



## Behavior of calcium oxalate in sodium aluminate solutions

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Received 24 December 2015; accepted 30 December 2016

**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.  $\text{Na}_2\text{CO}_3$  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  $\text{CaO}$  to  $\text{Al}_2\text{O}_3$ ,  $\text{CO}_3^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ , and  $\text{SO}_4^{2-}$  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

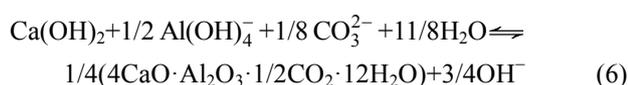
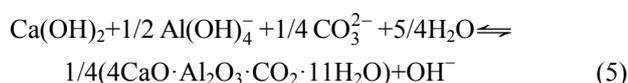
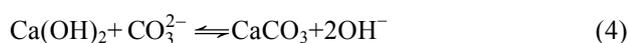
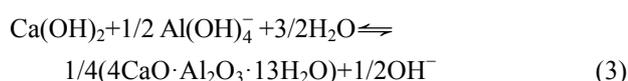
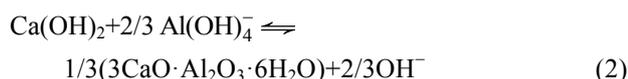
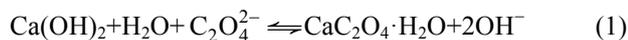
practical as comparison with the above theoretical results. Moreover, the slurry containing calcium oxalate is practically pumped into the washing tanks of red mud with a relatively high concentration solution (caustic soda  $\rho(\text{Na}_2\text{O}) > 40 \text{ g/L}$ , alumina  $\rho(\text{Al}_2\text{O}_3) > 40 \text{ g/L}$ ) 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

$\text{Al}(\text{OH})_4^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ , or  $\text{SO}_4^{2-}$  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 ( $\text{OH}^-$  is expressed as  $\text{Na}_2\text{O}$ ) 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.

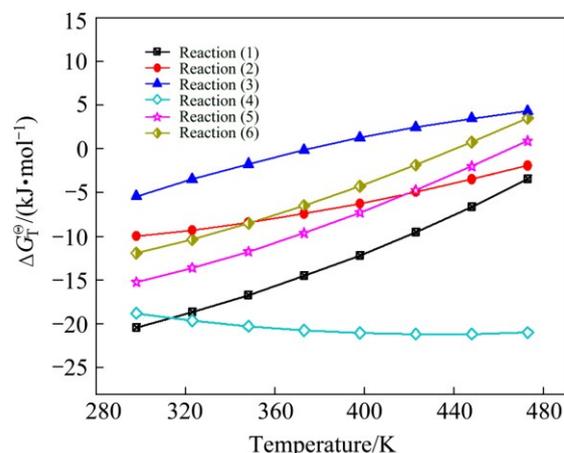
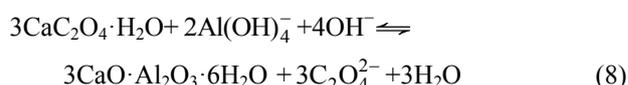


Fig. 1 Relationship between temperature and Gibbs free energy of calcium-containing compounds

Figure 1 illustrates that  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ ,  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaCO}_3$ ,  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$ , 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,  $\text{CaCO}_3$  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  $\text{CaCO}_3$  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,

the occurrence of the reaction in Eq. (8) leads to alumina loss, this process is defined as anti-causticisation.

The mean activity coefficients of NaOH, NaAl(OH)<sub>4</sub>, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and Na<sub>2</sub>CO<sub>3</sub> are obtained on the basis of Bromley's model expressed as follows [26–28]:

$$\lg \gamma_{MX} = \frac{-A_m |Z_M Z_X| I^{1/2}}{1 + I^{1/2}} + \frac{v_M F_M}{v} + \frac{v_X F_X}{v} \quad (9)$$

$$F_M = \sum_i \left( \frac{0.06 + 0.6 B_{Mi} |Z_M Z_i|}{1 + \left( \frac{1.5}{|Z_M Z_i|} \right)} + B_{Mi} \right) \left( \frac{|Z_M| + |Z_i|}{2} \right)^2 m_i \quad (10)$$

This model uses a similar expression to the  $F_X$  term. In these equations,  $i$  and  $j$  represent the different ions of M and X in a given solution, respectively;  $A_m$  (Debye–Hückel constant) is 0.5100 kg<sup>1/2</sup>/mol<sup>1/2</sup> at 298.15 K [27]; and  $Z_i$  and  $v_i$  denote the ionic charge and stoichiometric coefficient of each ion, respectively, ( $v=v_M+v_X$ );  $I$  refers to ionic strength;  $B_{Mi}$  is Bromley's coefficient;  $m_i$  is the mass molar concentration of ions (mol/kg); and  $B_{NaOH}$ ,  $B_{NaAl(OH)_4}$ ,  $B_{Na_2C_2O_4}$  and  $B_{Na_2CO_3}$  are 0.0759, 0.0188, -0.045, and 0.0001, respectively [27]. Thus, the solubility of calcium oxalate in different solutions was calculated at 298.15 K according to the following equations:

$$m_{[C_2O_4^{2-}]_{Tr(7)}} = \frac{\gamma_{Na_2CO_3}^3}{\gamma_{Na_2C_2O_4}^3} \cdot \exp\left(\frac{-\Delta G_{Tr(7)}^\ominus}{RT}\right) \quad (11)$$

