



Behavior of calcium oxalate in sodium aluminate solutions



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Abstract: The stability of calcium oxalate is critical for the removal of sodium oxalate from sodium aluminate solutions. This study investigated the behavior of calcium oxalate in sodium aluminate solution containing sodium carbonate. Results show that calcium oxalate can be converted to tricalcium aluminate hydrate (TCA) and calcium carbonate in sodium aluminate solution and sodium carbonate solution, respectively. Elevating temperature, extending residence time, or increasing caustic soda concentration enhances the conversion ratio of calcium oxalate in sodium aluminate solution; as a consequence, anti-causticisation occurs. Stability of calcium-containing compounds in sodium aluminate solution containing sodium carbonate differs from that in sodium aluminate solution or sodium carbonate solution. Na_2CO_3 in aluminate solution accelerates the transformation of calcium oxalate; thus, alumina is lost because of $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CO}_2\cdot 11\text{H}_2\text{O}$ and TCA formation. Calcium carbonate, $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CO}_2\cdot 11\text{H}_2\text{O}$ and calcium oxalate can change into TCA in sodium aluminate solution at elevated temperature. Calcium oxalate remains relatively stable in dilute aluminate solution within a short residence time at low temperature. Thus, a novel process for removal of sodium oxalate by lime causticisation was presented and employed in an alumina refinery in China.

Key words: calcium oxalate; sodium aluminate solution; sodium carbonate; lime causticisation; activity coefficient

1 Introduction

Sodium oxalate, generated in the Bayer process by decomposition of organic compounds in bauxite, is a well-known organic impurity in sodium aluminate solution [1]. Low solubility and easy co-precipitation with alumina trihydrate (ATH) in seeded precipitation processes lead to low seed precipitation rate, fine ATH, poor alumina quality, considerable caustic soda loss, and difficult slurry filtration [2–6]. Moreover, sodium oxalate deteriorates the settlement property of red mud and promotes the formation of scales in evaporation equipment and precipitation tanks [7,8]. Sodium oxalate, together with sodium carbonate and sodium sulfate in aluminate solution, further accelerates the formation of scales on equipment surface and exacerbates seeded precipitation [9].

Sodium oxalate can be removed from solutions through various methods, including crystallization [10,11], fine ATH washing [12,13], precipitation [14], wet oxidation [15], ion exchange [16], adsorption [17], and causticisation [14,18,19]. Compared with other

methods, lime causticisation is extensively applied because of several advantages, such as caustic soda recovery, convenient operation, and low cost. Thus, lime causticisation has been improved. ZHAO et al [20] proposed that lime can be added to oxalate-rich aluminate solution to form insoluble calcium oxalate. The addition of lime depends on the stoichiometric coefficients of CaO to Al_2O_3 , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, and SO_4^{2-} in solutions according to the common understanding that tricalcium aluminate hydrate (TCA), calcium carbonate and calcium oxalate can be formed in aluminate solutions containing sodium carbonate. To avoid the negative effect of aluminate anion and remove both sodium oxalate and sodium sulfate, ROSENBERG et al [14,21] presented a two-step causticisation process. In this process, hydrocalumite is formed in the first step and calcium oxalate is produced in the second step. In ROSENBERG's [21] subsequent patents, the utilization ratio of lime is enhanced from 20% to 80%, and alumina loss is reduced by adding sodium carbonate to recover alumina from TCA. These studies focused on calcium oxalate formation and causticisation efficiency, while more lime is required and lower efficiency occurs in

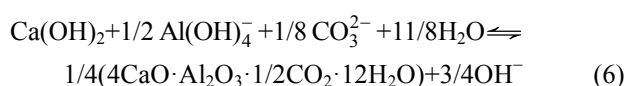
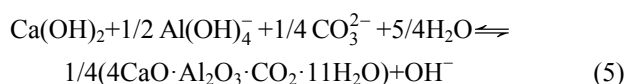
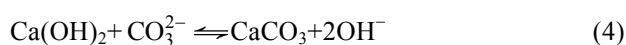
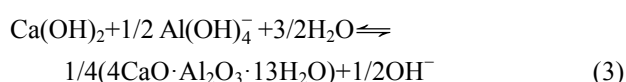
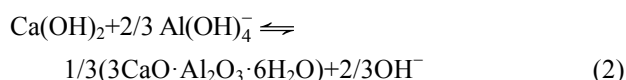
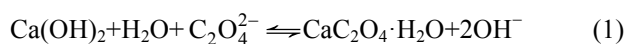
practical as comparison with the above theoretical results. Moreover, the slurry containing calcium oxalate is practically pumped into the washing tanks of red mud with a relatively high concentration solution (caustic soda $\rho(\text{Na}_2\text{O}) > 40 \text{ g/L}$, alumina $\rho(\text{Al}_2\text{O}_3) > 40 \text{ g/L}$) for 3–10 h at 90 °C to 100 °C to simplify the treatment of causticisation slurry. An interconvertible reaction may occur among calcium-containing compounds during the washing of red mud because the solubilities of these calcium-containing compounds vary [22]. Consequently, lime causticisation efficiency is further reduced. However, the behavior of calcium oxalate in sodium aluminate solutions has been rarely reported, and the influence of sodium carbonate in aluminate solutions on causticisation remains unclear.

