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Behavior of calcium silicate in leaching process ①

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Abstract: Based on the thermodynamic calculation, the mole ratio of CaO to SiO_2, temperature and A/S of bauxite have a profound influence on the mole ratio of $2CaO\cdot SiO_2$ to $CaO\cdot SiO_2$ in sinter. $CaO\cdot SiO_2$ and β-$2CaO\cdot SiO_2$ appear stable in caustic solution but unstable in soda solution, and $CaO\cdot SiO_2$ is more stable than β-$2CaO\cdot SiO_2$ under the same leaching condition. Compared with the conventional sinter, the rate of alumina extraction of the new sinter is large and the secondary reaction is restricted in the leaching, which might be mainly due to the more content of $CaO\cdot SiO_2$ in sinter and better stability of $CaO\cdot SiO_2$ in leaching.

Key words: sinter; leaching; β-$2CaO\cdot SiO_2$; $CaO\cdot SiO_2$

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1 INTRODUCTION

In general, alumina can't be produced economically by Bayer process in China because the bauxite characterizes in diaspore and about 80% bauxite exist in low degree of the mass ratio of alumina to silica(A/S) which varies from 4 to 9[1]. And about 40% of alumina is produced by sintering process in China.

In the burden of conventional sintering process, sodium carbonate, bauxite(or added red mud from Bayer process) and lime are mixed according to that the mole ratio of Na_2O to(Al_2O_3+ Fe_2O_3) is 1 and the mole ratio of lime to silica is 2, and then the mixture is sintered. The objective of sintering is to convert alumina in bauxite into sodium aluminate($Na_2O\cdot Al_2O_3$) decomposed easily into caustic solution and to convert silica into calcium silicate($m CaO\cdot SiO_2$) stabilized in caustic solution[2]. The ratio of Na_2O to (Al_2O_3+ Fe_2O_3) or that of CaO to SiO_2 sharply affects the composition of sinter and rate of alumina extraction in leaching. Since some new technologies in sintering process were succeeded by changing the ratio of CaO to SiO_2[3-5], the composition of sinter, especially property of calcium silicate, showed different. And the studies on sintering process in Russia mainly focused on nepheline[6], but other countries pay little attention to the sintering process. So it is necessary to study the behavior of sinter in the new sinter system.

In the paper, the effects of bauxite and the ratio of CaO to SiO_2 on the composition of sinter are studied in thermodynamics. With the comparison of rate of alumina extraction between the conventional sinter and the new sinter in leaching, and analyzing XRD patterns of the new sinter and the red mud, the behavior of calcium silicate is discussed in detail.

2 FORMATION OF CALCIUM SILICATE AND THEIR STABILITY

In general, there are β-$2CaO\cdot SiO_2$, $CaO\cdot SiO_2$ when the silica converts into calcium silicate. However, studies are confined to β-$2CaO\cdot SiO_2$, and little attention is paid to $CaO\cdot SiO_2$. Supposing that the formation of calcium silicate comes from lime and quartz, the calculation results of the reaction Gibbs free energy show that β-$2CaO\cdot SiO_2$ and $CaO\cdot SiO_2$ can be easily formed because the formation Gibbs free energy is much less than -80 kJ/mol. And the formation of β-$2CaO\cdot SiO_2$ is prior to that of $CaO\cdot SiO_2$.

The main mineral containing silica is kaolinite in China. In the sintering process, H_2O firstly is removed, and then the reaction equations at high temperature can be written as follows:

$$4CaO+ Al_2O_3\cdot 2SiO_2+ Na_2CO_3 = 2[2CaO\cdot SiO_2]+ Na_2O\cdot Al_2O_3+ CO_2 \quad (1)$$

$$2CaO+ Al_2O_3\cdot 2SiO_2+ Na_2CO_3 = 2[CaO\cdot SiO_2]+ Na_2O\cdot Al_2O_3+ CO_2 \quad (2)$$

Based on the theory of reaction equilibrium, the mole ratio of $2CaO\cdot SiO_2$ to $CaO\cdot SiO_2$ can be deducted as:

$$\frac{x(2CaO\cdot SiO_2)}{x(CaO\cdot SiO_2)} = \exp[(\Delta G_2 - \Delta G_1)/2RT]\cdot x(CaO) \quad (3)$$

where ΔG_2, ΔG_1 represents the reaction free energy of

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Eqns. (2) and (1) respectively, x(CaO) represents the mole fraction of CaO. The thermodynamic data are from Refs. [7] and [8].

