

Nucleation during gibbsite precipitation with seeds from sodium aluminate solution processed under ultrasound^①

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Abstract: The secondary nucleation during gibbsite precipitation with seeds from sodium aluminate solution processed by ultrasound was examined by particle size distribution(PSD) analyses. Experiments indicate that at low temperature($< 65\text{ }^{\circ}\text{C}$) and with low frequency ultrasound, the precipitation efficiency and also the secondary nucleation can be improved. Solution processed by low frequency ultrasound has more nuclei than common liquor does at low temperature. At $55\text{ }^{\circ}\text{C}$, precipitation efficiency can be improved by 5.31%, and the effect promoted by low frequency ultrasound decreases with the increase of temperature.

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

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1 INTRODUCTION

It is known^[1-4] that nucleation can be hastened by ultrasound during the crystallization of solutions. For sodium aluminate solution with high viscosity and surface tension, primary nucleation is difficult to take place without seeds under industrial conditions^[5-8]. When gibbsite is precipitated from liquor with seeds, there are many secondary nuclei near the defects and active sites of surfaces of seeds and secondary nucleation depends much on the quality of seeds. According to particle distribution data^[9-11], the diameters of new critical nuclei deprived of surfaces of seeds are $1\text{--}3\text{ }\mu\text{m}$.

CHEN et al^[12] have indicated that primary nucleation of sodium aluminate solutions can not be promoted by ultrasound at industrial concentration. Because of the quick formation of crystal units with ultrasound, a lot of secondary nuclei on the surface of seeds can therefore be produced. These nuclei are hexagonal slices with diameter of less than $1\text{ }\mu\text{m}$, and can easily enter liquors by agitation. It is important to study the amount of secondary nuclei, its influence on agglomeration, growth and the particle size distribution(PSD) of gibbsite products, and the appropriate conditions under which the decomposition with seeds of sodium aluminate solutions can be promoted by ultrasound.

2 EXPERIMENTAL

Fresh, supersaturated sodium aluminate solu-

tions($\alpha_K: 1.4\text{--}1.62$, $c(\text{NaOH}) = 4.5\text{--}5.3\text{ mol/L}$) were obtained by dissolving $\text{Al}(\text{OH})_3$ (industry grade from the Henan Branch Aluminium Company) into NaOH (chemistry grade). The liquors were processed for 10 min by low or high frequency ultrasound at reaction temperature, then ploughed quickly into stainless steel reactor. The other experimental conditions were as follows: temperature $55\text{--}65\text{ }^{\circ}\text{C}$, agitation rate 400 r/min and primary seeds concentration 600 g/L.

The seeds and gibbsite samples were washed with distilled water for 3 times, then PSD was analyzed in Mastersizer 2000 apparatus.

3 RESULTS AND DISCUSSION

3.1 PSD affected by breakage

It is suggested by many researchers that the diameters of secondary nuclei are $1\text{--}3\text{ }\mu\text{m}$ during the decomposition of sodium aluminate solution. The investigation on the changes of PSD is very important to the principles of secondary nucleation. During decomposition of sodium aluminate solution with seeds, because of the interaction among seeds, between particles and wall of reactor, and between particles and muddler at agitation condition, the seeds are easily broken. As a result, the amount of fine particles increase and the PSD of seeds and mensuration of nucleation particles are affected. It is necessary to study the influence of breakage on secondary nucleation of sodium aluminate solution processed by ultrasound, especially on PSD of seeds. For higher viscosity of

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liquors and ineluctable nucleation, the breakage of seeds in distilled water is measured qualitatively to review the effect of sodium aluminate solution in this article.

PSD of seeds at 400 r/min and 55 °C in distilled water are shown in Fig. 1. It shows that seeds can be broken because of agitation. PSD of seeds are affected at the beginning of agitation, but after 2 h, it almost keep constant with agitation. It indicates that the breakage of seeds reaches steady on experiment conditions, and does not affect the PSD of seeds obviously during the decomposition of sodium aluminate solution. It is also known from Fig. 1 that the diameter of the broken fine granules is all above 3 μm , and does not affect on the secondary nucleation.

