Secondary reaction mechanism of leaching process of calcium aluminate slag

Hui-lan SUN1,2, Bo WANG1,2, Jian-xin ZHANG1, Shu-feng ZONG1, Jia-jia LIU1
1. School of Materials Science and Engineering, Hebei University of Science and Technology, Shijiazhuang 050018, China;
2. Hebei Key Laboratory of Material Near-net Forming Technology, Hebei University of Science and Technology, Shijiazhuang 050018, China

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Abstract: SiO2 in calcium aluminate slag exists in the form of γ-2CaO·SiO2 which is more stable than β-2CaO·SiO2. 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 γ-2CaO·SiO2 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. SiO2 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·7Al2O3 and γ-2CaO·SiO2. The alumina of 12CaO·7Al2O3 is easily leached into sodium carbonate solution.

The crystal form of 2CaO·SiO2 of calcium aluminate slag is γ type [8], but that of soda–lime sinter is β type [9]. The different crystal structures of dicalcium silicate have different influences on alumina leaching of sinters. β-2CaO·SiO2 of soda–lime sinter will react with NaOH, Na2CO3 and NaAl(OH)4. Then, sodium hydrate alumino–silicate and hydrogarnet are formed [10–13]. In this way, Al(OH)4− and Na+ 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 γ-2CaO·SiO2 is inert in sodium aluminate solution, and it normally does not react with other phases [14]. But our former research indicates that partial γ-2CaO·SiO2 will be decomposed and cause secondary reaction in the solution with high sodium carbonate concentration [15]. The secondary reaction of γ-2CaO·SiO2 is seldom reported. Therefore, in this work, the effects of sodium carbonate concentration, leaching time and leaching temperature on the decomposition of γ-2CaO·SiO2 were studied and the secondary reaction mechanism was discussed.

2 Experimental

2.1 Materials
CaCO3, Na2CO3, NaOH and SiO2 used in the
experimental studies are analytical pure reagents. Al(OH)₃ used in the experiment is an industrial pure reagent.

2.2 Equipments

Muffle furnace, gas shielded MoSi₂ 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 MoSi₂ furnace and the vessel was a graphite crucible. The smelting temperature was 1500 °C and the holding time was 1 h. After smelting, the melt was cooled at the speed of 5 °C/min, and it was taken out at the temperature of 400 °C. After grinding, the particle size of the slag is less than 74 μm.

The calcium aluminate slag is synthesized by chemical reagents. Its \( \frac{m(\text{Al}_2\text{O}_3)}{m(\text{SiO}_2)} \) (the mass ratio of \( \text{Al}_2\text{O}_3 \) to \( \text{SiO}_2 \)) and \( \frac{n(\text{CaO})}{n(\text{Al}_2\text{O}_3)} \) (the mole ratio of \( \text{CaO} \) to \( \text{Al}_2\text{O}_3 \), excluding the \( \text{CaO} \) of \( 2\text{CaO}·\text{SiO}_2 \)) 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 \( 12\text{CaO}·7\text{Al}_2\text{O}_3 \) and \( \gamma-2\text{CaO}·\text{SiO}_2 \), whose contents are 46.57% and 52.96%, respectively according to Rietveld analysis. Pure \( 12\text{CaO}·7\text{Al}_2\text{O}_3 \) and \( \gamma-2\text{CaO}·\text{SiO}_2 \) are synthesized at 1500 °C by chemical reagents separately.

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

<table>
<thead>
<tr>
<th></th>
<th>( \text{Al}_2\text{O}_3 )</th>
<th>( \text{SiO}_2 )</th>
<th>( \text{CaO} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24.13</td>
<td>18.56</td>
<td>57.31</td>
</tr>
</tbody>
</table>

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 g/L, \( \alpha_c=1.6 \) (mole ratio of \( \text{Na}_2\text{O} \) to \( \text{Al}_2\text{O}_3 \)) and liquid–solid ratio of 4.5 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).

\[
\eta_A = 1 - \frac{m(\text{Al}_2\text{O}_3)_{\text{residue}}}{m(\text{Al}_2\text{O}_3)_{\text{slag}}} \tag{1}
\]

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 \( \gamma-2\text{CaO}·\text{SiO}_2 \) \((\Delta \rho(\text{SiO}_2))\) 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 \( \gamma-2\text{CaO}·\text{SiO}_2 \)