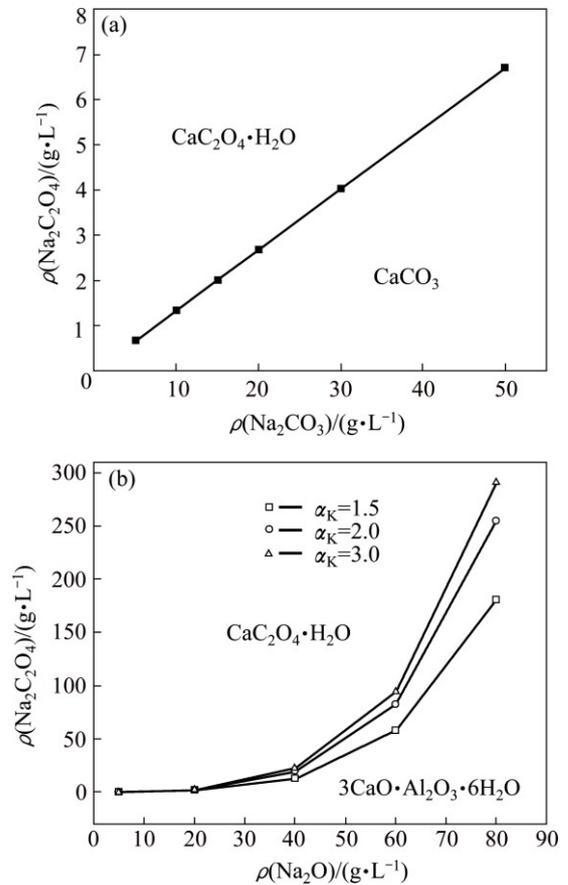
$$m_{[C_2O_4^{2-}]_{Tr(8)}} = m_{[Al(OH)_4^-]}^{2/3} m_{[OH^-]}^{4/3} \frac{\gamma_{NaOH}^{8/3} \gamma_{NaAl(OH)_4}^{4/3}}{\gamma_{Na_2C_2O_4}^3} \exp\left(\frac{-\Delta G_{Tr(8)}^\ominus}{3RT}\right) \quad (12)$$

where  $\Delta G_{Tr(7)}^\ominus$  and  $G_{Tr(8)}^\ominus$  refer to Gibbs free energies of Eqs. (7) and (8) at 298.15 K, respectively.  $R$  is the molar gas constant equal to 8.314 J/(mol·K). Subscripts of Tr (7) and Tr (8) refer to Eqs. (7) and (8), respectively.

Figure 2 shows the stable area of calcium-containing compounds in different solutions.

Figure 2(a) indicates that the increase in Na<sub>2</sub>CO<sub>3</sub> concentration linearly enhances C<sub>2</sub>O<sub>4</sub><sup>2-</sup> concentration. This result suggests that a great amount of calcium oxalate is converted into calcium carbonate in the sodium carbonate solution. The stable area of CaCO<sub>3</sub>, which is located below the line in Fig. 2(a), also enlarges as the Na<sub>2</sub>CO<sub>3</sub> concentration increases. This observation is similar to the stable area of calcium oxalate, that is, this area broadens as the sodium oxalate concentration increases. Figure 2(b) shows that the Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>

concentration increases slightly with the increase of caustic soda concentration in the solution when the  $\rho(\text{Na}_2\text{O})$  is lower than 20 g/L. While, the Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> concentration increases significantly as the caustic soda concentration increases at  $\rho(\text{Na}_2\text{O}) > 40$  g/L. This trend demonstrates that calcium oxalate is stable in the extremely dilute aluminate solution. An increase in  $\alpha_k$  enlarges the stable area of calcium oxalate; as a consequence, the decomposition of calcium oxalate in a solution containing low alumina concentration is prevented. This result also suggests that the increase in alumina concentration promotes the transformation of calcium oxalate to TCA, as presented in Eq. (8). Thus, calcium oxalate is unstable in sodium carbonate solution or the concentrated sodium aluminate solution.



**Fig. 2** Stability of calcium oxalate in sodium carbonate (a) and sodium aluminate (b) solutions ( $\alpha_k$  is the molar ratio of caustic soda (Na<sub>2</sub>O) to alumina (Al<sub>2</sub>O<sub>3</sub>) in solutions. The upper areas of the line in Figs. 2(a) and (b) are the stable areas of CaC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O, the lower right corners of Figs. 2(a) and (b) are the stable areas of CaCO<sub>3</sub> and 3CaO·Al<sub>2</sub>O<sub>3</sub>·6H<sub>2</sub>O, respectively)

### 2.3 Stability of calcium-containing compounds in sodium aluminate solutions with sodium carbonate

Sodium aluminate solutions in alumina refineries contain high concentration of sodium carbonate, which

complicates the system [22]. As such, the behavior of calcium oxalate in this complex system should be urgently investigated. The alumina concentration decreases markedly in a series of washing tanks through reversal washing. To enhance our understanding of the relationship between the alumina concentration and the stability of calcium oxalate, the free caustic soda concentrations were calculated in Eqs. (1), (2), (4), and (5) at 298.15 K according to the following equations:

$$m_{[\text{OH}^-]_{r(1)}} = m_{[\text{C}_2\text{O}_4^{2-}]_{r(1)}}^{1/2} \frac{\gamma_{\text{Na}_2\text{C}_2\text{O}_4}^{3/2}}{\gamma_{\text{NaOH}}^2} \cdot \exp\left(\frac{-\Delta G_{\text{Tr}(1)}^\ominus}{2RT}\right) \quad (13)$$

$$m_{[\text{OH}^-]_{r(2)}} = m_{[\text{Al}(\text{OH})_4^-]_{r(2)}} \frac{\gamma_{\text{NaAl}(\text{OH})_4}^2}{\gamma_{\text{NaOH}}^2} \cdot \exp\left(\frac{-3\Delta G_{\text{Tr}(2)}^\ominus}{2RT}\right) \quad (14)$$

