



## Secondary reaction mechanism of leaching process of calcium aluminate slag

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**Abstract:** SiO<sub>2</sub> in calcium aluminate slag exists in the form of  $\gamma$ -2CaO·SiO<sub>2</sub> which is more stable than  $\beta$ -2CaO·SiO<sub>2</sub>. However, it is decomposed by sodium carbonate solution during leaching process, leading to the secondary reaction. The extent of secondary reaction and reaction mechanism of calcium aluminate slag were studied using XRD. The results show that the decomposition rate of  $\gamma$ -2CaO·SiO<sub>2</sub> increases with the increase in leaching time and sodium carbonate concentration. The main products of secondary reaction are the mixture of hydrogarnet and sodium hydrate alumina–silicate. SiO<sub>2</sub> concentration rises firstly and then drops with the increase of leaching temperature. XRD results indicate that the stable product of secondary reaction at low temperature is hydrogarnet. But hydrogarnet is transformed into sodium hydrate alumina–silicate at high temperature.

**Key words:** calcium aluminate slag; secondary reaction; alumina; leaching

### 1 Introduction

With the significantly increasing alumina production capability in recent years, the discrepancy between the supply and the demand of the materials of bauxite in China is increasingly serious [1]. One of the methods to solve this discrepancy is to explore and utilize new alumina-containing materials [2–4]. Calcium aluminate process (lime sintering process) is a method to leach alumina from iron-bearing bauxite, fly ash and alumina-containing slags [5–7]. In this process, iron-bearing bauxite is sintered with limestone at 1500 °C. The main phases of the sinter are 12CaO·7Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -2CaO·SiO<sub>2</sub>. The alumina of 12CaO·7Al<sub>2</sub>O<sub>3</sub> is easily leached into sodium carbonate solution.

The crystal form of 2CaO·SiO<sub>2</sub> of calcium aluminate slag is  $\gamma$  type [8], but that of soda–lime sinter is  $\beta$  type [9]. The different crystal structures of dicalcium silicate have different influences on alumina leaching of sinters.  $\beta$ -2CaO·SiO<sub>2</sub> of soda–lime sinter will react with NaOH, Na<sub>2</sub>CO<sub>3</sub> and NaAl(OH)<sub>4</sub>. Then, sodium hydrate alumino–silicate and hydrogarnet are formed [10–13]. In

this way, Al(OH)<sub>4</sub><sup>−</sup> and Na<sup>+</sup> are leached out from sinter and then precipitated into the red mud again. Thus, alumina leaching rate of sinter decreased. This is called the secondary reaction. Secondary reaction will cause the alumina loss of the leaching process. And the decomposed silicon dioxide will come into the crude liquor and complicate the desilication system.

It has been reported that  $\gamma$ -2CaO·SiO<sub>2</sub> is inert in sodium aluminate solution, and it normally does not react with other phases [14]. But our former research indicates that partial  $\gamma$ -2CaO·SiO<sub>2</sub> will be decomposed and cause secondary reaction in the solution with high sodium carbonate concentration [15]. The secondary reaction of  $\gamma$ -2CaO·SiO<sub>2</sub> is seldom reported. Therefore, in this work, the effects of sodium carbonate concentration, leaching time and leaching temperature on the decomposition of  $\gamma$ -2CaO·SiO<sub>2</sub> were studied and the secondary reaction mechanism was discussed.

### 2 Experimental

#### 2.1 Materials

CaCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH and SiO<sub>2</sub> used in the

experimental studies are analytical pure reagents.  $\text{Al}(\text{OH})_3$  used in the experiment is an industrial pure reagent.

## 2.2 Equipments

Muffle furnace, gas shielded  $\text{MoSi}_2$  furnace, magnetic stirring constant temperature water bath, X-ray diffraction analyzer (PANalytical PW3040/60) and spectrophotometer (722S) were used.

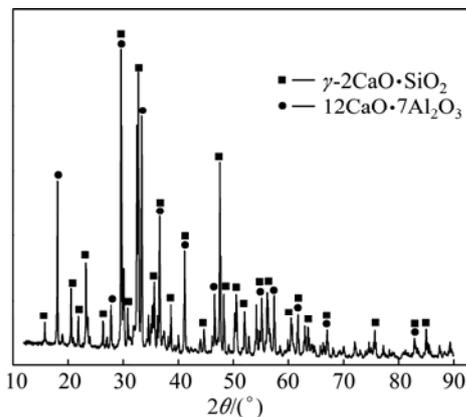
## 2.3 Smelting of calcium aluminate slag

The smelting experiments were carried out in a gas shielded  $\text{MoSi}_2$  furnace and the vessel was a graphite crucible. The smelting temperature was  $1500\text{ }^\circ\text{C}$  and the holding time was 1 h. After smelting, the melt was cooled at the speed of  $5\text{ }^\circ\text{C}/\text{min}$ , and it was taken out at the temperature of  $400\text{ }^\circ\text{C}$ . After grinding, the particle size of the slag is less than  $74\text{ }\mu\text{m}$ .

