Effect of Lithium on the Seed Precipitation Process

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Abstract

The bauxite deposits in the Henan and Shanxi regions of China are rich in lithium content. During the digestion process, lithium enters the sodium aluminate solution, where lithium ions, as impurity ions, negatively affects the precipitation process. This study investigates the behaviour of lithium ions during seed precipitation, thus clarifying the precipitation patterns of lithium during the process. The results acquired indicate that during the initial stage of precipitation, lithium ions rapidly precipitate from the sodium aluminate solution. With a precipitation time of 1 hour, the precipitation rate of lithium exceeds 90 %, and at 2 hours, it exceeds 99 %. Lithium ions significantly influence the microstructure of aluminium hydroxide, with fine particles either existing independently or adhering to the surface of larger aluminium hydroxide crystals, leading to product particle refinement. The presence of lithium in the aluminium hydroxide product affects both its purity and strength; moreover, higher lithium content results in an increased attrition index of alumina and reduced product strength.

Keywords: Lithium ions, Seed precipitation, Precipitation rate.

1. Introduction

The seed precipitation of sodium aluminate solution is one of the key processes in alumina production with Bayer process, significantly affecting the process output, quality of alumina products, and overall technical indicators. It is generally recognized [1] that when the Li_2O content in alumina products is controlled below 0.05 %, no negative impact will be exerted on the technical-economic indicators or stable operation of aluminium smelters. By reverse calculation, the corresponding lithium ion concentration in the pregnant liquor is approximately 0.02 g/L. However, in some Chinese alumina refineries using high-lithium bauxite, the Li^+ concentration in the pregnant liquor even reaches 0.15 g/L, which not only causes production issues but also creates opportunities for lithium extraction from the system. Domestic and international researchers have conducted studies on the influence of lithium ions on the precipitation process. Prestudge [2] observed that during the precipitation of aluminium hydroxide by adding sodium hydroxide to aluminium chloride, Li^+ ions could modify the structure of pseudo-boehmite. Xiaobin Li [3] suggested that in the seed precipitation process of diaspore-type bauxite for alumina production, Li^+ ions in the solution had no impact on the precipitation rate or particle size distribution (PSD). Wenqiang Huang [4] investigated the impact of lithium ions on the seed precipitation process and concluded that lithium ions could enhance the precipitation rate of sodium aluminate solution while increasing the lithium content in the products. Since lithium-containing aluminium hydroxide preferentially nucleates during precipitation, the nucleated particles are very fine, leading to a significant increase in the total quantity of particles in the sodium aluminate solution. However, the influence of lithium ions on the seed precipitation process of sodium aluminate solution has not been systematically investigated.

This study investigates the influence of lithium ions on the seed precipitation process in sodium aluminate solution under the existing precipitation system for producing diaspore-type bauxite with the Bayer process. It examines the distribution patterns of lithium ions during precipitation and reveals the reaction behaviour of lithium ions as well as the migration and transformation mechanisms. The study aims to provide a theoretical foundation for the efficient separation, enrichment, and extraction of lithium from sodium aluminate solutions.

2. Change in Lithium Ion Concentration During Precipitation Process

Under the precipitation conditions of an initial temperature of 69 °C, a final temperature of 54 °C, seed dosage of 500 g/L, and a precipitation time of 2 hours, the influence of different lithium ion concentrations (0.05 g/L and 0.5 g/L) on the lithium precipitation rate during seed precipitation was investigated using green liquor, as shown in Figure 1, for the following conditions: an initial precipitation temperature of 69 °C, a final precipitation temperature of 54 °C, a seed dosage of 500 g/L, and a precipitation duration of 2 hours.

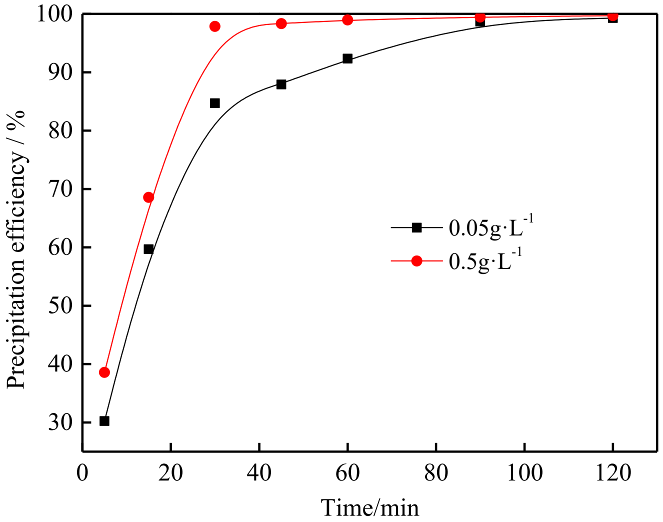

Figure 1. Impact of precipitation time on lithium precipitation rate from sodium aluminate solution.

