# Crystallization and Separation of Potassium-Containing Salts in Sodium Aluminate Solution

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## Abstract

The dissolution of potassium-containing minerals in bauxite leads to a large amount of potassium ions entering the sodium aluminate solution, which severely affects the seed precipitation rate of the sodium aluminate solution, as well as the crystal morphology, particle size, and quality of the precipitated products. To achieve the economical and efficient removal of potassium ions from sodium aluminate solution, a single-stage double salt crystallization (SDSC) process is proposed, using $Na_2SO_4$ as an additive to remove potassium in the form of the double salt $3K_2SO_4 \cdot Na_2SO_4 \cdot 9H_2O$. The potassium removal performance and mechanisms under different crystallization regimes and solution compositions are systematically studied. The results show that increasing the amount of additive and reaction temperature promotes the crystallization of the $3K_2SO_4 \cdot Na_2SO_4 \cdot 9H_2O_3$ double salt, thereby improving the potassium removal rate. However, the increase in caustic soda concentration leads to an increase in the number of chain polymers and ion pairs in the solution, hindering solute diffusion, which significantly reduces the potassium removal rate. Under optimal conditions, the potassium removal rate from the sodium aluminate solution can reach 85.68 %, with the potassium concentration dropping from 120 to 24.54 g/L. Additionally, molecular dynamics simulation results indicate that carbonate and oxalate in the sodium aluminate solution exhibit strong interactions with the (0 0 1) face of $3K_2SO_4 \cdot Na_2SO_4 \cdot 9H_2O$, and their adsorption on the crystal face inhibits crystal growth.

**Keywords:** Sodium aluminate solution, Alumina, Potassium ions, Double salt crystallization, Molecular dynamics simulation.

## 1. Introduction

The Bayer process is an industrial chemical process widely used for producing alumina from bauxite [1, 2]. During the Bayer process, impurities such as silicates, organic compounds, and inorganic salts from bauxite and additives are dissolved in the alkaline solution, thus entering the sodium aluminate solution, and gradually accumulate during the recycling process [3, 4]. The concentrated impurities not only increase caustic soda loss but also raise the viscosity of the solution [5]. Furthermore, inorganic anions and impurities such as oxalates can co-precipitate with aluminium hydroxide, leading to a decrease in the quality of the final alumina product [6, 7]. Researchers have conducted extensive studies on the removal of impurities like silica, titanium, iron, vanadium, and organic compounds from sodium aluminate solution, developing various impurity removal techniques such as precipitation, electrochemical methods, solvent extraction, and ion exchange [8, 9]. However, there has been limited focus on the removal of potassium from sodium aluminate solution, and corresponding technological developments are still in their early stages.

Potassium in bauxite primarily exists in minerals such as illite ($(K_{0.75}(Al_{1.75}R)(Si_{3.5}Al_{0.5}O_{10})(OH)_2)$), potassium feldspar, mica, and others. During the digestion process, potassium enters the sodium aluminate solution and concentrates as the solution undergoes repeated cycles. Although a small amount of potassium may enter bauxite residue and be discharged with it, most potassium remains in the solution. When using potassium-rich bauxite, the potassium concentration in industrial sodium aluminate solution can reach 100–120 g/L. The presence of potassium reduces the nucleation rate of aluminium hydroxide and prolongs the induction period of seed crystals during precipitation [10]. Therefore, the growth rate of aluminium hydroxide crystals in potassium aluminate solution is significantly slower than in sodium aluminate solution [11]. Moreover, the high potassium concentration during seed crystal precipitation can easily trigger secondary nucleation, leading to the formation of numerous small particles, which impacts the precipitation process and product quality. Consequently, controlling the potassium ion concentration at a lower level during alumina production is crucial for improving both alumina yield and quality.

Due to the similar chemical properties of potassium and sodium, separating them in an alkaline solution is challenging. Xue et al. [12] developed a solvent extraction method to treat potassium aluminate solution, using alkylphenols as extractants, followed by back-extraction for potassium recovery; however, this method could only remove about 40% of the potassium. Crystallization is a commonly used technique for solution purification and is widely applied in separating salts with similar chemical properties. Studies show that potassium can be recovered as potassium carbonate from Bayer spent liquor through multi-stage vacuum evaporation and cooling crystallization processes [13]. Ma et al. [14] extracted potassium nitrate from Bayer spent liquor through multi-stage recrystallization. However, the crystallization processes mentioned above are complex, energy-intensive, slow in reaction rate, and require several days for the separation process.

Therefore, this study proposes an energy-efficient single-stage double salt crystallization (SDSC) process, using $Na_2SO_4$ as an additive to remove potassium from sodium aluminate solution in the form of the double salt ($3K_2SO_4 \cdot Na_2SO_4 \cdot 9H_2O$). The impact of various reaction conditions on potassium removal is systematically investigated, and the micro-morphology and phase composition of the crystallization products are analysed. Additionally, molecular dynamics simulations are used to explore the mechanism by which impurity ions affect the crystallization process. This research provides a theoretical and technical foundation for the efficient removal of potassium in the Bayer process.

## 2. Experimental Methods

### 2.1 Preparation of Sodium Aluminate Solution

The chemicals used in the experiment included sodium aluminate, sodium hydroxide, potassium hydroxide, and sodium sulphate (analytical grade, Tianjin Kemiou Chemical Reagent Co., Ltd.). These chemicals were mixed in specific proportions and dissolved under heating. After filtration, a potassium-containing sodium aluminate solution was obtained. The concentrations of alumina and caustic soda in the sodium aluminate solution were determined by EDTA (ethylenediaminetetraacetic acid) complexometric titration and acid-base titration, respectively.

### 2.2 Crystallization Removal of Potassium

Potassium removal experiments were conducted using sodium sulphate as an additive. Solid sodium sulphate was added to the potassium-containing sodium aluminate solution. After stirring and dissolution, the solution was placed in a constant-temperature water bath at 90 °C and evaporated for 60 minutes to reach a supersaturated state. The solution was then maintained at various temperatures to promote crystallization, with the stirring speed held constant at 60 rpm during the crystallization process. The crystallization temperature T was set between 50–90 °C, crystallization time $t$ ranged from 10 to 120 minutes, the initial potassium concentration was 40–120 g/L, and the caustic soda concentration in the sodium aluminate solution was 100–350 g/L.

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