The calcium aluminate slag is synthesized by chemical reagents. Its  $m(\text{Al}_2\text{O}_3)/m(\text{SiO}_2)$  (the mass ratio of  $\text{Al}_2\text{O}_3$  to  $\text{SiO}_2$ ) and  $n(\text{CaO})/n(\text{Al}_2\text{O}_3)$  (the mole ratio of  $\text{CaO}$  to  $\text{Al}_2\text{O}_3$ , excluding the  $\text{CaO}$  of  $2\text{CaO}\cdot\text{SiO}_2$ ) are 1.3 and 1.7, respectively. Table 1 shows the chemical composition of the slag and Fig. 1 shows the XRD results of the slag. XRD result indicates that the main phases in the slag are  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  and  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$ , whose contents are 46.57% and 52.96%, respectively according to Rietveld analysis. Pure  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  and  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  are synthesized at  $1500\text{ }^\circ\text{C}$  by chemical reagents separately.

**Table 1** Chemical composition of slag (mass fraction, %)

$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{CaO}$
24.13	18.56	57.31



**Fig. 1** XRD pattern of calcium aluminate slag

## 2.4 Leaching of calcium aluminate slag

The sodium aluminate solution obtained from the slag was treated according to the carbonization precipitation process. Circulating mother liquid was used to leach new calcium aluminate slag. The conditions of

the leaching solution are: caustic alkali concentration of  $7\text{ g/L}$ ,  $\alpha_k=1.6$  (mole ratio of  $\text{Na}_2\text{O}$  to  $\text{Al}_2\text{O}_3$ ) and liquid–solid ratio of  $4.5\text{ mL/g}$ .

## 2.5 Methods of analysis

The contents of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{Na}_2\text{O}$  in samples and filtrate were analyzed by XRF. Alumina leaching rate is calculated according to Eq. (1).

$$\eta_A = 1 - \frac{m(\text{Al}_2\text{O}_3)/m(\text{SiO}_2)_{\text{residue}}}{m(\text{Al}_2\text{O}_3)/m(\text{SiO}_2)_{\text{slag}}} \quad (1)$$

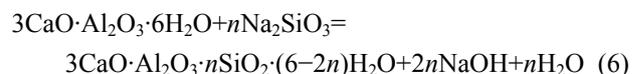
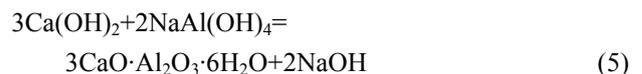
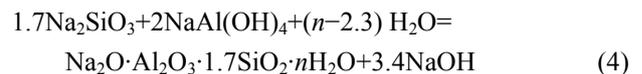
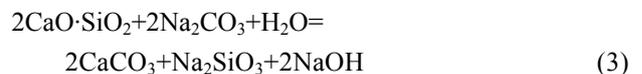
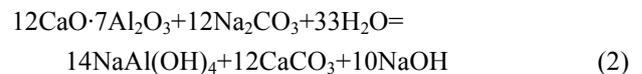
where  $\eta_A$  is alumina leaching rate;  $m(\text{Al}_2\text{O}_3)$  is the mass of  $\text{Al}_2\text{O}_3$  in slag or residue;  $m(\text{SiO}_2)$  is the mass of  $\text{SiO}_2$  in slag or residue.

Phase components of calcium aluminate slag and leaching residues were identified by X-ray diffraction (PANalytical PW3040/60). The concentration of  $\text{SiO}_2$  in leaching solution was determined with silico–molybdenum blue spectrophotometer. Thus, the decomposition property of  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  ( $\Delta\rho(\text{SiO}_2)$ ) during alumina leaching process is defined as the concentration change of  $\text{SiO}_2$  after alumina leaching.

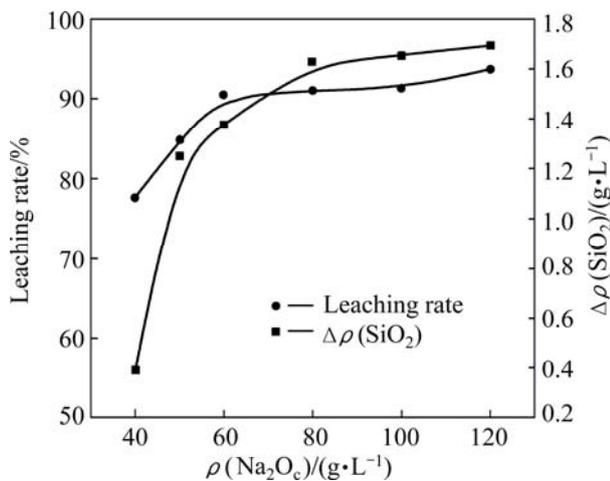
## 3 Results and discussion

### 3.1 Effect of sodium carbonate concentration on decomposition of $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$

The reaction between  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{CO}_3$  (Eq. (2)) can realize the recovery of alumina from calcium aluminate slag. Meanwhile,  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  will also react with  $\text{Na}_2\text{CO}_3$ , leading to the decomposition of dicalcium silicate (Eq. (3)) and the loss of alumina extracted into solution (Eq. (4)–(6)). Therefore, the effect of sodium carbonate concentration (abbr.,  $\text{Na}_2\text{O}_c$ ) on decomposition characteristics of  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  was studied. The results are shown in Fig. 2.



