposition fraction at 15 h can be enhanced by 16 kHz ultrasound treatment, while there are no significant effect at 33 kHz and 50 kHz, i.e., the ultrasonic treatment at 16 kHz can accelerate the decomposition rate in the precipitation process. The difference of average decomposition fraction at 15 h between the level with 16 kHz ultrasonic treatment and the level without ultrasound treatment is 1.9%. The changes of average decomposition fraction versus temperature and initial α_k are considered as linear. The effect of 16 kHz ultrasound treatment on decomposition is equivalent to that of 9.2°C temperature drop or an increase of 0.33 in initial α_k.

Similarly, 16 kHz ultrasound treatment can significantly enhance the particle number percentage at size below 2 μm at 15 h, while the ultrasound treatment at frequency 33 kHz and 50 kHz has little effect on particle size distribution. The difference of particle number ratio between the level with 16 kHz ultrasound treatment and the level without ultrasound treatment is 6%, which is equivalent to the effect of 13.4°C temperature drop or 0.93 of initial α_k increase.

It is shown in Table 2 that both the particle number percentage and the decomposition fraction reach the maximum at run No.1. In order to further study the ultrasound effects on the precipitation process, experiments were conducted to compare the precipitation under the conditions for run No.1 with the corresponding process without ultrasound treatment. The comparison of particle size distribution at 8 h are demonstrated in Fig.1. It is shown that both distributions are of the same mode, but the particle number percentage at size below 2 μm of the product obtained with ultrasound treatment is much larger than that without ultrasound treatment. The changes of particle number percentage below 2 μm with time were demonstrated in Fig.2, showing that the particle number percentage is increased after about 2 h, but the percentage drops a little after 15 h.

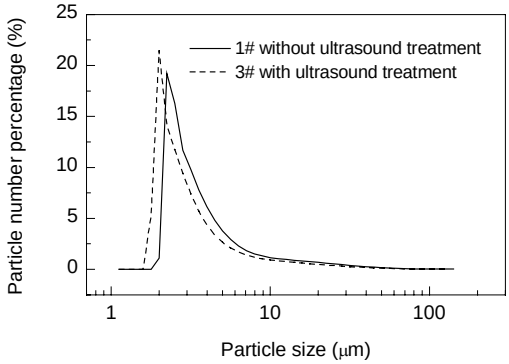


Fig.1 Comparison of the particle size distribution at 8 h of gibbsite obtained with and without ultrasound

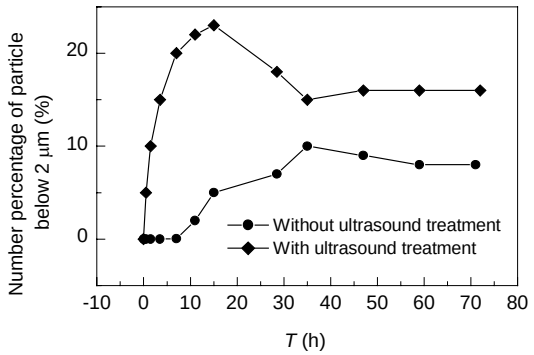
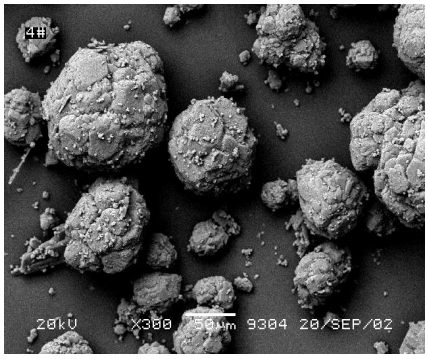


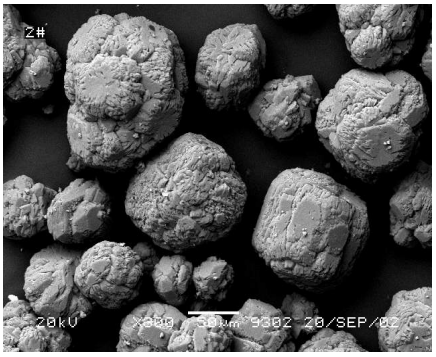
Fig.2 Comparison of the changes with time of particle number at the sizes below 2 μm of gibbsite obtained with and without ultrasound

The SEM photographs (20 kV, ×300) of particles obtained by both processes at 2 h are illustrated in Fig.3. It is shown that the fine particles either adhering on the seeds or being broken off are numerous by the process with ultrasound treatment in contrast to that without ultrasound treatment.

The particle size distribution and SEM photograph show that the ultrasound treatment on sodium aluminate solutions can enhance the particle number with size below 2 μm, i.e., ultrasonication can accelerate the nucleation and increase the number of fine particles.



(a) With ultrasound treatment



(b) Without ultrasound treatment

Fig.3 Comparison of SEM photographs of gibbsite obtained

4 DISSCUSION AND CONCLUSION

The chemical effects of ultrasound (yield or reaction rate improvement, chemical switching, etc.) are mainly based on cavitation[10–12]: during the rarefaction period of the wave, if the acoustic pressure is low enough, “voids” are created in the liquid and bubbles (filled with dissolved gases or liquid vapor) are generated. Under the cavitation conditions the bubbles grow quickly and implode violently. Very high pressure and temperature are generated inside and around the bubbles. That may induce the breakage of chemical bonds and result in the formation of free radicals. Ultrasonication then acts as a “chemical catalyst”. The effect of ultrasound on gibbsite precipitation can also be explained by the generation of some kind of free radicals which can decrease the activation energy of precipitation process. Margulis et al.[9,12] reported that it was much easier to generate free radicals in solution by treating with ultrasound at low frequency than that at high frequency, which lends support to explain why the ultrasound treatment has effect only at 16 kHz. Zhao et al.[7] detected by Raman spectrum that a peak at 540 cm^{-1} disappeared in sodium aluminate solution after ultrasound treatment, which proved the decrease of $Al_2O(OH)_6$ dimer in the solution. The decrease of $Al_2O(OH)_6$ dimer could also be observed during the nucleation process[2]. The mechanism of ultrasound effect on precipitation can be primarily explained as follows: free radicals are generated by cavitation as the solution being treated with ultrasound, subsequently, the free radicals promote the decrease of dimers and then formation of nuclei.

The following conclusions may be drawn:

(1) 16 kHz ultrasound treatment can enhance the rate of gibbsite precipitation from sodium aluminate solutions.

(2) 16 kHz ultrasound treatment can also enhance the secondary nucleation rate in gibbsite precipitation.

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