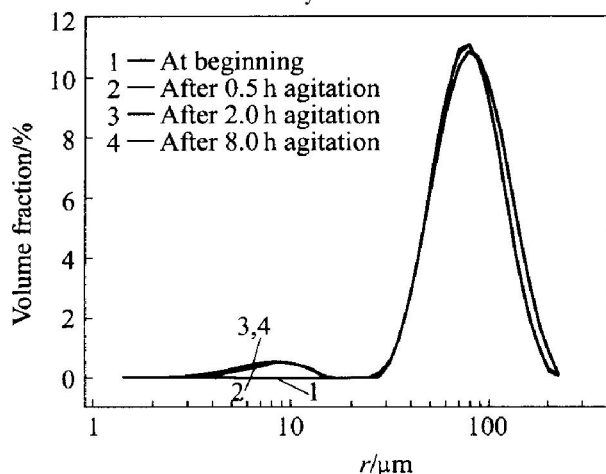


Fig. 1 Particle size distribution (PSD) of seeds in distilled water at 55 °C at agitation rate of 400 r/min

3.2 Influence of temperature on decomposition of sodium aluminate solution

Precipitation efficiency ($\eta/\%$) of sodium aluminate solutions promoted by ultrasound at 50, 55, 60 and 65 °C with time are plotted in Figs. 2–5 respectively. All primary seed concentrations are fixed at 600 g/L, and NaOH concentrations are between 5.0–5.2 mol/L. The reaction periods are all longer than 45 h.

Experiments show that the variation trends of precipitation efficiency of sodium aluminate solutions promoted by ultrasound are similar to that of the common precipitation of liquor. The higher the temperature, the faster the reaction speed and the higher the precipitation efficiency at the beginning of the reaction. There is obvious increment of precipitation efficiency during the gibbsite precipitation processed by low frequency ultrasound compared with that without ultrasound at 50 and 55 °C. For example, the precipitation efficiency by low frequency ultrasound is 5%–6% higher than that without ultrasound after 45 h or later at 55 °C. With increasing the reaction temperature, this kind increment becomes smaller. There is little difference between precipitation ef-

ficiencies at 60 °C, and curves are almost superposed at 65 °C, which indicates that the decomposition of sodium aluminate solution can not be promoted by ultrasound at higher temperature.

It can also be seen from Fig. 3 that there is no

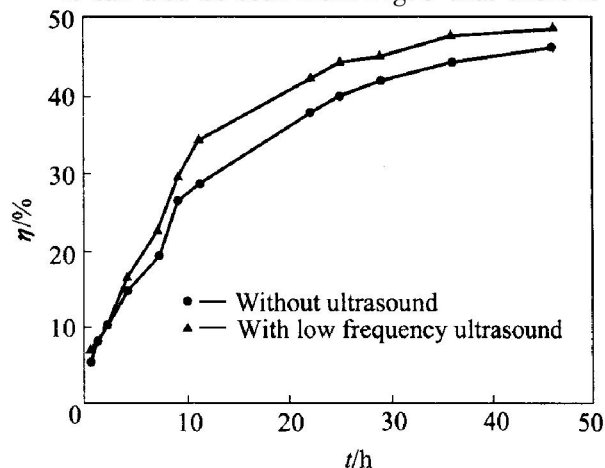


Fig. 2 Change of precipitation efficiency of sodium aluminate solution with time at 50 °C

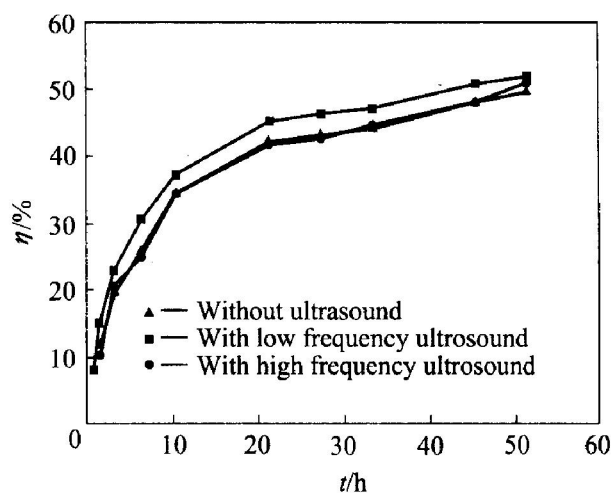


Fig. 3 Change of precipitation efficiency of sodium aluminate solution with time at 55 °C

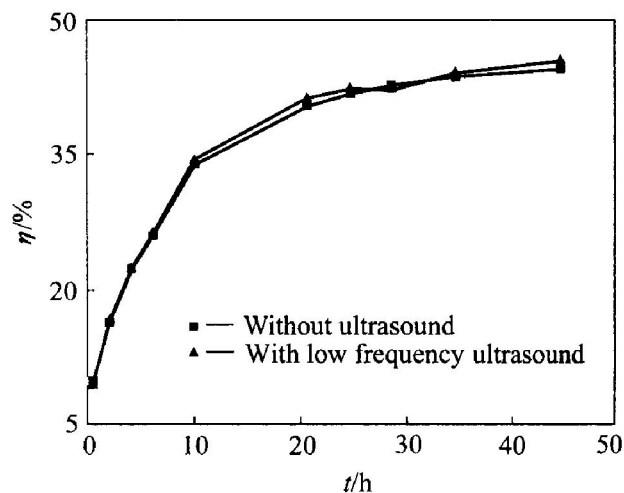


Fig. 4 Change of precipitation efficiency of sodium aluminate solution with time at 60 °C