The results indicate that the  $\Delta\rho(\text{SiO}_2)$  concentration increases obviously when  $\text{Na}_2\text{O}_c$  concentration increases from  $40\text{ g/L}$  to  $80\text{ g/L}$ . The increasing rate of  $\Delta\rho(\text{SiO}_2)$  decreases as the  $\text{Na}_2\text{O}_c$  concentration continuously increases.



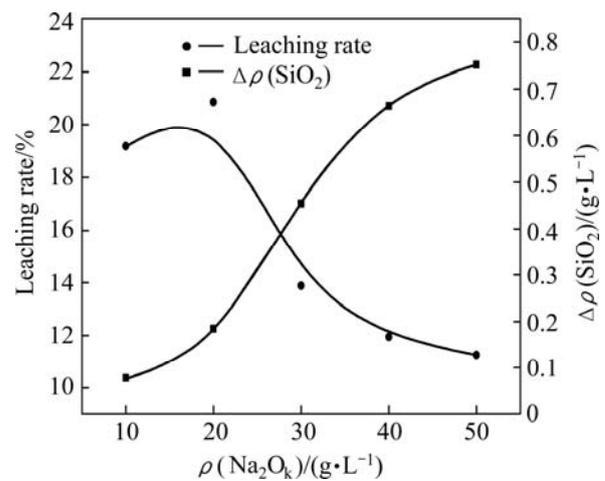
**Fig. 2** Effect of  $\text{Na}_2\text{O}_c$  on leaching rate of slag and decomposability of  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  (Conditions:  $\rho(\text{Na}_2\text{O}_k)=7\text{ g/L}$ ,  $\alpha_k=1.6$ , temperature  $75\text{ }^\circ\text{C}$ ,  $t=120\text{ min}$ , and liquid-solid ratio  $4.5\text{ mL/g}$ )

The values of  $\Delta\rho(\text{SiO}_2)$  vary from  $0.4\text{ g/L}$  to  $1.7\text{ g/L}$ , indicating that the decomposition of  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  is serious when  $\text{Na}_2\text{O}_c$  concentration is up to  $80\text{ g/L}$ .

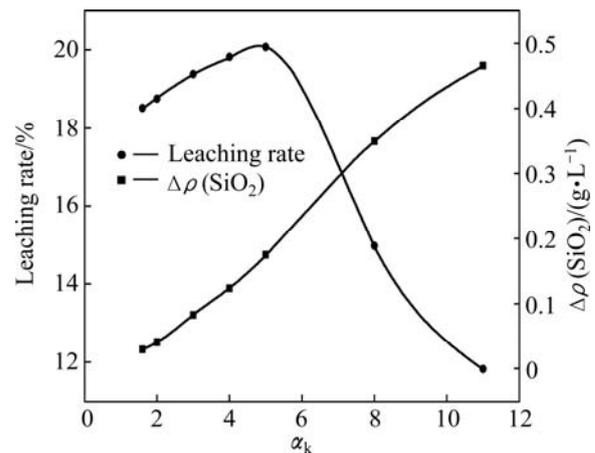
The change trend of alumina leaching rate under different  $\text{Na}_2\text{O}_c$  concentrations is similar to that of  $\Delta\rho(\text{SiO}_2)$ . When liquid-solid ratio is  $4.5\text{ mL/g}$ , calcium aluminate slag will consume  $\text{Na}_2\text{O}_c$  at approximately  $50\text{--}60\text{ g/L}$  according to Eq. (2). Therefore, the alumina leaching rate increases from  $77.59\%$  to  $90.49\%$  under different  $\text{Na}_2\text{O}_c$  concentrations. Further extension of  $\text{Na}_2\text{O}_c$  has little effect on the improvement of alumina leaching ratio.

