Precipitating sandy aluminium hydroxide from sodium aluminate solution by the neutralization of sodium bicarbonate

Yan Li, Yifei Zhang, Chao Yang, Yi Zhang

* Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

ARTICLE INFO

Article history:
Received 19 December 2008
Received in revised form 24 March 2009
Accepted 25 March 2009
Available online 31 March 2009

Keywords:
Precipitation
Sodium aluminate solution
Sodium bicarbonate solution
Aluminium hydroxide

ABSTRACT

In the sinter process for alumina production, it is still difficult to produce sandy aluminium hydroxide by the carbonation of sodium aluminate solution. Therefore, a precisely controllable and feasible process for the precipitation of sandy aluminium hydroxide from the supersaturated sodium aluminate solution neutralized by sodium bicarbonate aqueous solution is proposed for the first time, in which the neutralization reagent (NaHCO₃) can be efficiently recycled by the carbonation of the produced sodium carbonate aqueous solution. The influencing factors of the precipitation, i.e. the pH value, the initial NaOH concentration, the temperature and the addition rate of neutralization agent, were investigated. All the aluminium hydroxides precipitated in the research were identified as gibbsite type. The gibbsite products had regular globular morphology and narrow size distribution whose minimum residue on a 44 µm mesh was 92–94%.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The Bayer process and the sinter process are commonly used for the production of alumina from bauxite ores, in which alumina is obtained by the calcination of aluminium hydroxide, and the quality of the alumina largely depends on that of the aluminium hydroxide. The Bayer process is basically used for the extraction of alumina from the bauxite ores with the mass ratio of alumina to silica (A/S) above 9 (Misra, 1986). In the process, aluminium hydroxide is precipitated from the supersaturated sodium aluminate solution by supplying large quantity of gibbsite seed particles, and the spent caustic solution is recycled to extract alumina from the bauxite. The sinter process is widely used to process the poor-grade diasporic bauxite ores by sintering the bauxite pre-mixed with sodium carbonate solution. The precipitation of aluminium hydroxide is promoted by bubbling carbon dioxide gas into the supersaturated sodium aluminate solution, i.e., the carbonation process (Misra, 1986, Zhao et al., 2004), meanwhile the caustic in the sodium aluminate solution is converted to sodium carbonate which is recycled to extract alumina from the bauxite in the sintering process (Bi, 2006). Before 1970s, alumina was produced in two different grades, i.e. floury and sandy. During the last decades, the sandy alumina was more desirable because of the increased concerns of environmental influence and energy cost in electrolytic aluminium industry (Arnswald et al., 1995, Gnyra and Brown, 1975). In order to produce eligible sandy alumina with the minimum residue of 90% on a 44 µm mesh, aluminium hydroxide obtained from sodium aluminate solution must have a minimum residue of 92–94% on a 44 µm mesh (Satapathy and Padhi, 1990). The eligible sandy aluminium hydroxide can be obtained by the Bayer process, however, in which the crystallization of aluminium hydroxide has a lower recovery ratio about 50% during the unusually long precipitation period about 48–72 h (Addai-Mensah and Ralston, 1999). For the sinter process, the decomposition ratio of the sodium aluminate by the carbonation is over 90% within 4 h, but the carbonation process is difficult to produce eligible sandy aluminium hydroxide with low fine particle content and narrow size distribution (Wang et al., 2005). In the gas–liquid reactive crystallization process of the carbonation, the low solubility of the precipitated aluminium hydroxide crystals and the relatively high concentration of carbon dioxide near the interface in the solution result in high local supersaturation, and further lessen the size of the precipitated aluminium hydroxide particles. Wachi and Jones (Wachi and Jones, 1991) also presented the high fine particle content was induced by the high resistance of gas–liquid interfacial mass transfer and the high interfacial supersaturation. Up to now, there is no successful example for producing sandy aluminium hydroxide from the sodium aluminate solution by the carbonation process.