The reaction between \( 12\text{CaO}·7\text{Al}_2\text{O}_3 \) and \( \text{Na}_2\text{CO}_3 \) (Eq. (2)) can realize the recovery of alumina from calcium aluminate slag. Meanwhile, \( \gamma-2\text{CaO}·\text{SiO}_2 \) 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 \( \gamma-2\text{CaO}·\text{SiO}_2 \) was studied. The results are shown in Fig. 2.

\[
12\text{CaO}·7\text{Al}_2\text{O}_3 + 12\text{Na}_2\text{CO}_3 + 33\text{H}_2\text{O} = 14\text{NaAl(OH)}_4 + 12\text{CaCO}_3 + 10\text{NaOH} \tag{2}
\]

\[
2\text{CaO}·\text{SiO}_2 + 2\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = 2\text{CaCO}_3 + 2\text{Na}_2\text{SiO}_3 + 2\text{NaOH} \tag{3}
\]

\[
1.7\text{Na}_2\text{SiO}_3 + 2\text{NaAl(OH)}_4 + (n-2.3) \text{H}_2\text{O} = \text{Na}_2\text{O}·\text{Al}_2\text{O}_3·1.7\text{SiO}_2·n\text{H}_2\text{O} + 3.4\text{NaOH} \tag{4}
\]

\[
3\text{Ca(OH)}_2 + 2\text{NaAl(OH)}_4 = 3\text{CaO}·\text{Al}_2\text{O}_3·6\text{H}_2\text{O} + 2\text{NaOH} \tag{5}
\]

\[
3\text{CaO}·\text{Al}_2\text{O}_3·6\text{H}_2\text{O} + n\text{Na}_2\text{SiO}_3 = 3\text{CaO}·\text{Al}_2\text{O}_3·n\text{SiO}_2·(6-2n)\text{H}_2\text{O} + 2n\text{NaOH} + n\text{H}_2\text{O} \tag{6}
\]

The results indicate that the \( \Delta \rho(\text{SiO}_2) \) concentration increases obviously when \( \text{Na}_2\text{O}_c \) concentration increases from 40 g/L to 80 g/L. The increasing rate of \( \Delta \rho(\text{SiO}_2) \) decreases as the \( \text{Na}_2\text{O}_c \) concentration continuously increases.
The values of $\Delta \rho(\text{SiO}_2)$ vary from 0.4 g/L to 1.7 g/L, indicating that the decomposition of $\gamma$-$2\text{CaO} \cdot \text{SiO}_2$ is serious when Na$_2$O$_c$ concentration is up to 80 g/L.

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

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

In order to avoid the effect of sodium carbonate on decomposition of $\gamma$-$2\text{CaO} \cdot \text{SiO}_2$, its concentration is fixed at 7 g/L in this section. The effects of Na$_2$O$_k$ concentration and $\alpha_k$ on the alumina leaching rate of calcium aluminate slag and the decomposition of $\gamma$-$2\text{CaO} \cdot \text{SiO}_2$ 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 Na$_2$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 Na$_2$O$_k$ concentration (Fig. 3) and $\alpha_k$ (Fig. 4) increase. The maximum values of $\Delta \rho(\text{SiO}_2)$ concentration are 0.75 g/L and 0.47 g/L when Na$_2$O$_c$ concentration is 50 g/L (Fig. 3) and $\alpha_k$ is 11 (Fig. 4). Both of the two values are lower than 1.69 g/L which is obtained when Na$_2$O$_c$ concentration is 120 g/L (Fig. 2). These results indicate that Na$_2$O$_c$ concentration and $\alpha_k$ have important effect on the decomposability of $\gamma$-$2\text{CaO} \cdot \text{SiO}_2$, but they are not the main factors compared to Na$_2$O$_c$.

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

The effect of leaching time on the alumina leaching rate of calcium aluminate slag and the decomposition of $\gamma$-$2\text{CaO} \cdot \text{SiO}_2$ 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 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 $\gamma$-$2\text{CaO} \cdot \text{SiO}_2$

Figure 6 shows alumina leaching rate and decomposability under different leaching temperatures. The $\Delta \rho(\text{SiO}_2)$ concentration increases to 1.73 g/L when
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·7Al2O3 and γ-2CaO·SiO2 are also carried out separately under the same conditions. The molecular formulas of sodium hydrate alumino-silicate and hydrogarnet are Na2O·Al2O3·1.7SiO2·nH2O and 3CaO·Al2O3·nSiO2·(6−2n)H2O (n=0.1), respectively. Thus, the mass ratios of Al2O3 to SiO2 in sodium hydrate alumino-silicate and hydrogarnet are 1.0 and 17, respectively.