### 3.2 Effect of $\text{Na}_2\text{O}_k$ concentration and $\alpha_k$ on decomposition of $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$

In order to avoid the effect of sodium carbonate on decomposition of  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$ , its concentration is fixed at  $7\text{ g/L}$  in this section. The effects of  $\text{Na}_2\text{O}_k$  concentration and  $\alpha_k$  on the alumina leaching rate of calcium aluminate slag and the decomposition of  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  are shown in Fig. 3 and Fig. 4. It can be seen that the leaching rates of samples are less than  $21\%$  under these conditions. This is because the  $\text{Na}_2\text{O}_c$  is not enough to react with  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  according to Eq. (2). The  $\Delta\rho(\text{SiO}_2)$  concentration increases when  $\text{Na}_2\text{O}_k$  concentration (Fig. 3) and  $\alpha_k$  (Fig. 4) increase. The maximum values of  $\Delta\rho(\text{SiO}_2)$  concentration are  $0.75\text{ g/L}$  and  $0.47\text{ g/L}$  when  $\text{Na}_2\text{O}_k$  concentration is  $50\text{ g/L}$  (Fig. 3) and  $\alpha_k$  is  $11$  (Fig. 4). Both of the two values are lower than  $1.69\text{ g/L}$  which is obtained when  $\text{Na}_2\text{O}_c$  concentration is  $120\text{ g/L}$  (Fig. 2). These results indicate that  $\text{Na}_2\text{O}_k$  concentration and  $\alpha_k$  have important effect on the decomposability of  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$ , but they are not the main factors compared to  $\text{Na}_2\text{O}_c$ .



**Fig. 3** Effect of  $\text{Na}_2\text{O}_k$  concentration on leaching rate of slag and decomposability of  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  (Conditions:  $\rho(\text{Na}_2\text{O}_c)=7\text{ g/L}$ ,  $\alpha_k=1.6$ , temperature= $75\text{ }^\circ\text{C}$ ,  $t=120\text{ min}$ , and liquid-solid ratio  $4.5\text{ mL/g}$ )



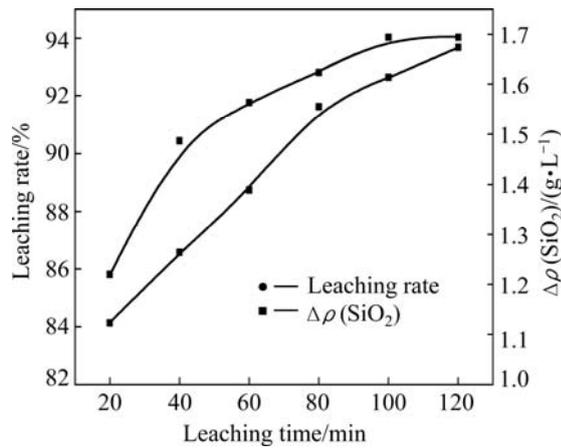
**Fig. 4** Effect of  $\alpha_k$  on leaching rate of slag and decomposability of  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  (Conditions:  $\rho(\text{Na}_2\text{O}_k)=7\text{ g/L}$ ,  $\rho(\text{Na}_2\text{O}_c)=7\text{ g/L}$ , temperature  $75\text{ }^\circ\text{C}$ ,  $t=120\text{ min}$ , and liquid-solid ratio  $4.5\text{ mL/g}$ )

### 3.3 Effect of leaching time on decomposition of $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$

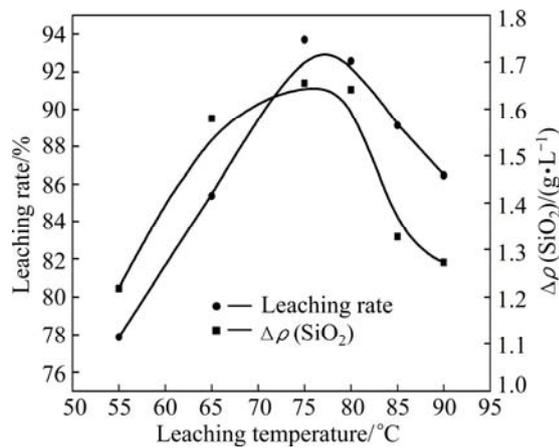
The effect of leaching time on the alumina leaching rate of calcium aluminate slag and the decomposition of  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  is shown in Fig. 5. It can be seen that the leaching rate and the  $\Delta\rho(\text{SiO}_2)$  concentration increase with increasing leaching time. When leaching time is up to  $80\text{ min}$ , its effect becomes little. The inflection point of leaching ratio does not appear under this condition because the reaction extent of secondary reaction is lower than that of leaching reaction.