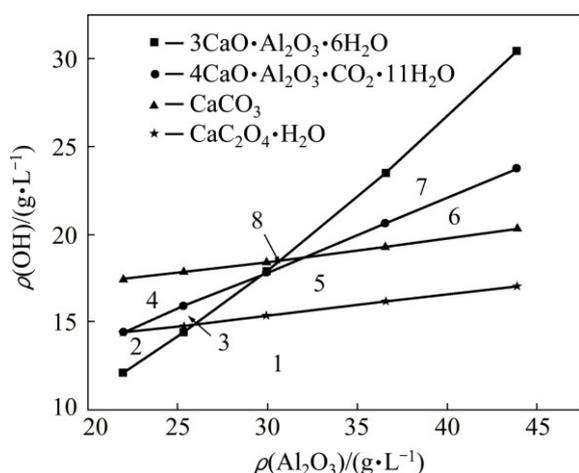
$$m_{[\text{OH}^-]_{r(4)}} = m_{[\text{CO}_3^{2-}]_{r(4)}}^{1/2} \frac{\gamma_{\text{Na}_2\text{CO}_3}^{3/2}}{\gamma_{\text{NaOH}}^2} \cdot \exp\left(\frac{-\Delta G_{\text{Tr}(4)}^\ominus}{2RT}\right) \quad (15)$$

$$m_{[\text{OH}^-]_{r(5)}} = m_{[\text{Al}(\text{OH})_4^-]_{r(5)}}^{1/2} m_{[\text{CO}_3^{2-}]_{r(5)}}^{1/4} \frac{\gamma_{\text{NaAl}(\text{OH})_4} \gamma_{\text{Na}_2\text{CO}_3}^{3/4}}{\gamma_{\text{NaOH}}^2} \cdot \exp\left(\frac{-\Delta G_{\text{Tr}(5)}^\ominus}{RT}\right) \quad (16)$$

where the free caustic soda concentration  $m_{[\text{OH}^-]}$  is equal to the caustic soda concentration (caustic soda in NaOH and NaAl(OH)<sub>4</sub>) minus the caustic soda concentration in NaAl(OH)<sub>4</sub>.

$\Delta G_{\text{Tr}(1)}^\ominus$ ,  $\Delta G_{\text{Tr}(2)}^\ominus$ ,  $\Delta G_{\text{Tr}(4)}^\ominus$ , and  $\Delta G_{\text{Tr}(5)}^\ominus$  represent Gibbs free energies of Eqs. (1), (2), (4), and (5) at 298.15 K, respectively.

The results are shown in Fig. 3.



**Fig. 3** Influence of alumina concentration on stability of calcium-containing compounds ( $\rho(\text{Na}_2\text{O})=40$  g/L;  $\rho(\text{Na}_2\text{C}_2\text{O}_4)=15$  g/L;  $\rho(\text{Na}_2\text{CO}_3)=0$  g/L)

The stable area of calcium-containing compounds is located below the corresponding line; the unstable area is located above the corresponding line because

$\rho(\text{OH}^-) > \rho(\text{OH}^-)_{\text{eq}}$ .

The stable area of calcium-containing compounds: 1) TCA,  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ,  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$ , and  $\text{CaCO}_3$ ; 2)  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ,  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$ , and  $\text{CaCO}_3$ ; 3)  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$  and  $\text{CaCO}_3$ ; 4)  $\text{CaCO}_3$ ; 5) TCA,  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$ , and  $\text{CaCO}_3$ ; 6)  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$  and TCA; 7) TCA; and 8) TCA and  $\text{CaCO}_3$ .

In terms of activity coefficient, the increase in the  $\text{Al}_2\text{O}_3$  concentration almost linearly increases  $\text{OH}^-$  equilibrium concentration for each calcium-containing compound (Fig. 3). Figure 3 shows that calcium-containing compounds can co-exist in dilute solutions with low caustic soda concentration (area 1). On the basis of the upper left area above the line in Fig. 3, we can observe that calcium oxalate is more stable than TCA at an alumina concentration of  $\rho(\text{Al}_2\text{O}_3) < 25$  g/L (area 2), and calcium carbonate is a relatively stable substance at different concentrations of alumina and caustic soda (areas 1, 2, 3, 4, 5, and 8). Calcium oxalate can be converted to  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$ , TCA, and calcium carbonate (areas 3 and 4). In addition, calcium oxalate,  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$ , and calcium carbonate are converted to TCA as the alumina concentration increases (areas 6 and 7). Figure 3 also illustrates that the increase in the free caustic soda concentration can largely reduce the stability of hydrocalumite as the  $\text{Al}_2\text{O}_3$  concentration remains constant. However, TCA is the most stable substance, but calcium oxalate is preferentially decomposed in a solution with high concentrations of caustic soda and alumina ( $\rho(\text{Al}_2\text{O}_3) > 30$  g/L).  $\text{CaCO}_3$  can be converted to  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$  and TCA as the alumina concentration increases. These findings are remarkably different from that shown in Fig. 1. Therefore, the behavior of calcium-containing compounds in the complex system differs from that in the single system of sodium carbonate or sodium aluminate. In addition, lime causticisation should not be performed in concentrated sodium aluminate solutions unless calcium oxalate is converted to other calcium-containing compounds.