Figure 1 shows that as the precipitation reaction proceeds, the lithium precipitation rate increases rapidly, with higher lithium concentrations in the green liquor leading to greater precipitation rates. At a precipitation time of 60 minutes, the lithium precipitation rate exceeds 90 %, and at a precipitation time of 2 hours, it exceeds 99 %, indicating that nearly all lithium ions in the solution have entered the aluminium hydroxide particles. This demonstrates that lithium ions enter the products during the initial stage of precipitation, and their behaviour in the alumina production process is a one-way process without cyclic accumulation.

Figure 2 shows the impact of lithium ion concentration on the precipitation rate during the initial precipitation stage, with the following conditions: an initial precipitation temperature of 69 °C, a final precipitation temperature of 54 °C and a seed charge of 500 g/L. It can be seen that during the initial precipitation stage, the precipitation rate of sodium aluminate solution increases with the rise of the lithium ion concentration in the solution, and the higher the lithium ion concentration, the more pronounced its effect on the precipitation rate. At a precipitation time of 2 hours, when the lithium ion concentration in green liquor is 0.05 g/L, the precipitation rate is 21.65 %, whereas at a lithium ion concentration of 0.5 g/L in green liquor, the precipitation rate reaches 23.70 %. This demonstrates that increasing the lithium ion concentration in the solution enhances the seed precipitation rate of sodium aluminate solution in the initial precipitation stage.

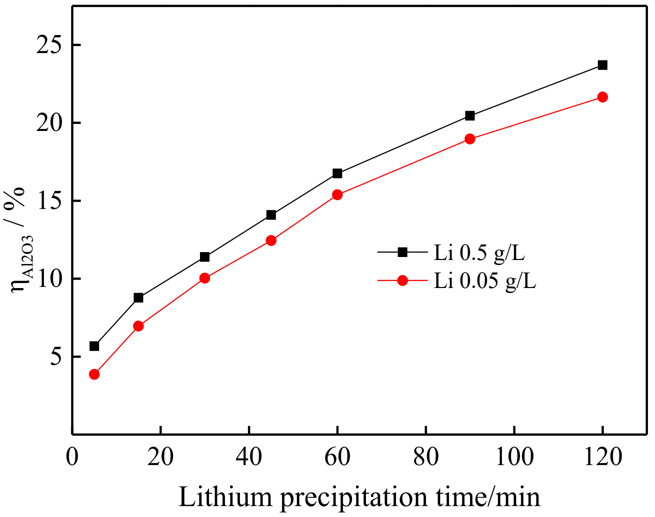

Figure 2. Impact of lithium ion concentration on the precipitation rate during initial precipitation stage.

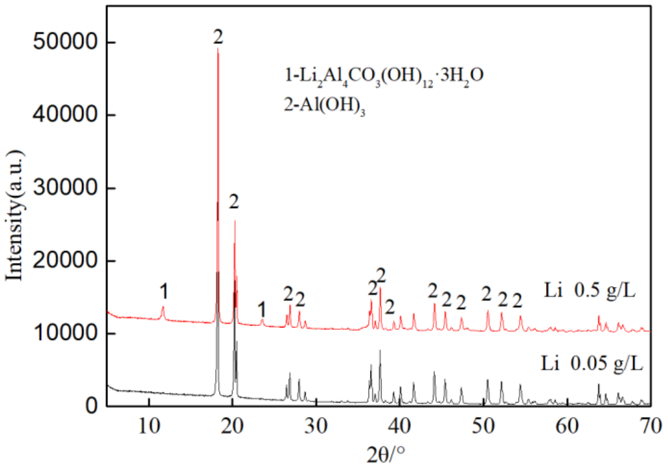

Figure 3. Phase composition of aluminium hydroxide at 2 hours of precipitation.