For the precipitation of sandy aluminium hydroxide in the sinter process, a precisely controllable and feasible precipitation process of supersaturated sodium aluminate solution neutralized by sodium bicarbonate aqueous solution but carbon dioxide is proposed in this research. In the novel process, part of the sodium carbonate solution produced in the precipitation can react with carbon dioxide to...
regenerate sodium bicarbonate (Hou, 1942), whilst the other sodium carbonate solution can be used to extract alumina from bauxite ores by the sintering process (Misra, 1986; Bi, 2006). Compared to the gas–liquid reactive crystallization of the carbonation process, the liquid–liquid reactive crystallization using sodium bicarbonate aqueous solution to neutralize the sodium aluminate solution is generally quite controllable, especially in modulating the supersaturation of the solution, and has significant advantages in the production of the precipitate with narrow size distribution and qualified morphology.

The reactions taking place in the proposed process are as follows:

1. \( \text{HCO}_3^- \) neutralizes free hydroxyl in the supersaturated sodium aluminate solution.

\[
\text{HCO}_3^- + \text{OH}^- = \text{CO}_3^{2-} + \text{H}_2\text{O}
\]  

2. \( \text{Al(OH)}_3^- \), the dominating aluminate ions in the supersaturated sodium aluminate solution under the condition of pH > 10 (Li et al., 2005), decomposes to \( \text{OH}^- \) and \( \text{Al(OH)}_3 \) precipitate.

\[
\text{Al(OH)}_3^- = \text{Al(OH)}_3 + \text{OH}^- 
\]

In the above process to produce aluminium hydroxide, both reactions of the neutralization (1) and the decomposition (2) mainly take place in the bulk solution. The progress of the reaction (2) crucially depends on the reaction (1) which is a fast reaction of neutralization and its progress can be easily controlled by the addition of sodium bicarbonate aqueous solution. It suggests that the supersaturation of the aluminate solution, as well as the rate of the precipitation could be crucially operated to produce qualified sandy aluminium hydroxide with narrow size distribution and qualified morphology. So that the influencing parameters of the precipitation process, i.e. pH value of the solution, caustic soda concentration, precipitation temperature and the addition rate of sodium bicarbonate aqueous solution, were investigated.

2. Materials and methods

Precipitation experiments were performed in a 400 mL cylindrical stainless steel crystallizer with a mechanical stirrer, a pH electrode and an inlet for sodium bicarbonate aqueous solution. The crystallizer was immersed in a water bath thermostatically controlled within \( \pm 0.5 \) °C.

Aluminium hydroxide (AR), sodium hydroxide (AR), sodium bicarbonate (AR) and deionized water were used in the experiments. Sodium bicarbonate aqueous solution was prepared by the dissolution of sodium bicarbonate in deionized water, whilst sodium bicarbonate solution by the dissolution of aluminium hydroxide into hot alkaline solution. The NaOH concentrations of the prepared sodium aluminate solution varied while the molar ratios of NaOH to Al \( \text{(OH)}_3 \) (MR) were constant at 1.5. The concentrations of the aluminate solutions are listed in Table 1, in which C is the caustic concentration in \( \text{g NaOH} / \text{L} \), \( A \) is the concentration of aluminium hydroxide in \( \text{g Al} \text{(OH)}_3 / \text{L} \) while \( A_{\text{eq}} \) the equilibrium concentration of \( \text{Al(OH)}_3 \) at the crystallization temperatures, is calculated by the method proposed by the reference (Misca and White, 1971).

50 mL of the supersaturated sodium aluminate solution with a certain NaOH concentration in the crystallizer was agitated at 300 rpm (sufficient to bring the slurry in full suspension). When the sodium aluminate solution was heated to a certain temperature within \( \pm 0.5 \) °C, a measured volume of freshly prepared sodium bicarbonate aqueous solution was added to the crystallizer at constant rate, e.g. 1 mL/min, until the set pH value reached. After the start of the addition of sodium bicarbonate solution, the samples of the slurry were taken and filtered, and the \( \text{Al(OH)}_3 \) content of the filtrate was analyzed by the ICP-AES method. To obtain the purified samples of the precipitates, the filter cakes were re-dispersed in hot deionized water, filtered and dried at 80 °C for 24 h.