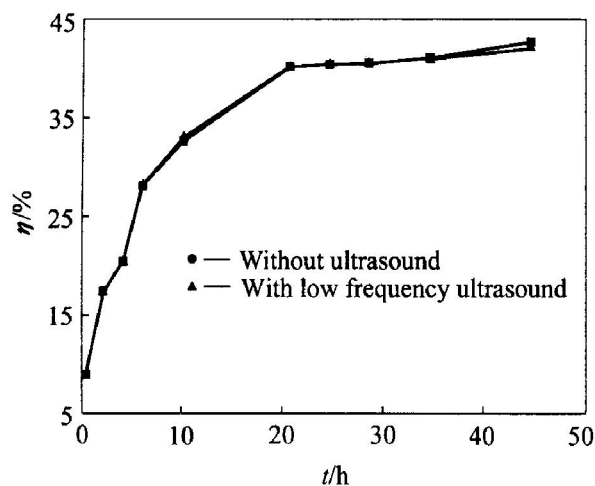


Fig. 5 Change of precipitation efficiency of sodium aluminate solution with time at 65 °C

difference between precipitation efficiency processed with high frequency ultrasound and that without ultrasound at 55 °C, which indicates that high frequency ultrasound can not promote the decomposition of sodium aluminate solutions with seeds.

3.3 PSD of seeds during decomposition of sodium aluminate solutions processed by ultrasound

It can be known from all PSD curves from Fig. 6 to Fig. 12 that the diameter of the least granules formed from sodium aluminate solutions processed by ultrasound is larger than 1 μm. It indicates that the critical diameter of secondary nuclei which enter into liquor because of agitation does not change with ultrasound frequency.

Figs. 6 and 7 show the PSD of gibbsite products corresponding to experiments of Figs. 3, 4 and 5 after 45 h agitation respectively. It can be discovered from Fig. 6 that the 1–10 μm range in PSD are obviously different from that of products yielded with ultrasound and without ultrasound at 55 °C. There is an obviously broad peak at this area with low frequency ultrasound, while a weak peak with high frequency ultrasound, and almost no particle less than 3 μm on common condition. It can be indicated from Fig. 7 that there is a little distribution between 1 μm and 3 μm at 60 °C with low frequency ultrasound, and almost no distribution in this range at 65 °C. All these results show that whether the frequency is high or low, the PSD of products can be affected by ultrasound to a certain degree. At low temperature and with low frequency ultrasound, there are more fine nuclei than those in common precipitation. The higher the temperature, the less the fine nuclei. At high temperature and with high frequency ultrasound, the precipitation efficiency and fine nuclei are almost the same as those of common precipitation. From above results, conclusions can be drawn that ultrasound

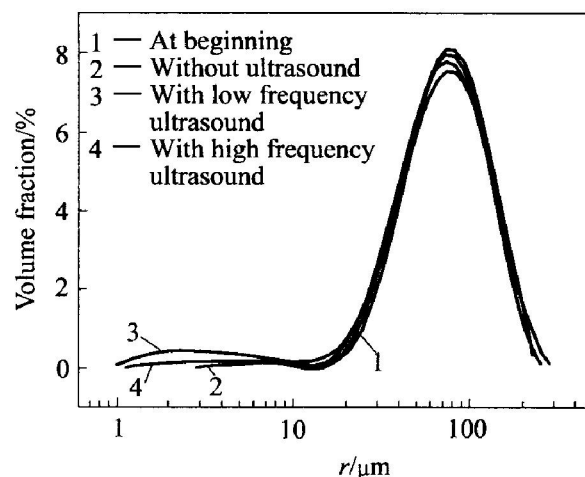


Fig. 6 PSD of product at seed concentration of 600 g/L, $\alpha_k = 1.58$, 55 °C and $c(\text{NaOH}) = 5.0 \text{ mol/L}$