From the ratio of Δρ(Al2O3) and Δρ′(SiO2), 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 β-2CaO·SiO2, 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, Na2CO3 and NaAl(OH)4 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).

\[
β-2CaO·SiO_2+2OH^-+2H_2O=2Ca(OH)_2+H_2SiO_4^{2-}
\]  

(7)

2) The decomposition of dicalcium silicate is mainly caused by Na2CO3. And the decomposition

<table>
<thead>
<tr>
<th>Temperature/°C</th>
<th>Calcium aluminate</th>
<th>12CaO·7Al2O3*</th>
<th>γ-2CaO·SiO2**</th>
<th>(ρ(Al_2O_3)/ρ′(SiO_2))</th>
<th>(ρ(Al_2O_3)/ρ′(SiO_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>50.24</td>
<td>1.65</td>
<td>50.88</td>
<td>1.76</td>
<td>0.64</td>
</tr>
<tr>
<td>80</td>
<td>49.63</td>
<td>1.73</td>
<td>51.43</td>
<td>2.11</td>
<td>1.80</td>
</tr>
<tr>
<td>85</td>
<td>47.79</td>
<td>1.22</td>
<td>51.92</td>
<td>2.39</td>
<td>4.13</td>
</tr>
</tbody>
</table>

* The data of the column are obtained when 12CaO·7Al2O3 is the only raw material. ** The data of the column are obtained when γ-2CaO·SiO2 is the only raw material. Δρ(Al2O3) is the difference value between column 2 and column 4. Δρ′(SiO2) is the difference value between column 3 and column 5.
reaction is shown in Eq. (8):

$$\beta-2\text{CaO} \cdot \text{SiO}_2 + 2\text{CO}_3^{2-} + 2\text{H}_2\text{O} = 2\text{CaCO}_3 + \text{H}_2\text{SiO}_4^{2-} + 2\text{OH}^-$$  

(8)

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

$$3(2\text{CaO} \cdot \text{SiO}_2) + 4\text{Al(OH)}_4^- + 6\text{H}_2\text{O} + 2\text{OH}^- = 2(3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}) + 3\text{H}_2\text{SiO}_4^{2-}$$  

(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 NaOH, Na$_2$CO$_3$ and NaAl(OH)$_4$. The results indicate that the stability of dicalcium silicate in the solution is decreased in the following sequence: NaOH, NaAl(OH)$_4$, Na$_2$CO$_3$. That is to say, Na$_2$CO$_3$ has the strongest decomposability on $\beta$-2CaO·SiO$_2$. Furthermore, BI [14] believed that dicalcium silicate could be decomposed thoroughly under pure Na$_2$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, $\gamma$-2CaO·SiO$_2$ is more stable, but Na$_2$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 CaCO$_3$ and $\gamma$-2CaO·SiO$_2$ in leaching residues under different conditions. Small quantity of 12CaO·7Al$_2$O$_3$ remains in the residues. The product of secondary reaction is only sodium hydrate alumino–silicate 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 alumino–silicate with leaching time increasing (Fig. 8, Eq. (10)). Sodium hydrate alumino-silicate and hydrogarnet are formed at 55 °C, but the latter disappears when the leaching temperature is up to 80 °C (Fig. 9).
According to Eq. (10), 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). NaAl(OH) 4 formed by Eq. (10) increases to 120 g/L under the studied conditions. The occurrence of secondary reaction is sodium hydrate alumino-silicate and hydrogarnet when leaching calcium aluminosilicate slag. But it is not stable in sodium carbonate solution. The occurrence of secondary reaction causes the loss of alumina from solution.

1) The dominant factor of the decomposition of dicalcium silicate is Na_2CO_3. The concentration of decomposed SiO_2 increases to 1.71 g/L when the Na_2CO_3 concentration increases to 120 g/L under the studied conditions.

2) 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.

4 Conclusions

1) γ-2CaO-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 Na_2CO_3. The concentration of decomposed SiO_2 increases to 1.71 g/L when the Na_2CO_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


铝酸钙炉渣浸出过程的二次反应机理

孙会兰 1,2, 王波 1,2, 张建新 1, 宗书凤 1, 刘佳佳 1

1. 河北科技大学 材料科学与工程学院，石家庄 050018；
2. 河北科技大学 河北省材料近净成形技术重点实验室，石家庄 050018

摘 要: SiO₂以γ-2CaO·SiO₂的形式存在于铝酸钙炉渣中，γ-2CaO·SiO₂比β-2CaO·SiO₂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，γ-2CaO·SiO₂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SiO₂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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