The phase of the precipitates was identified by X-ray diffraction, using the Siemens D5000 X-ray diffractometer with CuK\( \alpha \) radiation. The morphology of the precipitates was observed by the scanning electron microscope images, using a JEOL JEM 2100F instrument operated at 200 kV. The particle sizes distribution of the precipitates was measured by a Malvern Mastersizer-Laser particle size analyzer.

3. Results and discussion

3.1. Titration curves

The titration of the supersaturated sodium aluminate solution by sodium bicarbonate aqueous solution at the rate of 1 mL/min was carried out (Expt.1 in Table 1). The titration curve (pH vs \( V_{\text{NaHCO}_3} \)) at 70 °C is shown in Fig. 1. Different from the reference (Panias and Krestou 2007), there are four distinct regions in the diagram. In Region 1 (pH > 13.46), the spontaneous chemical reaction between the added \( \text{HCO}_3^- \) ions and the free hydroxide ions in the supersaturated sodium aluminate solution takes place. At the end of Region 1, or the start of Region 2, aluminium hydroxide begins to precipitate, which is indicated by the change of the color of the solution from clear to opaque, and the obvious increase of the buffering capacity of the aluminate solution. In Region 2 (13.38 < pH < 13.46), because of the
high buffering capacity of the supersaturated sodium aluminate solution, the pH value is almost constant, which suggests that the rate of the HCO$_3^-$ addition was basically equal to the rate of the hydroxide ions liberation in the solution according to the chemical reaction (2). In Region 2, the transformation of the opaque phase into a white precipitate was easily detected in the experiment, indicating the formation of solid particles in the aqueous solution. In Region 3 (10.31 < pH < 13.38), the pH value decreases with the addition of HCO$_3^-$, which implies that the rate of the HCO$_3^-$ addition is higher than the rate of hydroxide ions liberation, therefore aluminium hydroxide can continuously precipitate out of the solution. In Region 4 (pH < 10.31), with the further addition of HCO$_3^-$, the concentration of Na$_2$CO$_3$ in the suspension increases gradually and is above its equilibrium concentration. After the filtration of the suspension, Na$_2$CO$_3$ precipitates from the filtrate and the filtrate becomes gelatinous.

3.2. Aluminate decomposition curve

The decomposition ratio of sodium aluminate in the solution is defined as

\[
\eta = \frac{(m_0 - m_t)}{m_0}
\]

Where:

\( \eta \) – the decomposition ratio of the sodium aluminate in the solution.

\( m_0 \) – the mass of aluminium hydroxide in the initial sodium aluminate solution.

\( m_t \) – the mass of aluminium hydroxide in the solution at time \( t \).

The decomposition curves of the sodium aluminate solution at 70 °C under various initial NaOH concentrations (from Expt.5 to Expt.9 in Table 1) are presented in Fig. 2. These curves show the effects of the added volume of sodium bicarbonate aqueous solution and the initial NaOH concentrations on the decomposition ratio of the sodium aluminate in solution. In the experiments shown in Fig. 2, it was found that the decomposition ratio of sodium aluminate was increasing with the addition of the sodium bicarbonate, and that the final decomposition ratio was determined by the amount of sodium bicarbonate added to the sodium aluminate solution. Furthermore, when the volume of the added sodium bicarbonate aqueous solution was less than 60 mL, the decomposition ratio of sodium aluminate in the solution was zero, namely, the aluminium hydroxide did not begin to precipitate, corresponding to the Region 1 in Fig. 1. As the volume from 60 mL up to 80 mL, the aluminate in solution began to decompose, while the decomposition rate was slow and equal to the rate of the HCO$_3^-$ addition, which was in accordance with the Region 2. As soon as the volume from 80 mL up to 120 mL, a steep increase of the decomposition ratio was observed, and this was consistent with the sharp decrease of pH in Region 3. From then on, the upward trend of the decomposition ratio was not so apparent as before. Fig. 2 also shows that the lower the initial NaOH concentration of the solution, the larger the decomposition ratio of the sodium aluminate. It can be explained as that the less the total amount of the initial Al(OH)$_4^-$ in the system, the quicker the complete of the reactions (1) and (2).