### 3.4 Effect of leaching temperature on decomposition of $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$

Figure 6 shows alumina leaching rate and decomposability under different leaching temperatures. The  $\Delta\rho(\text{SiO}_2)$  concentration increases to  $1.73\text{ g/L}$  when



**Fig. 5** Effect of leaching time on leaching rate of slag and decomposability of  $\gamma$ -2CaO·SiO<sub>2</sub> (Conditions:  $\rho(\text{Na}_2\text{O}_k)=7$  g/L,  $\alpha_k=1.6$ , temperature 75 °C,  $\rho(\text{Na}_2\text{O}_c)=120$  g/L, and liquid–solid ratio 4.5 mL/g)



**Fig. 6** Effect of leaching temperature on leaching rate of slag and decomposability of  $\gamma$ -2CaO·SiO<sub>2</sub> (Conditions:  $\rho(\text{Na}_2\text{O}_k)=7$  g/L,  $\alpha_k=1.6$ ,  $t=120$  min,  $\rho(\text{Na}_2\text{O}_c)=120$  g/L, and liquid–solid ratio 4.5 mL/g)

leaching temperature is 80 °C, and then decreases subsequently. It has been reported that reaction temperature rise will enhance the equilibrium solubility of silica solution. It indicates that the solubilised silica is transferred into the residue when leaching temperature is higher than 80 °C. There are two transferred forms of silica in residue: sodium hydrate alumino–silicate and

hydrogarnet. Both will cause the loss of alumina leached into solution.

The inverted V trend of alumina leaching rate also proves the existence of the secondary reaction. The maximum value of leaching rate is 93.69% at the inflection point (75 °C). The results of different leaching temperatures are shown in Table 2. The leaching experiments of pure 12CaO·7Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -2CaO·SiO<sub>2</sub> are also carried out separately under the same conditions. The molecular formulas of sodium hydrate alumino–silicate and hydrogarnet are Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·1.7SiO<sub>2</sub>·*n*H<sub>2</sub>O and 3CaO·Al<sub>2</sub>O<sub>3</sub>·*n*SiO<sub>2</sub>·(6–2*n*)H<sub>2</sub>O (*n*≈0.1), respectively. Thus, the mass ratios of Al<sub>2</sub>O<sub>3</sub> to SiO<sub>2</sub> in sodium hydrate alumino–silicate and hydrogarnet are 1.0 and 17, respectively.

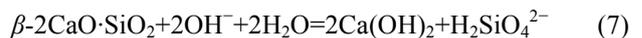
From the ratio of  $\Delta\rho(\text{Al}_2\text{O}_3)$  and  $\Delta\rho'(\text{SiO}_2)$ , it can be concluded that the products of secondary reaction are the mixture of sodium hydrate alumino–silicate and hydrogarnet. With the increase of leaching temperature, hydrogarnet tends to be transformed into sodium hydrate alumino–silicate. The amount of secondary reaction becomes large and then alumina leaching rate decreases obviously when leaching temperature is up to 85 °C. The further study of secondary reaction mechanism is discussed in the next section.

### 3.5 Mechanism of secondary reaction of calcium aluminate slag

#### 3.5.1 Principle of secondary reaction

About 30% of sinter produced during soda–lime sintering process is  $\beta$ -2CaO·SiO<sub>2</sub>, which will be decomposed and cause the loss of alumina. The phenomenon mentioned above is called “secondary reaction” [16]. There are three main phases as NaOH, Na<sub>2</sub>CO<sub>3</sub> and NaAl(OH)<sub>4</sub> in sodium aluminate solution. But the dominant factors of the decomposition of dicalcium silicate have not been determined at present. These opinions may be described as follows [17–20].

1) The decomposition of dicalcium silicate is mainly caused by NaOH. And the decomposition reaction is shown in Eq. (7).



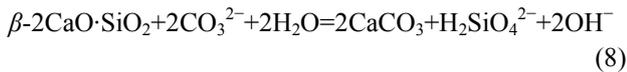
2) The decomposition of dicalcium silicate is mainly caused by Na<sub>2</sub>CO<sub>3</sub>. And the decomposition

**Table 2** Liquid results of leaching solution at different temperatures

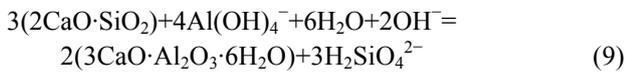
Temperature/ °C	Calcium aluminate		12CaO·7Al <sub>2</sub> O <sub>3</sub> *	$\gamma$ -2CaO·SiO <sub>2</sub> **	$\rho(\text{Al}_2\text{O}_3)/$	$\rho'(\text{SiO}_2)/$	$\rho(\text{Al}_2\text{O}_3)/$
	$\rho(\text{Al}_2\text{O}_3)/(\text{g}\cdot\text{L}^{-1})$	$\rho(\text{SiO}_2)/(\text{g}\cdot\text{L}^{-1})$	$\rho(\text{Al}_2\text{O}_3)/(\text{g}\cdot\text{L}^{-1})$	$\rho(\text{SiO}_2)/(\text{g}\cdot\text{L}^{-1})$	(g·L <sup>-1</sup> )	(g·L <sup>-1</sup> )	$\rho'(\text{SiO}_2)$
75	50.24	1.65	50.88	1.76	0.64	0.11	5.82
80	49.63	1.73	51.43	2.11	1.80	0.38	4.74
85	47.79	1.22	51.92	2.39	4.13	1.17	3.53