### 3 Experimental

#### 3.1 Materials

Sodium aluminate solution was prepared by industrial aluminum hydroxide (Chalco) and sodium hydroxide based on  $\alpha_k$  (1.4–3.0).  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3$ , and other reagents were of analytical grade.

#### 3.2 Experimental procedure

Experiments were carried out in a 150 mL

continuously rotating steel bomb immersed in glycerol and heated by electricity ( $\pm 1$  °C). Different solutions (sodium aluminate solution, sodium carbonate solution, or sodium aluminate solution with sodium carbonate) and calcium oxalate were added to the steel bomb. After the reaction was completed at a given temperature and duration, the slurry was filtered. The resulting solution was then obtained by diluting the filtrate with distilled water to produce the final of 500 mL to determine the concentrations of  $\text{Al}_2\text{O}_3$  and  $\text{C}_2\text{O}_4^{2-}$ . The dried sludge was used to identify the contents of calcium-bearing compounds.

### 3.3 Characterization

The alumina ( $\text{Al}_2\text{O}_3$ ) and caustic soda ( $\text{Na}_2\text{O}$ ) concentrations in the resulting solution were determined through titration. The sodium oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ ) concentration was obtained by using an ICS-90A ion chromatograph (DIONEX) [29]. The X-ray diffraction patterns of the sample were obtained by using a powder diffractometer (D8-Advance, Bruker Corporation). The elemental distribution of the sludge was observed with an energy dispersive spectrometer (EDS, JSM-6360LV, Electronic, Ltd.).

### 3.4 Data processing

The conversion ratio of calcium oxalate in either sodium carbonate solution or sodium aluminate solution was calculated according to the following formula:

$$\eta = \frac{m_1}{m_0} \times 100\% \quad (17)$$

where  $m_0$  and  $m_1$  correspond to  $\text{C}_2\text{O}_4^{2-}$  contents in calcium oxalate and in solution (g), respectively.

The mass fraction of the corresponding calcium-containing compound (taking  $\text{CaCO}_3$  for example) in sludge ( $\omega$ ) was calculated using the following formula, with the total calcium ( $[\text{Ca}]_T$ ) content remaining constant:

$$\omega = \frac{[\text{CaCO}_3]}{[\text{Ca}]_T} \times 100\% \quad (18)$$

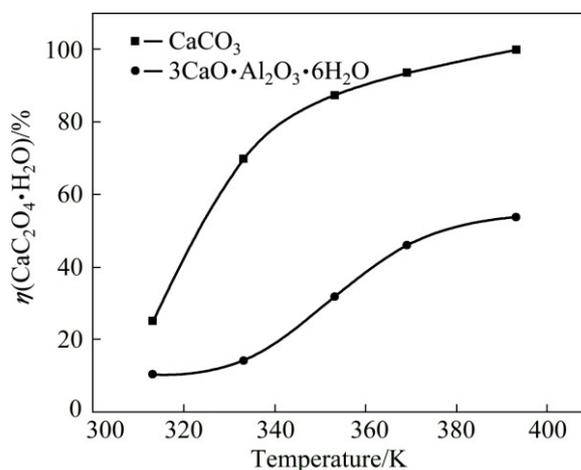
where subscript T refers to the total calcium content and the other subscripts denote the contents of the corresponding calcium-containing compounds.

The  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and  $\text{CaCO}_3$  contents in the sludge were obtained on the basis of the concentration variation of oxalate anion and carbonate anion in the solution; the TCA and  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$  contents were calculated according to the total mass of the sludge and concentration variation of alumina before and after reaction. The mass fraction of the calcium-containing compounds was then determined.

## 4 Results and discussion

### 4.1 Influence of temperature on reaction between calcium oxalate and different solutions

In practice, causticisation temperature varies in causticisation-related processes, including lime causticisation reaction, clarification, and washing operation. In the aluminate solution containing sodium carbonate, calcium oxalate may react with sodium carbonate (expressed as  $\text{Na}_2\text{O}_c$ ) or sodium aluminate solution, as expressed in Eqs. (7) and (8). Figure 4 illustrates the variation in the conversion ratio of calcium oxalate in the aluminate solution or the carbonate solution to describe the influence of reaction temperature on the stability of calcium oxalate in the aluminate solution.

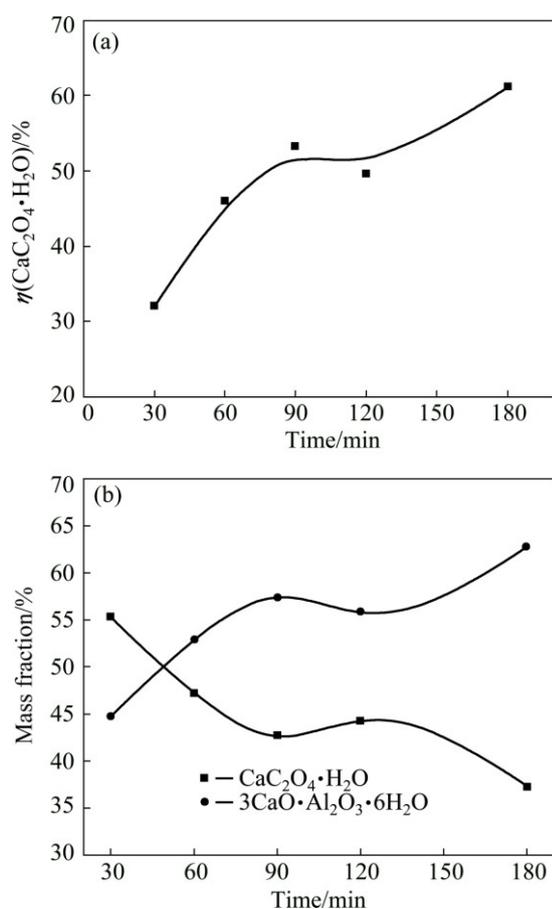


**Fig. 4** Influence of temperature on conversion ratio of calcium oxalate (Sodium aluminate solution:  $\rho(\text{Na}_2\text{O})=37.46$  g/L,  $\alpha_k=2.90$ ; sodium carbonate solution:  $\rho(\text{Na}_2\text{O}_c)=30$  g/L; 60 min)