3.3. Phase identification of aluminium hydroxide precipitate

The washed precipitates dried at 80 °C for 24 h were examined for the crystal phase using XRD technique. The phase compositions of the precipitates from sodium aluminate solutions at the various final pH values of the solution (Expt.12, 14, 15 in Table 1) and precipitation temperatures (from Expt.10 to Expt.13 in Table 1) were identified as the typical gibbsite type of aluminium hydroxide. Furthermore, the same XRD patterns were also observed for all the precipitates produced in this research.

3.4. Particle size distribution of aluminium hydroxide precipitate

The contrast experiments using two different neutralization agents, namely carbon dioxide and sodium carbonate solution were carried out in the same crystallizer to compare the difference of their precipitates. The particle size distribution of the two precipitates is shown in Fig. 3. It was observed that the gibbsite obtained from the process of carbon dioxide neutralization had the bimodal particle size distribution, which was similar to that of the industrial gibbsite precipitated by the carbonation process. However, the gibbsite from the process of sodium bicarbonate solution neutralization gave the monomodal particle size distribution. Thus, the process of sodium bicarbonate solution neutralization would be more potential to produce the gibbsite with qualified narrow size distribution from sodium aluminate solution.

The addition rate of the NaHCO$_3$ aqueous solution into the sodium aluminate solution has significant influence on supersaturation, especially the local supersaturation around the droplet of the NaHCO$_3$ solution, and then, on the particle size distribution of the produced crystals. It was observed that a colloidal suspension was produced in this research. Three experiments were carried out at
different addition rates of sodium bicarbonate aqueous solution, i.e. 0.5 mL/min, 1 mL/min and 2 mL/min (from Expt.2 to Expt.4). The particle size distributions of the crystals precipitated at the three different addition rates are shown in Fig. 4. The median particle size of the crystals increased with the decrease of the addition rate of the sodium bicarbonate aqueous solution, e.g., from 57 µm with the addition rate at 2 mL/min to 81 µm at 1 mL/min, and over 100 µm at 0.5 mL/min. It can be extrapolated that the decrease of the nucleation rate with the slowness of the addition rate of the sodium bicarbonate aqueous solution was more significant than the decrease of the crystal growth and agglomeration rates in the precipitation process. In addition, it can be observed that 1 mL/min is a moderate addition rate to produce gibbsite with a minimum residue of 92–94% on a 44 µm mesh and a median diameter between 80 and 100 µm.

The NaOH concentration or the aluminate concentration (MR was constant at 1.5 in the research) is another important factor for the precipitation of gibbsite by the sodium bicarbonate neutralization process. The particle size distributions of gibbsite precipitated at various NaOH concentrations (Expt.5 to Expt.9 and 12 in Table 1) are presented in Fig. 5. The lower initial NaOH concentration in the sodium aluminate solution resulted in more fine particles precipitated (Fig. 5), which was likely to be attributed to the less crystal growth and agglomeration rates, and the formation of excess secondary nuclei at a lower Al(OH)₃ concentration.