Figure 3 shows the phase composition of aluminium hydroxide at 2 hours of precipitation. As can be seen from the figure, compared with the seed, the phase composition of aluminium hydroxide undergoes significant changes at 2 hours of precipitation. When the lithium ion concentration in the green liquor is 0.05 g/L, the characteristic peaks of $Li_2Al_4CO_3(OH)_{12}\cdot 3H_2O$ appear in the product, indicating that lithium ions in the sodium aluminate solution precipitate as lithium hydrotalcite and enter the aluminium hydroxide. The seed precipitation process involves the crystallization and precipitation of aluminium hydroxide from supersaturated sodium aluminate solution, which belongs to a chemical crystallization process. During crystallization, the transformation of $Al(OH)_4^-$ tetrahedra into $Al(OH)_6^-$ octahedra occurs [5]. In this transformation process, lithium ions may undergo coprecipitation reaction with aluminate ions, leading to the precipitation of lithium ions into the aluminium hydroxide products.

3. Impact of Lithium Concentration on Precipitation Rate

Figure 4 shows the variation trend of seed precipitation rate over time in sodium aluminate solutions with different lithium ion concentrations, with the following conditions: an initial precipitation temperature of 69 °C, a final precipitation temperature of 54 °C, and a seed charge of 500 g/L). The results indicate that lithium ions significantly influence the precipitation rate. In the initial stage, the precipitation rate increases with higher lithium ion concentrations. However, during the middle and later stages, the precipitation rate decreases as the lithium ion concentration rises. According to crystallization theory in solutions, there are two fundamental processes for crystal formation from a solution [5]: nucleation and growth. When the solution's supersaturation is high, the driving force for nucleation is strong, and the solution is predominantly for nucleation. As the reaction proceeds, the supersaturation of the solution decreases rapidly. Once the supersaturation drops to a certain level, the driving force for nucleation diminishes, and crystal growth becomes the dominant factor. The seed precipitation process involves both nucleation and crystal growth. Due to the excessively high surface tension of sodium aluminate solutions, spontaneous nucleation is often difficult to occur, and most nucleation during seed precipitation is secondary nucleation. In the initial stage of precipitation, the sodium aluminate solution exhibits high supersaturation [4], and the solution is primarily in the nucleation phase, resulting in the formation of numerous secondary crystal nucleus. The presence of lithium ions facilitates the generation of secondary crystal nucleus of aluminium hydroxide in the supersaturated sodium aluminate solution, thereby shortening the induction period for aluminium hydroxide precipitation and increasing the precipitation rate. However, the lithium-containing compounds precipitated exhibit a flaky morphology (Figure 7) and adhere to the surface of aluminium hydroxide, forming a dense film that hinders crystal growth of aluminium hydroxide, leading to a decline in the precipitation rate in the middle and later stages of precipitation. The findings of this study contradict those of previous study [3], which may be attributed to the difference in precipitation system between the reported literature and this paper. The literature reported isothermal precipitation at room temperature, whereas this study employs continuous cooling precipitation. The distinct precipitation conditions lead to different supersaturation levels of the sodium aluminate solution, thereby significantly affecting the precipitation rate.

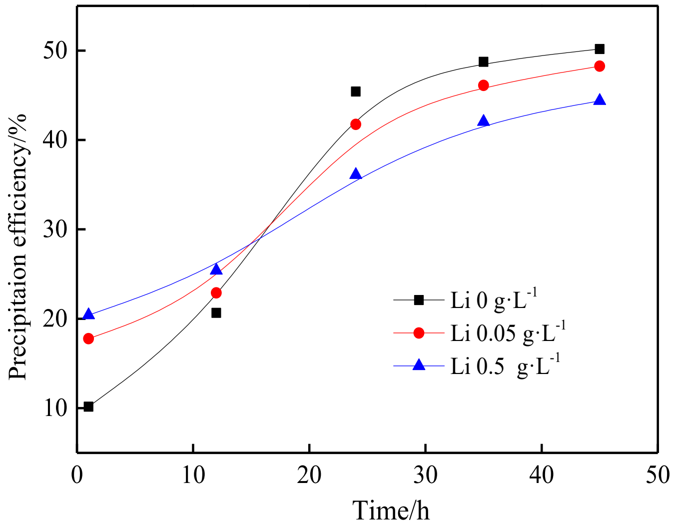

Figure 4. Impact of lithium ions on precipitation rate.

4. Impact of Lithium on Particle Size of Aluminium Hydroxide Products

The particle size of aluminium hydroxide product is one of the critical physico-chemical properties of alumina, significantly impacting the operational environment and technical-economic indicators in downstream aluminium electrolysis processes. Fine particles not only increase dust generation and worsen the working environment but also lead to blocked feed inlets, higher power consumption, and increased fluoride salt consumption. To control the particle size of alumina products, it is essential to regulate the particle size of aluminium hydroxide during precipitation. Figures 5 and 6 show the PSD curves of aluminium hydroxide generated respectively at lithium concentrations of 0, 0.05 and 0.5 g/L. Conditions were: an initial precipitation temperature of 69 °C, a final precipitation temperature of 54 °C, a seed charge of 500 g/L, and a precipitation duration of 45 hours.