The bauxite 1 or bauxite 2 is taken as experimental material. The ingredients are listed in Table 1 and 2. A/S values for bauxite 1 and bauxite 2 are 4.76 and 9.62, respectively.

Table 1 Ingredients of bauxite 1 (mass fraction, %)

Al_2O_3	SiO_2	CaO	TiO_2	Fe_2O_3
65.80	13.82	0.26	1.32	5.10

Table 2 Ingredients of bauxite 2 (mass, fraction, %)

Al_2O_3	SiO_2	CaO	TiO_2	Fe_2O_3
69.91	7.27	1.62	3.18	2.67

Providing that the mole ratio of Na_2O to (Al_2O_3 + Fe_2O_3) is 1, and based on the facts that all the main phases of the sinter are formed at 1 173 K detected by XRD[6]. Effects of mole ratio of CaO to SiO_2 and A/S of bauxite on the mole ratio of $2CaO \cdot SiO_2$ to $CaO \cdot SiO_2$ from 1 200 K to 1 700 K are calculated, and the results are given in Figs. 1 and 2.

The results indicate that the mole ratio of $2CaO \cdot SiO_2$ to $CaO \cdot SiO_2$ becomes less as the temperature increases when the mole ratio of CaO to SiO_2 is the same. That means the content of $CaO \cdot SiO_2$ in the sinter increases at high temperature. On the other hand, the mole ratio of CaO to SiO_2 also has profound influence on the mole ratio of $2CaO \cdot SiO_2$ to $CaO \cdot SiO_2$ in the sinter at the same temperature. The decrease of the mole ratio of CaO to SiO_2 increases the content of $CaO \cdot SiO_2$ in the sinter, e.g. when $x(CaO)/x(SiO_2)$ is 2.5 and 1 at 1 600 K (as shown in Fig. 1), $x(2CaO \cdot SiO_2)/x(CaO \cdot SiO_2)$ is 9.72 and 4.62, respectively. At the same time, the A/S value of the bauxite also affects the ratio of $2CaO \cdot SiO_2$ to $CaO \cdot SiO_2$; for example, when $x(CaO)/x(SiO_2)$ is 2, $x(2CaO \cdot SiO_2)/x(CaO \cdot SiO_2)$ in sinter from bauxite1 and 2 at 1 600 K is 8.21 and 4.90, respectively.

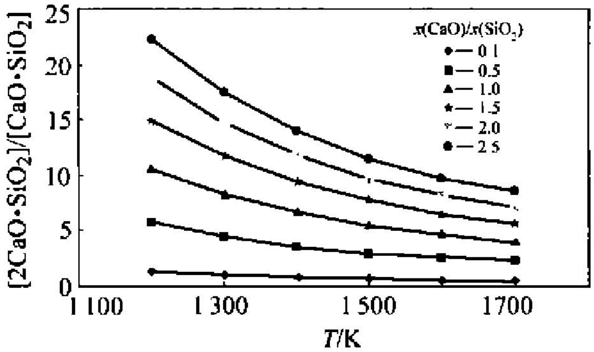

Fig. 1 Effect of temperature and mole ratio of CaO to SiO_2 on mole ratio of $2CaO \cdot SiO_2$ to $CaO \cdot SiO_2$ in bauxite 1