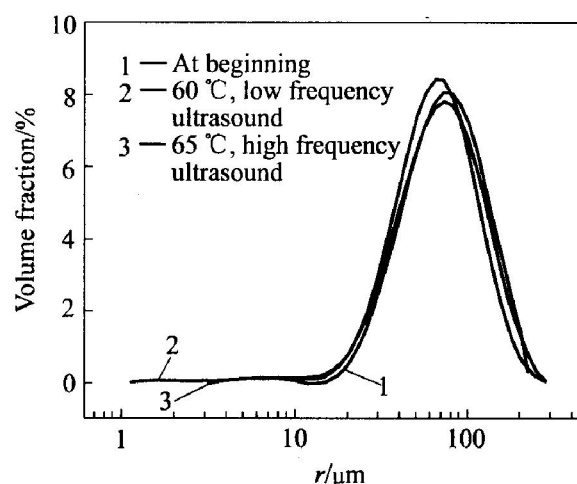


Fig. 7 PSD of product at seed concentration of 600 g/L, $\alpha_k = 1.64$, $c(\text{NaOH}) = 5.2 \text{ mol/L}$

with low frequency can promote the decomposition of sodium aluminate solution with seeds at low temperature by facilitating secondary nucleation on surfaces of seeds at the beginning of decomposition.

The PSD of gibbsite from liquor processed by low frequency ultrasound at different temperatures (45–65 °C) are plotted in Figs. 8, 9 and 10, respectively. It can be seen that the distributions in 1–3 μm range are increased with increasing precipitation time. But the volume fraction in this area at 65 °C is less than that at 45 °C and 55 °C. It indicates that at low temperature, more fine nuclei of 1–3 μm can be promoted by low frequency ultrasound, and the promotion to secondary nucleation will be decreased with decreasing temperature.

PSD at low primary seed concentration (200 g/L) with and without ultrasound in Fig. 11 and Fig. 12 shows that there are no obvious difference except that the main peaks in fine size range with ultrasound are smaller than those without ultrasound.

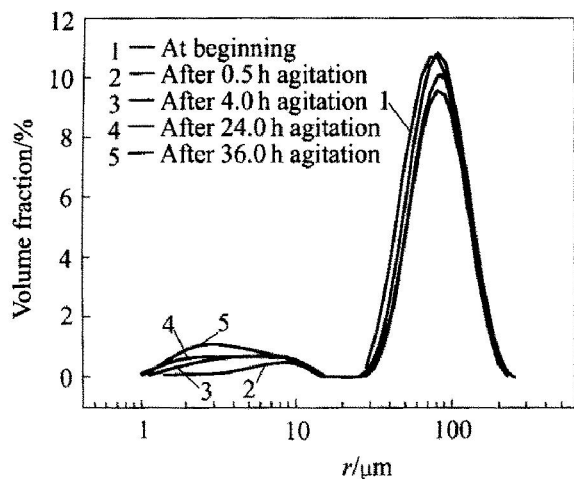


Fig. 8 Evolution of PSD with time at seed concentration of 600 g/L, $\alpha_k = 1.435$, 45 °C, $c(\text{NaOH}) = 4.5 \text{ mol/L}$ with low frequency ultrasound

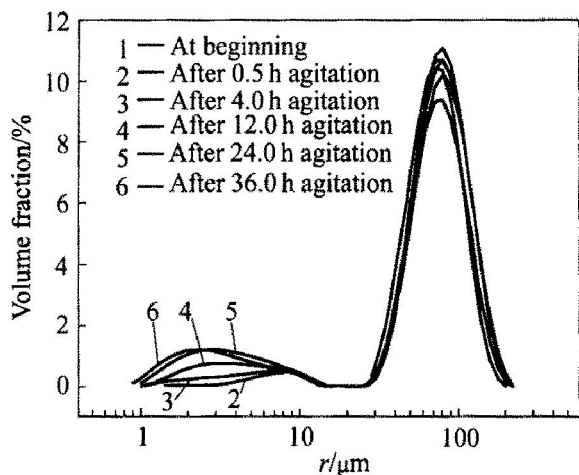


Fig. 9 Evolution of PSD with time at seed concentration of 600 g/L, $\alpha_k = 1.435$, 55 °C, $c(\text{NaOH}) = 4.5 \text{ mol/L}$ with low frequency ultrasound

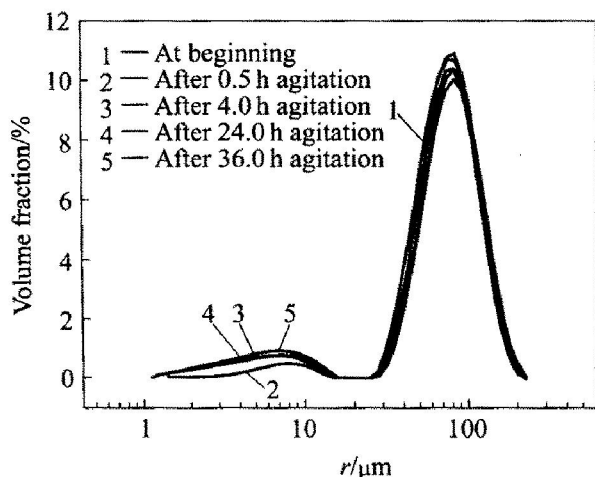


Fig. 10 Evolution of PSD with time at seed concentration of 600 g/L, $\alpha_k = 1.435$, 65 °C, $c(\text{NaOH}) = 5.3 \text{ mol/L}$ with low frequency ultrasound