Figure 4 shows that increasing temperature favors the increase in the conversion ratio of calcium oxalate, which illustrates that increasing temperature accelerates the transformation of calcium oxalate into calcium carbonate and TCA in the sodium carbonate solution and in the sodium aluminate solution, respectively. The conversion ratio of calcium oxalate increases remarkably in the sodium carbonate solution as temperature increases because calcium carbonate is preferentially formed at high temperature (Fig. 1). By contrast, the conversion ratio of calcium oxalate almost remains constant at temperatures of  $<330$  K and then increases significantly with temperature rising in sodium aluminate solution. This finding indicates that an increase in temperature causes significant anti-causticisation; the calcium oxalate-containing slurry should not return to the aluminate solution at high temperature.

#### 4.2 Influence of residence time on reaction between calcium oxalate and aluminate solution

The slurry or the concentrated slurry (underflow) after settling is practically pumped to the second washing tank ( $\rho(\text{Na}_2\text{O})$  30–45 g/L) to simplify the process. The slurry then flows through the third tank, fourth tank and the final washing tank for 5–8 h at 90–95 °C. Thus, residence time is a critical factor to ensure sufficient causticisation. The influence of residence time on the conversion ratio of calcium oxalate in the sodium aluminate solution is presented in Fig. 5.

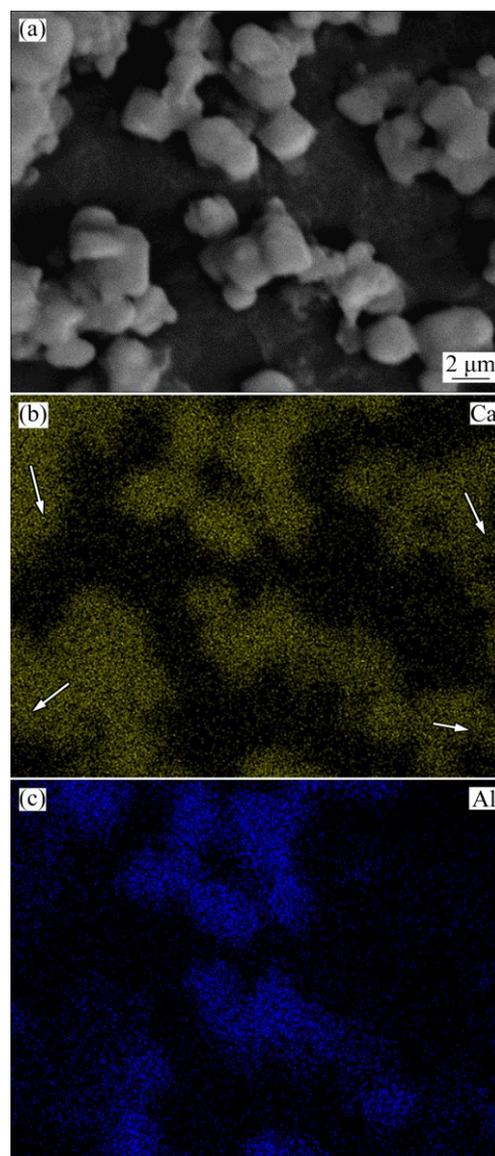


**Fig. 5** Influence of residence time on conversion ratio of calcium oxalate (a) and mass distribution of calcium oxalate and TCA (b) (Sodium aluminate solution:  $\rho(\text{Na}_2\text{O})=37.46$  g/L,  $\alpha_k=2.90$ ; 96 °C)

Figure 5(a) indicates that the conversion ratio of calcium oxalate remarkably increases with residence time in the sodium aluminate solution because of the transformation of calcium oxalate into TCA. Figure 5(b) shows that the content of calcium oxalate in the sludge decreases but the content of TCA increases with time; as a consequence, alumina is lost. For example, up to 44.75% TCA in the sludge in the first 30 min demonstrates that anti-causticisation readily occurs in the aluminate solution. Figure 5 also illustrates that calcium oxalate must be discharged alone to prevent sodium

oxalate from returning to the sodium aluminate solution when anti-causticisation occurs.

To further investigate the distribution of calcium-containing compounds in the sludge after causticisation occurs, the EDS element maps (Fig. 6) are presented. The highlighted areas in Figs. 6(b) and 6(c) are the main distribution areas of Ca and Al elements, respectively.