\* The data of the column are obtained when 12CaO·7Al<sub>2</sub>O<sub>3</sub> is the only raw material. \*\* The data of the column are obtained when  $\gamma$ -2CaO·SiO<sub>2</sub> is the only raw material.  $\Delta\rho(\text{Al}_2\text{O}_3)$  is the difference value between column 2 and column 4.  $\Delta\rho'(\text{SiO}_2)$  is the difference value between column 3 and column 5.

reaction is shown in Eq. (8):



3) The decomposition of dicalcium silicate is mainly caused by  $\text{NaAl}(\text{OH})_4$ . And the decomposition reaction is shown in Eq. (9):



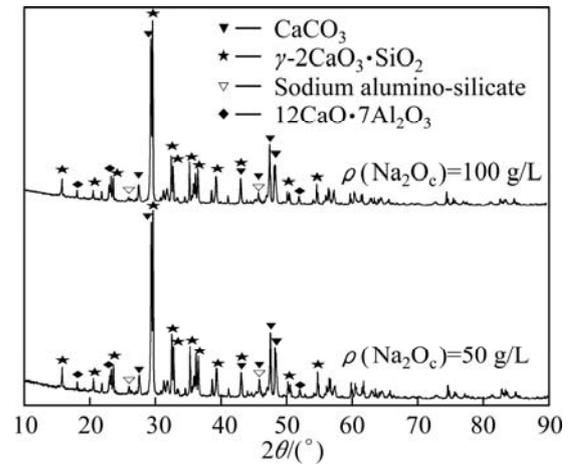
Therefore,  $\beta$  type dicalcium silicate can be decomposed by the phases mentioned above under proper conditions. CHEN et al [17] has studied the thermomechanics of the decomposition reaction with  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NaAl}(\text{OH})_4$ . The results indicate that the stability of dicalcium silicate in the solution is decreased in the following sequence:  $\text{NaOH}$ ,  $\text{NaAl}(\text{OH})_4$ ,  $\text{Na}_2\text{CO}_3$ . That is to say,  $\text{Na}_2\text{CO}_3$  has the strongest decomposability on  $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ . Furthermore, BI [14] believed that dicalcium silicate could be decomposed thoroughly under pure  $\text{Na}_2\text{CO}_3$  solution.

Our research is focused on lime sintering process which has two differences compared with soda–lime sintering process. Firstly, the crystal structure of dicalcium silicate of the former process is  $\gamma$  type with low activity; but that of the latter process is  $\beta$  type with high activity. Secondly, the sodium carbonate concentration in the former process is greater than that in the latter process, but the concentrations of caustic alkali and sodium aluminate show the contrary trend. Interestingly,  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  is more stable, but  $\text{Na}_2\text{CO}_3$  has the stronger decomposability in lime sintering process. Therefore, the mechanism of the secondary reaction between lime sintering process and soda–lime sintering process is different.

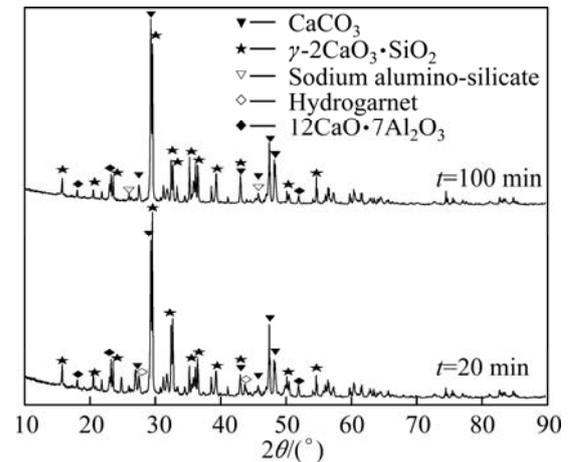
### 3.5.2 Mechanism of secondary reaction of calcium aluminate slag

XRD analysis of leaching residues formed under different conditions is used to study the mechanism of the secondary reaction. The XRD patterns are shown in Figs. 7 and 9.

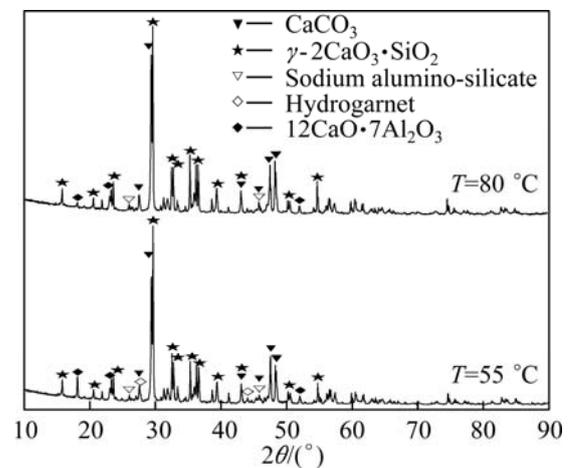
The XRD results (Figs. 7–9) show that there are large amounts of  $\text{CaCO}_3$  and  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  in leaching residues under different conditions. Small quantity of  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  remains in the residues. The product of secondary reaction is only sodium hydrate aluminosilicate when sodium carbonate concentrations are 50 g/L and 100 g/L, respectively (Fig. 7). Hydrogarnet is formed when leaching time is 20 min, but it will be transformed into sodium hydrate aluminosilicate with leaching time increasing (Fig. 8, Eq. (10)). Sodium hydrate aluminosilicate and hydrogarnet are formed at 55 °C, but the latter disappears when the leaching temperature is up to 80 °C (Fig. 9).