The effect of temperature on the median particle size ($d_{50}$) of gibbsite precipitates by the sodium bicarbonate neutralization process was studied at $MR = 1.5$, and initial NaOH concentration of 150 g/L in the sodium aluminate solution. Under the precipitation temperature ranging from 50 to 80 °C (Expt.10 to Expt.13 in Table 1), the variation of median particle sizes ($d_{50}$) against the precipitation temperatures is shown in Fig. 6. It was found that the $d_{50}$ increased rapidly at the precipitation temperature ranging from 50 to 70 °C, and then did slowly above 70 °C. It is known that particle enlargement is promoted by crystal growth and agglomeration, and the growth rate of gibbsite crystals is very slow, typically $\sim 5 \times 10^{-10} \text{ m/s}$, so that the crystal agglomeration is the dominant mechanism controlling the size and the morphology of the gibbsite product (Ilievski and Livk, 2006). Then the elevation of the agglomeration rate is used as an important method to counter the generation of fine particles and to maximize the production of eligible sandy aluminium hydroxide. And the precipitation temperature which improves the gibbsite agglomeration in the sodium aluminate solution will also enlarge the size of the gibbsite product. Thus, the particle size ($d_{50}$) of the aluminium hydroxide precipitated from the sodium aluminate solution by the sodium bicarbonate neutralization process obviously increased with the temperature under the experimental conditions.

The gibbsite products precipitated from the sodium aluminate solution by the sodium bicarbonate neutralization process under the various initial concentrations of sodium aluminate solution and addition rates of the sodium bicarbonate solution investigated in the research basically gave the monomodal particle size distribution, as shown in Figs. 3, 4 and 5, which was decidedly different from the bimodal particle size distribution of the gibbsite produced by the carbonation process (Wang et al., 2005). It significantly suggests that the process for the precipitation of sandy aluminium hydroxide from the supersaturated sodium aluminate solution neutralized by sodium bicarbonate aqueous solution was precisely controllable.

### 3.5. Morphology of aluminium hydroxide precipitate

From the scanning electron microscopic images of the typical gibbsite precipitates in this research (Fig. 7), it is suggested that the precipitate was made up of the regular and globular particles in uniform size, and there were quite few fine particles in the precipitates, which was in accordance with the narrow size distribution of the precipitate. Furthermore, the particles were agglomerated by the hexagonal prism shaped crystals, which implied that the morphology of the product was similar to that of the precipitate from the carbonation process (Watling, 2000).
It is known that gibbsite grown from sodium aluminate solution shows the very large dispersion in growth morphology and crystal size (Sweegers et al., 2001). Under industrial conditions, gibbsite often grow into the agglomerates of either hexagonal tablets or hexagonal prisms shaped crystals (Fleming et al., 2000). The agglomerates of hexagonal tablets usually grew from seeded sodium aluminate solutions, but the agglomerates with well-formed hexagonal prismatic faces were often derived from the carbonation of sodium aluminate solutions (Watling, 2000).

In the precipitation of gibbsite from the sodium aluminate solution by the sodium bicarbonate neutralization process, the hexagonal prismatic crystals of gibbsite, as in the carbonation process, were formed through the preferential growth of the basal faces, and then these prisms actinomorphically agglomerated.

4. Conclusions

The process for precipitating aluminium hydroxide from sodium aluminate solution neutralized by sodium bicarbonate solution has been investigated, which has several advantages compared with the carbonation process in the sinter process of alumina production. Different from the bimodal particle size distribution of the precipitate from the carbonation process, the precipitate from the proposed process has monomodal particle size distribution. The precipitate with monomodal particle size distribution and a minimum residue of 92–94% on a 44 µm mesh can be produced under the various initial concentrations of sodium aluminate solution and moderate addition rates of the sodium bicarbonate solution. Furthermore, part of the sodium carbonate solution produced in the precipitation process can react with carbon dioxide to regenerate the sodium bicarbonate, whilst the other sodium carbonate solution can be recycled to extract alumina from bauxite ores by the sintering process, therefore, the precipitation process is feasible for the industrialization.

The aluminium hydroxide produced by the process is the typical gibbsite. The morphology of the gibbsite is regular and quite globular particles. And the particles are the actinomorphic agglomerates of hexagonal prism shaped crystals, as the same as that produced by the carbonation process.

Acknowledgment

The authors acknowledge the National Basic Research Program of China (973 project 2007CB613501) and the National Key Technologies R & D Program of China (2006BAC02A05) for funding this work.

References