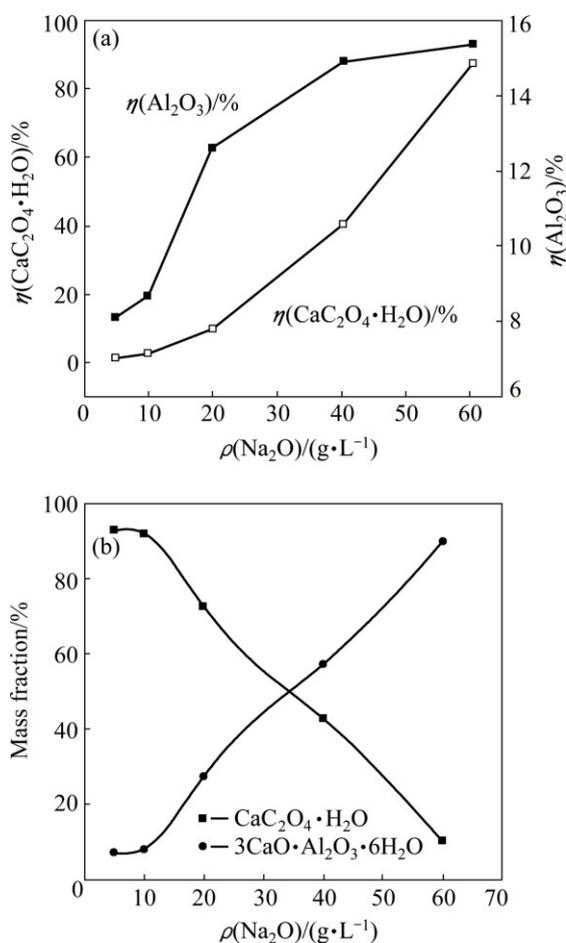
**Fig. 6** EDS element maps of sludge after calcium oxalate reacts with sodium aluminate solution (Ca is contributed by TCA and calcium oxalate; Al originates from TCA. Sodium aluminate solution:  $\rho(\text{Na}_2\text{O})=37.46$  g/L,  $\alpha_k=2.90$ ; 96 °C; 60 min. Arrows indicate the presence of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ )

In Fig. 6, TCA and calcium oxalate are presented as fine particles size (<5 μm). Calcium oxalate is difficult to distinguish from TCA on the basis of morphological characteristics. Comparing Fig. 6(b) with Fig. 6(c), TCA in the form of element Al is scattered on the surface of calcium oxalate. TCA also co-exists with calcium oxalate, as shown in Fig. 6(b). These findings demonstrate that

calcium oxalate is readily converted into TCA at temperatures higher than 90 °C.

### 4.3 Influence of caustic soda concentration on reaction of calcium oxalate with aluminate solution

The concentration of caustic soda in a series of washing tanks sharply decreases during the red mud washing process. Figure 7 displays the influence of caustic soda concentration on the calcium oxalate conversion ratio, alumina reaction ratio and the mass fraction of calcium-containing compounds in the sludge.

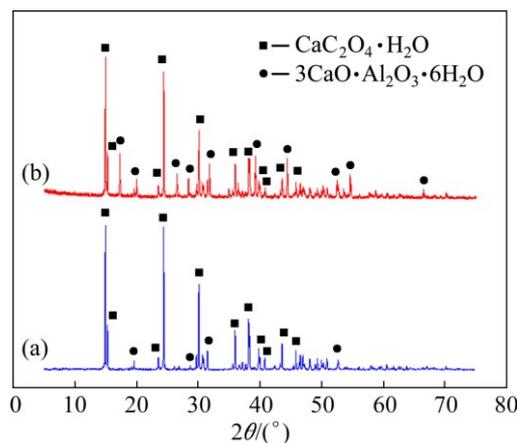


**Fig. 7** Influence of caustic soda concentration on conversion ratio of calcium oxalate (a) and mass distribution of calcium oxalate and TCA (b) (Sodium aluminate solution:  $\alpha_k=1.70$ ; 96 °C; 60 min)

Figure 7 shows that the increase in the  $\text{Na}_2\text{O}$  concentration significantly enhances the conversion ratio of calcium oxalate and the reaction ratio of alumina in the sodium aluminate solution at 96 °C. The conversion ratio of calcium oxalate remains less than 10%, and the mass fraction of TCA in the sludge is less than 27% in solution of  $\rho(\text{Na}_2\text{O}) < 20$  g/L. And then the conversion ratio of calcium oxalate and the mass fraction of TCA in the sludge significantly increase as the caustic soda

concentration increases. Therefore, the conversion of calcium oxalate into TCA can be inhibited by reducing the concentration of caustic soda in the sodium aluminate solution. The fact suggests that calcium oxalate should be discharged alone into red mud stock dump rather than currently pumped into the first or the second red mud washing tanks to match the caustic soda concentration.

The XRD patterns of the sludge after calcium oxalate reacting with the sodium aluminate solution at 96 °C are illustrated in Fig. 8.



**Fig. 8** XRD patterns of sludge after calcium oxalate reacts with sodium aluminate solution (Sodium aluminate solution: (a)  $\rho(\text{Na}_2\text{O})=10$  g/L, (b)  $\rho(\text{Na}_2\text{O})=40$  g/L,  $\alpha_k=1.70$ ; 96 °C; 60 min)

Many well-characteristic peaks in Fig. 8(a) are assigned to  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , and a few weak peaks of TCA appear in the sodium aluminate solution of  $\rho(\text{Na}_2\text{O})=10$  g/L. However, a number of peaks of TCA are also found in the sodium aluminate solution of  $\rho(\text{Na}_2\text{O})=40$  g/L (Fig. 8(b)). These results confirm that calcium oxalate is readily converted into TCA in the concentrated aluminate solution; as a result, anti-causticisation occurs.