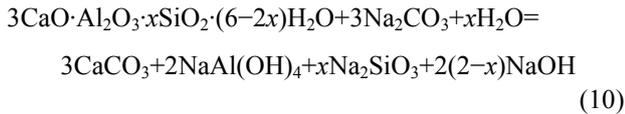
**Fig. 7** XRD patterns of leaching residue with different  $\text{Na}_2\text{O}_c$  concentrations (Conditions:  $\rho(\text{Na}_2\text{O}_k)=7$  g/L,  $\alpha_k=1.6$ , temperature 75 °C,  $t=120$  min, and liquid–solid ratio 4.5 mL/g)



**Fig. 8** XRD patterns of leaching residue with different leaching time (Conditions:  $\rho(\text{Na}_2\text{O}_k)=7$  g/L,  $\alpha_k=1.6$ , temperature 75 °C,  $\rho(\text{Na}_2\text{O}_c)=120$  g/L, and liquid–solid ratio 4.5 mL/g)



**Fig. 9** XRD patterns of leaching residue at different temperatures (Conditions:  $\rho(\text{Na}_2\text{O}_k)=7$  g/L,  $\alpha_k=1.6$ ,  $t=120$  min,  $\rho(\text{Na}_2\text{O}_c)=120$  g/L, and liquid–solid ratio 4.5 mL/g)



According to Eq. (10),  $\text{NaAl(OH)}_4$  will be formed in this reaction especially when silica saturation of hydrogarnet is low. And the macro phenomenon of the reaction is the increase in alumina leaching rate. This is another reason for the increase of leaching rate with increasing leaching time (Figs. 5 and 8).

High reaction temperature could promote not only Eq. (10) but also Eq. (4).  $\text{NaAl(OH)}_4$  formed by Eq. (10) is less than that consumed by Eq. (4). Thus, alumina leaching ratio decreases when leaching temperature is higher than 75 °C (Fig. 6).

## 4 Conclusions

1)  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  is decomposed during alumina leaching process of calcium aluminate slag. But it is not stable in sodium carbonate solution. The occurrence of secondary reaction causes the loss of alumina from solution.

2) The dominant factor of the decomposition of dicalcium silicate is  $\text{Na}_2\text{CO}_3$ . The concentration of decomposed  $\text{SiO}_2$  increases to 1.71 g/L when the  $\text{Na}_2\text{CO}_3$  concentration increases to 120 g/L under the studied conditions.

3) The products of secondary reaction are sodium hydrate alumino-silicate and hydrogarnet when leaching time is 20 min and leaching temperature is 55 °C. Hydrogarnet is transformed into sodium hydrate alumino-silicate with increasing leaching time and rising leaching temperature.