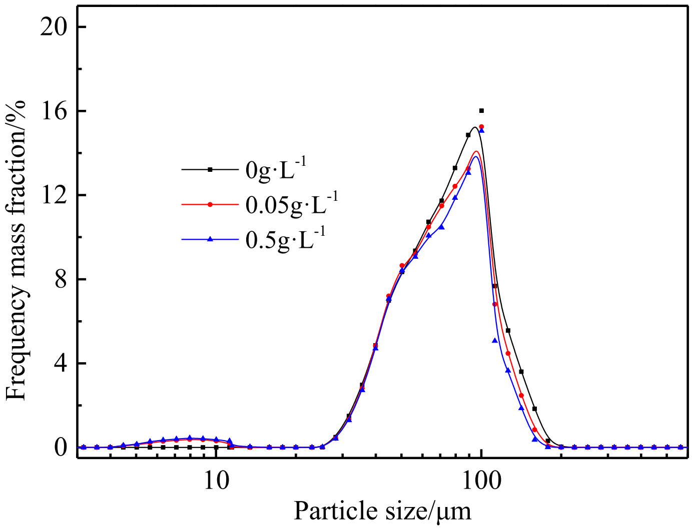

Figure 5. PSD of aluminium hydroxide precipitated at different lithium ion concentrations.

According to Figure 6, the PSD of aluminium hydroxide is mainly concentrated around 60 μm. As the lithium ion concentration increases, the PSD of aluminium hydroxide shows a finer trend, with a higher content of fine particles concentrated around 5 μm. The PSD diagram of aluminium hydroxide (Figure 6) reveals that as the lithium concentration rises, the content of coarse particles gradually decreases, particularly the most significant reduction in the 75–120 μm range. Meanwhile, the content of particles in the 45–75 μm and below 45 μm ranges increases progressively. This indicates that the influence of lithium ions leads to an increase in fine particles in the precipitated products, resulting in an overall finer size.

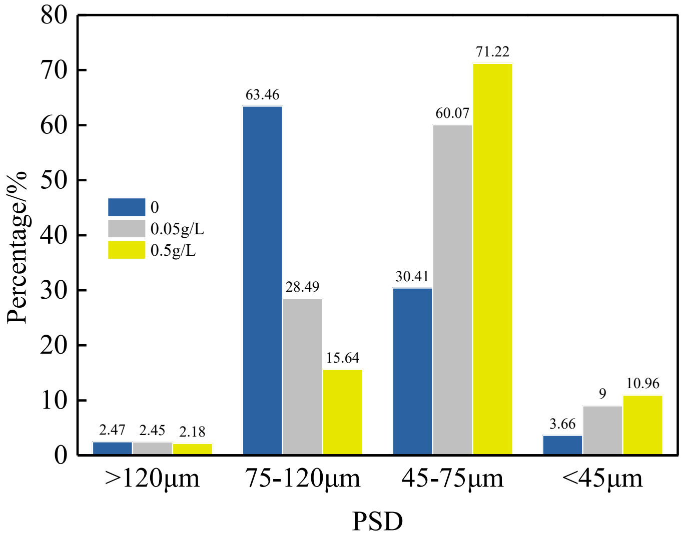

Figure 6. PSD of aluminium hydroxide precipitated at different lithium concentrations.