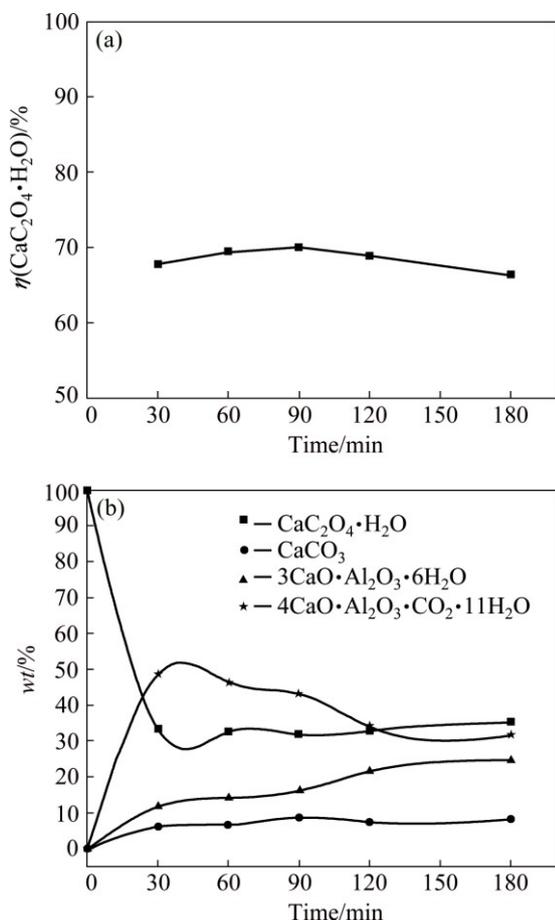
### 4.4 Influence of sodium carbonate in sodium aluminate solution on reaction of calcium oxalate with aluminate solution containing carbonate anion

Sodium carbonate is a harmful impurity in Bayer liquor [22] and is predominantly produced from the reaction of  $\text{CaCO}_3$  with  $\text{NaOH}$  at high temperature, as expressed in the following reaction:



The pregnant sodium aluminate solution in alumina refineries often contains 5–35 g/L  $\text{Na}_2\text{CO}_3$  (equal to 2.9–20.5 g/L  $\text{Na}_2\text{O}_c$ ). Figure 4 indicates that a part of calcium oxalate changes into calcium carbonate and TCA in the sodium carbonate solution and the sodium aluminate solution, respectively. Thus, the influence of

sodium carbonate on the behavior of calcium oxalate in the sodium aluminate solution should be elucidated. Results are shown in Fig. 9.

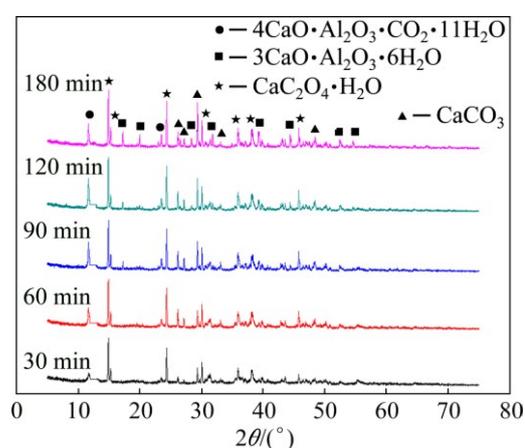


**Fig. 9** Influence of sodium carbonate in sodium aluminate solution on the conversion ratio of calcium oxalate (a) and the mass distribution of calcium-containing compounds (b) (Sodium aluminate solution:  $\rho(\text{Na}_2\text{O})=37.46$  g/L,  $\alpha_k=2.90$ ;  $\rho(\text{Na}_2\text{O}_c)=10$  g/L; 96 °C)

Figure 9(a) shows that calcium oxalate readily reacts with solution within 30 min, and the conversion ratio of calcium oxalate slightly increases and then slowly reduces from 30 to 180 min. Figure 9(a) also reveals that the 69.45% conversion ratio of calcium oxalate at 60 min differs from the 45.99% conversion ratio shown in Fig. 5. This difference indicates that sodium carbonate accelerates the transformation of calcium oxalate at 96 °C because of the simultaneous reaction, as expressed in Eqs. (7) and (8). Thus, the remarkable anti-causticisation in Chinese alumina refineries accounts for a large amount of sodium carbonate generated at increased temperature (Eq. (9)). Figure 9(b) shows that the calcium oxalate content sharply reduces at 30 min and then remains unchanged as the reaction time is extended. The calcium carbonate content (<10%) nearly remains constant. The TCA content consistently increases while the hydrocalmite

content increases initially and then decreases gradually with residence time. These results indicate that hydrocalmite can change into TCA, and this finding is consistent with that illustrated in Figs. 1 and 3 (area 7). The calcium carbonate content is considerably less than the TCA and hydrocalmite contents because TCA is more stable than  $\text{CaCO}_3$  in the sodium aluminate solution, as described in Fig. 3 (areas 6 and 7). Compared with Fig. 5, Fig. 9 demonstrates that calcium oxalate reacts more rapidly with solution; as a result, anti-causticisation and alumina loss occur.

The XRD patterns of the sludge are shown in Fig. 10.