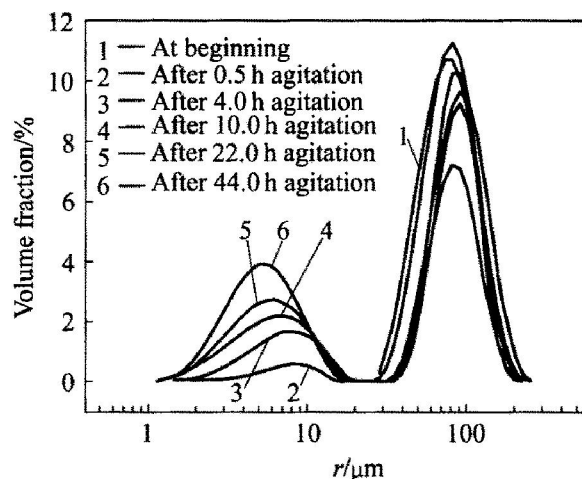


Fig. 11 Evolution of PSD with time at seed concentration of 200 g/L, $\alpha_k = 1.410$, 55 °C, $c(\text{NaOH}) = 4.5 \text{ mol/L}$ with low frequency ultrasound

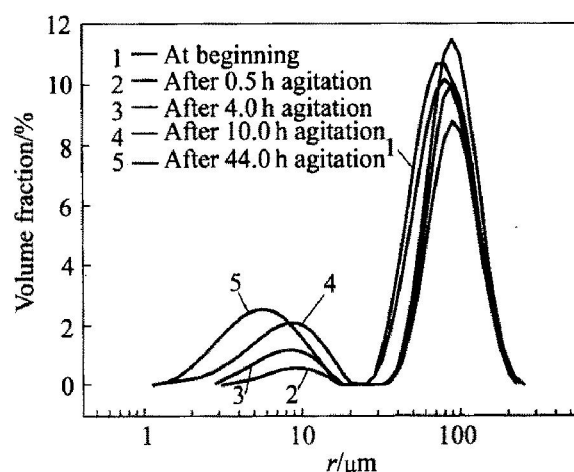


Fig. 12 Evolution of PSD with time at seed concentration of 200 g/L, $\alpha_k = 1.435$, 55 °C, $c(\text{NaOH}) = 4.9 \text{ mol/L}$ with low frequency ultrasound

Raman spectrum of sodium aluminate solution processed by 33 kHz ultrasound measured by $\text{Li}^{[4]}$ indicates that $\text{Al}_2\text{O}(\text{OH})_6^{2-}$ is dismissed and changed to other transition anions by 33 kHz ultrasound in solution so that the nucleation and growth of crystal can be accelerated, then the growth rate of growth unit is increased and the formation rate of hexagonal flakes is accelerated on the surface of seeds. Combined with SEM study of seeds from sodium aluminate solution^[6], it can be concluded that a lot of secondary nuclei can be promoted when gibbsite precipitation with seeds is processed by low frequency ultrasound. The diameters of new secondary nuclei on the surfaces of seeds are below 1 μm with thickness in nanometer grade. These new secondary nuclei enter liquors because of agitation. At low decomposition temperature, the secondary nucleation can increase the precipitation efficiency and the amount of 1–3 μm fine

particles.

4 CONCLUSIONS

1) The decomposition of sodium aluminate solutions can be promoted by ultrasound at low temperature.

2) A lot of fine secondary nuclei whose diameters are about 1 ~ 3 μm can be produced.

3) Ultrasound can not change the critical diameter at which the secondary nuclei enters liquor.

4) At low temperature (below 60 $^{\circ}\text{C}$), the PSD patterns of seeds during decompositions with ultrasound are not the same as that without ultrasound, and more fine granules exist with ultrasound.

5) At high temperature (above 65 $^{\circ}\text{C}$), there are almost no difference between the PSD patterns with and without ultrasound. It can be suggested that the increment of precipitation efficiency of sodium aluminate solutions with low frequency and at low temperature comes from the promotion of secondary nucleation when solutions are processed by ultrasound.

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