5. Impact of Lithium on Microstructure of Aluminium Hydroxide

The microscopic morphology of aluminium hydroxide obtained from green liquor of precipitation with different lithium concentrations was analysed, and the results are shown in Figure 7, which demonstrates that lithium ions in the green liquor significantly affect the microscopic morphology of aluminium hydroxide products. Under identical precipitation conditions for 3 hours, as the lithium ion concentration increases, fine particles gradually become more abundant, existing either as individual particles or attached to the surface of larger aluminium hydroxide crystals. As shown in Figures 7(a) and (b), the aluminium hydroxide seeds exhibit uniform particle size, composed of hexagonal prism aggregates with smooth surfaces. When no lithium ions are present in the green liquor, Figures 7(c) and (d) show that the crystal size of the precipitated products exhibits negligible change compared to the seeds, with the hexagonal prism crystals having smooth surfaces and very few fine particles attached. As seen in Figures 7(e) and (f), when the lithium ion concentration in the green liquor reaches 0.05 g/L, the quantity of fine particles in the precipitated product increases significantly. Further, Figures 7(g) and (h) reveal that when the lithium ion concentration in the green liquor rises to 0.5 g/L, a large quantity of fine particles appears in the precipitated product, adhering to the surface of aluminium hydroxide crystals in the form of small flakes. In the initial stage of precipitation, the sodium aluminate solution exhibits high supersaturation, and the solution is dominated by nucleation, resulting in many secondary nucleation crystals. This implies that lithium ions participate in the formation of aluminium hydroxide nuclei in some manner, shortening the induction period of secondary nucleation. The higher the lithium ion concentration in the sodium aluminate solution, the greater the quantity of secondary seeds generated, leading to more fine particles. These fine particles are prone to breaking into powders during calcination, often causing the product to fail meeting the sandy alumina standards and becoming a major source of dust in potrooms. From the perspective of microscopic morphology, the influence of lithium ions on the microstructure of precipitated products is also a reason for the finer particle sizes.

6. Impact of Lithium on Purity of Aluminium Hydroxide

Lithium ions in sodium aluminate solution enter the aluminium hydroxide product during the precipitation process, affecting the purity of aluminium hydroxide. Under the conditions of an initial precipitation temperature of 69 °C, a final precipitation temperature of 54 °C, seed dosage of 500 g/L, and precipitation time of 45 hours, the influence of different lithium ion concentrations in the green liquor (0 g/L, 0.05 g/L, 0.50 g/L) on the lithium content in the final product is shown in Table 1.

From Table 1, it can be observed that the lithium content in aluminium hydroxide products increases with the rising lithium ion concentration in the pregnant liquor. Under identical precipitation conditions, when the lithium ion concentration in the green liquor of precipitation increases from 0.05 to 0.50 g/L, the Li_2O content in aluminium hydroxide rises from 0.011 to 0.072 %. Meanwhile, as the lithium ion concentration increases, the Na_2O content in the product shows a slight decreasing trend. The alkalinity in aluminium hydroxide consists of three components: lattice alkali, intercrystalline alkali, and adherent alkali. The difference in sodium oxide content is primarily caused by lattice alkali and intercrystalline alkali. A possible explanation is that the ionic radius of Li^+ (0.06 nm) is smaller than that of Na^+ (0.095 nm), allowing Li^+ to potentially replace Na^+ and occupy the H^+ positions in the $Al(OH)_3$ crystal lattice.

7. Impact of Lithium Contents on Attrition Index

The fine particles of alumina are the primary source of alumina dust generated in the potrooms of smelters. The attrition index is an important indicator representing the strength of alumina, primarily describing the increase in fine alumina particles caused by collision and abrasion during transportation and handling processes. For aluminium hydroxide products obtained from green liquor with different lithium ion concentrations, the attrition index of alumina was tested after roasting at 1050 °C for 30 minutes. The results are shown in Table 2. It can be observed that as the lithium content in the alumina product increases, the attrition index also rises. Consequently, during transportation, alumina particles are prone to partial fragmentation and getting finer, adversely affecting the operational environment in the potrooms.