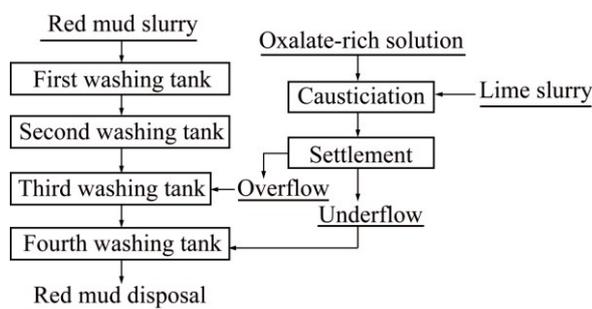


**Fig. 10** XRD patterns of sample after calcium oxalate reacts with sodium aluminate solution containing sodium carbonate (Sodium aluminate solution:  $\rho(\text{Na}_2\text{O})=37.46$  g/L,  $\alpha_k=2.90$ ;  $\rho(\text{Na}_2\text{O}_c)=10$  g/L; 96 °C)

Calcium oxalate ( $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ), hydrocalmite ( $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$ ), and calcium carbonate can be observed at 30 min (Fig. 10). The characteristic peak of TCA can be detected at 90 min, and the peak intensity increases gradually. This trend suggests that hydrocalmite is readily formed and subsequently converted to TCA. Calcium oxalate can also be converted to  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$  instead of  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CO}_2 \cdot 12\text{H}_2\text{O}$  [25] in the sodium aluminate solution containing sodium carbonate. Thus,  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$  is likely formed, as illustrated in Fig. 1.

On the basis of these findings, the following conclusions can be made. Calcium oxalate can be relatively stable in dilute aluminate solution ( $\rho(\text{Na}_2\text{O})$  and  $\rho(\text{Al}_2\text{O}_3)$  are preferably under 20 g/L) for a very short time at low temperatures. In an alumina refinery in Shangdong Province in China, a novel process (as shown in Fig. 11) was presented to remove sodium oxalate by lime causticisation [30]. In this process, lime was added according to the molar ratio of  $n(\text{CaO})/n(\text{Na}_2\text{C}_2\text{O}_4)=1.0-1.5$  and more than 90%  $\text{Na}_2\text{C}_2\text{O}_4$  changed into

$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . The formation of TCA and hydrocalmite was successfully inhibited in the diluted sodium aluminate solution. Moreover, as compared with the traditional lime causticisation, solid content in slurry then reduced significantly, leading to a better clarification by settlement for slurry after lime causticisation. Afterwards, the overflow was pumped into the third washing tank of red mud after the slurry well settled, the underflow was then pumped into the final washing tanks with  $\rho(\text{Na}_2\text{O})$  of 5 g/L and a residence time less than 2 h. As a result, the anti-causticisation of calcium oxalate was perfectly prevented the novel process reduces alumina loss by about 50% and saves around 60% lime. By contrast, the concentrated slurry in traditional lime causticisation is pumped into the second washing tank due to bad settlement property. This procedure causes significant anti-causticisation, which leads to large alumina loss and much sodium oxalate returning into aluminate solution.



**Fig. 11** Novel lime-causticisation flowsheet for removal of sodium oxalate

## 5 Conclusions

1) The increase in the concentration of sodium carbonate or caustic soda enlarges the stable area of calcium carbonate or TCA, respectively. Calcium oxalate is stable in dilute solutions at low temperatures; otherwise, calcium oxalate changes into  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CO}_2 \cdot 11\text{H}_2\text{O}$ ,  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$ ,  $\text{CaCO}_3$ , or TCA in aluminate solutions. The increase in the alumina concentration induces the conversion of calcium oxalate and  $\text{CaCO}_3$  to  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$  and TCA.  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$  is a more stable substance than  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CO}_2 \cdot 11\text{H}_2\text{O}$ .

2) Calcium oxalate can be converted to TCA and calcium carbonate in sodium aluminate solution and sodium carbonate solution, respectively. The conversion ratio of calcium oxalate in the sodium aluminate solution and anti-causticisation increase with temperature, residence time, and caustic soda concentration.

3) Sodium carbonate in sodium aluminate solution complicates the reaction behavior of calcium-containing

compounds; sodium carbonate in aluminated solution favors the formation of  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$  and TCA instead of calcium carbonate. Sodium carbonate significantly increases the conversion ratio of calcium oxalate and reduces the content of calcium oxalate in sludge.  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$  can be converted to TCA in the sodium aluminate solution at increased temperature. The formation of hydrocalmite and TCA causes alumina loss.

4) Anti-causticisation is inhibited when a novel process of lime causticisation was adopted in an alumina refinery. Compared with the traditional process, the novel process reduced about 50% alumina loss and saved around 60% lime addition.

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## 铝酸钠溶液中草酸钙的行为

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**摘要:** 草酸钙的稳定性对于铝酸钠溶液中草酸钠的脱除至关重要。研究了草酸钙在含有碳酸钠的铝酸钠溶液中的反应行为。结果表明, 在铝酸钠溶液和碳酸钠溶液中, 草酸钙能够分别被转化为铝酸三钙(TCA)和碳酸钙。在铝酸钠溶液中, 升高温度、延长反应时间以及增加苛性碱浓度会使得草酸钙的转化率增加, 进而发生反苛化反应。此外, 含钙化合物的稳定性在含有碳酸钠的铝酸钠溶液中与其在单一的铝酸钠或者碳酸钠溶液中不同。铝酸钠溶液中的碳酸钠会促进草酸钙的转化, 因此  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CO}_2\cdot 11\text{H}_2\text{O}$  和 TCA 的形成会导致氧化铝的损失。在铝酸钠溶液中, 温度升高会促进碳酸钙、 $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CO}_2\cdot 11\text{H}_2\text{O}$  和草酸钙转化为 TCA。在低温稀铝酸钠溶液中, 短停留时间操作条件下, 草酸钙可以保持相对稳定。研究的新型石灰苛化去除草酸钠工艺已经应用于国内某氧化铝厂。

**关键词:** 草酸钙; 铝酸钠溶液; 碳酸钠; 苛化; 活度系数

(Edited by Yun-bin HE)