## References

- [1] GU Song-qing. Alumina production technology with high efficiency and low consumption from Chinese bauxite resource [J]. *The Chinese Journal of Nonferrous Metals*, 2004, 14(1): 91–97. (in Chinese)
- [2] LIU Wan-chao, YANG Jia-kuan, XIAO Bo. Review on treatment and utilization of bauxite residues in China [J]. *International Journal of Mineral Processing*, 2009, 93(3): 220–231.
- [3] LIU Kui, CHEN Qi-yuan, HU Hui-ping, DING Zhi-ying, YIN Zhou-lan. Characteristics of scales formed from pressure leaching of Yuanjiang laterite [J]. *Hydrometallurgy*, 2011, 109(1–2): 131–139.
- [4] VESTOLA E A, KUUSENAHO M K N, RHI H M, TUOVINEN O H, PUHAKKA J A, PLUMB J J, KAKSONEN A H. Acid bioleaching of solid waste materials from copper, steel and recycling industries [J]. *Hydrometallurgy*, 2010, 103(1): 74–79.
- [5] HAYNES R J, ZHOU Y F, NAIDU R. Recycling and use of wastes/co-products from the iron/steel and alumina industries [J]. *International Journal of Environment and Waste Management*, 2011, 8(1): 174–211.
- [6] HUANG Zhao-hui, LIU Kai-qi, ZHAO Hong-wei, LI Zhuang. Study on extraction of alumina from sericite phyllite [J]. *Key Engineering Materials*, 2013, 544: 38–42.
- [7] GRZYMEK J, DERDACKA-GRZYMEK A, KONIK Z, STOK A, IWANCIW J. The new way of alumina lixiviation from sinters containing  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  in J. Grzymek's method [C]//*Light Metals 1988*. Warrendale: Minerals, Metals & Materials Society, 1988: 129–133.
- [8] WANG Bo, YU Hai-yan, SUN Hui-lan, BI Shi-wen. Effect of material ratio on leaching and self-disintegrating property of calcium aluminate slag [J]. *Journal of Northeastern University: Natural Science*, 2008, 29(11): 1593–1596. (in Chinese)
- [9] PADILLA R, SOHN H. Sodium aluminate leaching and desilication in lime-soda sinter process for alumina from coal wastes [J]. *Metallurgical Transactions B*, 1985, 16(4): 707–713.
- [10] ZHANG Ran, ZHENG Shi-li, MA Shu-hua, ZHANG Yi. Recovery of alumina and alkali in Bayer red mud by the formation of andradite–grossular hydrogarnet in hydrothermal process [J]. *Journal of Hazardous Materials*, 2011, 189(3): 827–835.
- [11] CHEN Bin, LI Xiao-bin, LIU Gui-hua. Behavior of  $\text{SiO}_2$  in the leaching process of alumina clinker with high concentration [J]. *Journal of University of Science and Technology of Beijing*, 2008, 15(5): 538–542.
- [12] LIU Gui-hua, LI Xiao-bin, PENG Zhi-hong, ZHOU Qiu-sheng. Behavior of calcium silicate in leaching process [J]. *Transactions of Nonferrous Metals Society of China*, 2003, 13(1): 213–216.
- [13] LI Xiao-bin, LIU Xiang-min, LIU Gui-hua, PENG Zhi-hong, LIU Ye-xiang. Study and application of intensified sintering process for alumina production [J]. *The Chinese Journal of Nonferrous Metals*, 2004, 14(6): 1031–1036. (in Chinese)
- [14] BI Shi-wen. *Process of alumina production* [M]. Beijing: Chemical Industry Press, 2006. (in Chinese)
- [15] SUN Hui-lan, YU Hai-yan, WANG Bo, ZHOU Huai-min, TU Gan-feng, BI Shi-wen. Study on synthesis and decomposition property of  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  [J]. *Mining and Metallurgical Engineering*, 2008, 28(5): 59–63. (in Chinese)
- [16] YU Hai-yan, PAN Xiao-lin, DING Ting-ting, ZHANG Wu, LIU Han, BI Shi-wen. Adsorption of sodium polyacrylate at interface of dicalcium silicate–sodium aluminate solution [J]. *Transactions of Nonferrous Metals Society of China*, 2011, 21(10): 2223–2226.
- [17] CHEN Bin, LI Xiao-bin, XU Hua-jun, PENG Zhi-hong, LIU Gui-hua, ZHOU Qiu-sheng. Thermodynamic analysis of secondary reactions in the clinker leaching process [J]. *Journal of Beijing University of Chemical Technology: Natural Science Edition*, 2007, 34(2): 189–192. (in Chinese)
- [18] LI Xiao-bin, XU Hua-jun, LIU Gui-hua, PENG Zhi-hong, ZHOU Qiu-sheng, LIU Yun-feng. Behavior of  $\text{SiO}_2$  during leaching process of alumina sinter [J]. *The Chinese Journal of Process Engineering*, 2006, 6(3): 431–434. (in Chinese)
- [19] LIU Gui-hua, LIU Yun-feng, LI Xiao-bin, PENG Zhi-hong, ZHOU Qiu-sheng, XU Hua-jun. Reducing loss of soda in red mud in process of Bayer digestion [J]. *The Chinese Journal of Nonferrous Metals*, 2006, 16(3): 555–559. (in Chinese)
- [20] XU Shuang. The secondary reaction in clinker digestion by sintering process [J]. *Metal Materials and Metallurgy Engineering*, 2008, 36(3): 56–59. (in Chinese)

## 铝酸钙炉渣浸出过程的二次反应机理

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**摘要:**  $\text{SiO}_2$  以  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  的形式存在于铝酸钙炉渣中,  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  比  $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$  稳定, 但是在氧化铝溶出过程中它仍然可以被碳酸钠溶液分解, 并引起二次反应。利用 XRD 研究铝酸钙炉渣二次反应的程度和机理。结果表明,  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$  的分解率随着浸出时间和碳酸钠浓度的增加而上升, 主要二次反应产物为水化石榴石和钠硅渣的混合物。溶液中  $\text{SiO}_2$  的浓度随着溶出温度的上升先增加而后降低。XRD 分析表明, 低温下二次反应的产物是水化石榴石, 而高温下水化石榴石则会转变为钠硅渣。

**关键词:** 铝酸钙炉渣; 二次反应; 氧化铝; 浸出

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