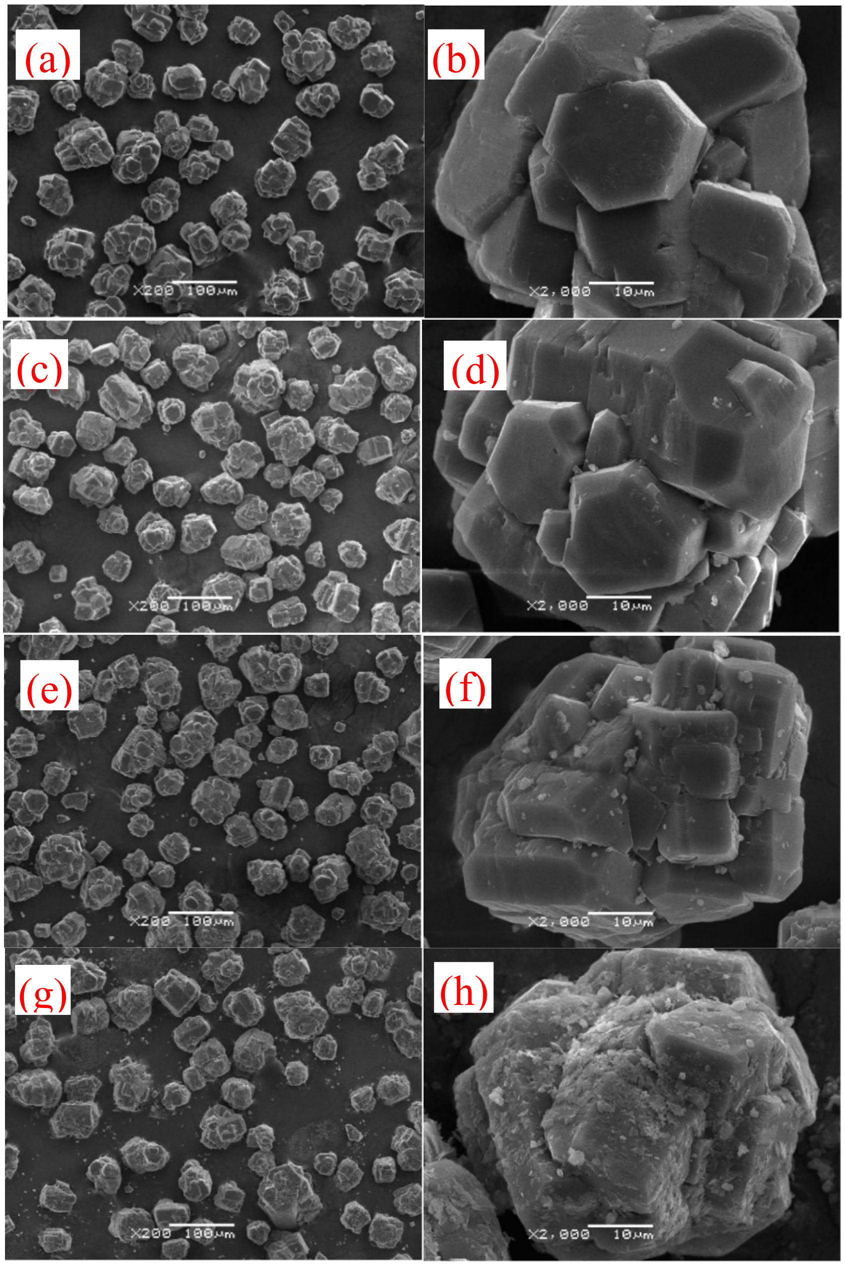

Figure 7. Micro-morphology of seeds (a, b) and aluminium hydroxide products from 3-hour precipitation of green liquors at different Li concentrations ((c, d) 0 g/L, (e, f) 0.05 g/L, (g, h) 0.5 g/L).

Table 1. Impurity content (wt%) in aluminium hydroxide products.

Pregnant liquor Li^+ concentration (g/L)	Impurity content in products			
	SiO_2	Fe_2O_3	Na_2O	Li_2O
0	0.024	0.0080	0.170	0
0.05	0.025	0.0078	0.167	0.011
0.50	0.024	0.0080	0.160	0.072

Table 2. Attrition index of alumina with different lithium contents.

No.	Li_2O content in alumina (%)	Attrition index (%)
1	0.0003	23.80
2	0.017	24.20
3	0.110	42.80

Note: No. 1, No. 2 and No. 3 correspond to lithium concentrations of 0, 0.05 and 0.5 g/L in the green liquor, respectively.

8. Conclusion

1. In the initial stage of precipitation, lithium precipitates rapidly from the sodium aluminate solution. At a precipitation time of 1 hour, the precipitation rate of lithium exceeds 90 %, and at 2 hours, it exceeds 99 %. Therefore, nearly all lithium ions in the pregnant liquor enter into aluminium hydroxide during the initial precipitation stage (within 2 hours).

2. In the initial stage of precipitation, lithium ions shorten the induction period for aluminium hydroxide precipitation in sodium aluminate solution, thereby enhancing the precipitation rate. In the middle and later stages, however, the lithium-containing aluminium hydroxide precipitates as flaky aggregates attached to the surface of aluminium hydroxide, which hinders the growth of seeds and consequently reduces the precipitation rate.

3. Lithium ions significantly influence the microstructure of aluminium hydroxide. Lithium ions increase the content of fine solid particles in the solution, with these fine particles existing either independently or attached to the surface of larger aluminium hydroxide crystals. As a result, lithium ions raise the proportion of fine particles (-45 µm) in the product, leading to finer particle sizes. The presence of lithium in the aluminium hydroxide product affects both its purity and strength. Moreover, higher lithium content results in an increased attrition index and reduced strength of alumina.

9. Acknowledgement

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