In this work, the stability of calcium oxalate in a $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{CO}_2-\text{H}_2\text{O}$ system was investigated on the basis of the thermodynamic calculations and conversion ratios of calcium oxalate in different solutions. The distribution of calcium-containing compounds after calcium oxalate reacted with different solutions was also determined. The study provides a guide to efficiently remove sodium oxalate from sodium aluminate solutions and to reduce alumina loss through lime causticisation, which is proven in an alumina refinery in China.

2 Thermodynamic calculation of reaction between calcium oxalate and sodium aluminate solution or sodium carbonate solution

2.1 Relationship between temperature and Gibbs free energy of reactions

$\text{Al}(\text{OH})_4^-$, CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, or SO_4^{2-} anions in sodium aluminate solution can react with calcium hydroxide to generate the corresponding calcium-containing compounds [12,14,20,23]. The following calcium-containing compounds can be formed in sodium aluminate solutions in alumina refineries without regard to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with a relatively high solubility.



These reaction equations indicate that the increase in caustic soda concentration (OH^- is expressed as Na_2O) is detrimental to the stability of calcium-containing compounds. Based on the thermodynamic data [20,24–26], Gibbs free energy of reactions at different temperatures was then calculated. Results are presented in Fig. 1.

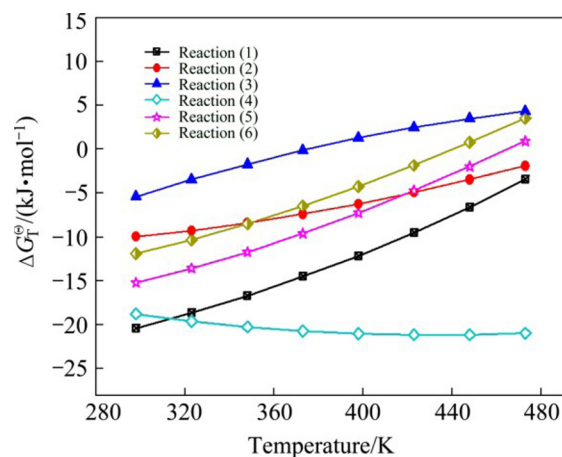
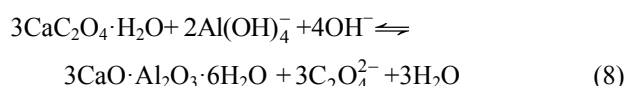


Fig. 1 Relationship between temperature and Gibbs free energy of calcium-containing compounds

Figure 1 illustrates that $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, CaCO_3 , $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$, and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CO}_2 \cdot 12\text{H}_2\text{O}$ ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{CO}_2 \cdot 12\text{H}_2\text{O}$ is known as hydrocalumite) can be formed by adding $\text{Ca}(\text{OH})_2$ at temperatures below 375 K. Among these compounds, CaCO_3 is the most stable and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ is decomposed at increased temperature. $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$ is more stable than $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CO}_2 \cdot 12\text{H}_2\text{O}$. Likewise, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is more stable than TCA at temperatures below 473 K. An increase in temperature promotes the transformation of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CO}_2 \cdot 12\text{H}_2\text{O}$, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$, and $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ into TCA. $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is also converted to CaCO_3 at temperatures above 317 K.

2.2 Stability of calcium oxalate in sodium carbonate solutions or sodium aluminate solutions

To understand the effect of sodium carbonate and aluminate anion on the stability of calcium oxalate, the behavior of calcium oxalate was discussed on the basis of the thermodynamic equilibrium calculation of the chemical reactions as Eq. (8)–(9) in the simulated oxalate-rich aluminate solution from fine ATH washing process.



Both reactions can release oxalate anion. Moreover,

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