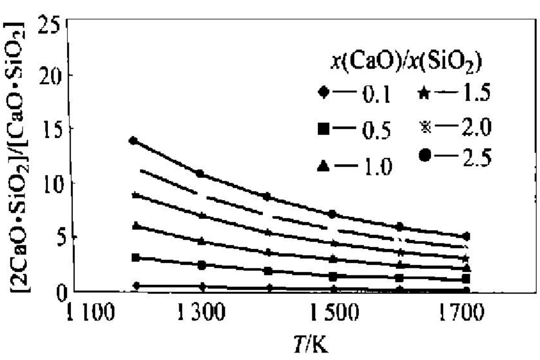

Fig. 2 Effect of temperature and mole ratio of CaO to SiO_2 on mole ratio of $2CaO \cdot SiO_2$ to $CaO \cdot SiO_2$ in bauxite 2

The stability of β-$2CaO \cdot SiO_2$ may be different from $CaO \cdot SiO_2$ whether in caustic solution or in soda solution. In general, the sinter is leached in caustic solution ($\rho(Na_2O_k) = 60 - 80$ g/L) with some sodium carbonate ($\rho(Na_2O_C) = 10 - 30$ g/L). In alumina production, the secondary reaction is attributed to the decomposition of calcium silicate, and the secondary reaction can be written as follows:

$$2CaO \cdot SiO_2 + 2OH^- + 2H_2O = 2Ca(OH)_2 + H_2SiO_4^{2-} \quad (4)$$

$$CaO \cdot SiO_2 + 2OH^- + H_2O = Ca(OH)_2 + H_2SiO_4^{2-} \quad (5)$$

and

$$2CaO \cdot SiO_2 + 2CO_3^{2-} + 2H_2O = 2CaCO_3 + H_2SiO_4^{2-} + 2OH^- \quad (6)$$

$$CaO \cdot SiO_2 + CO_3^{2-} + H_2O = CaCO_3 + H_2SiO_4^{2-} \quad (7)$$

The effect of temperature on the secondary reaction Gibbs free energy is given in Fig. 3 in caustic solution and in Fig. 4 in soda solution, respectively.

The result in Fig. 3 indicates that β-$2CaO \cdot$

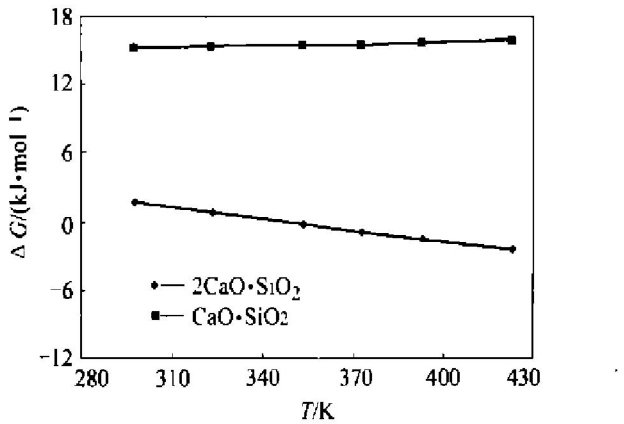

Fig. 3 Effect of temperature on reaction Gibbs energy when calcium silicate is leached in caustic solution

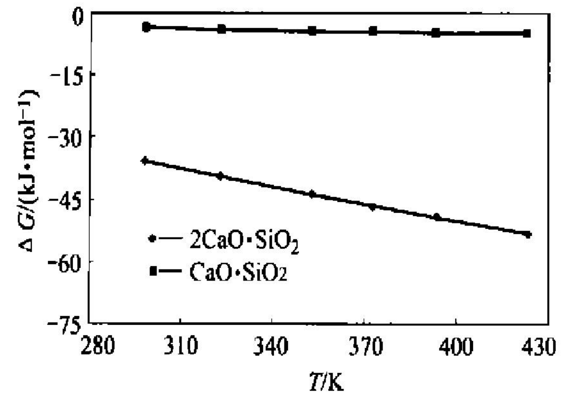

Fig. 4 Effect of temperature on reaction Gibbs energy when calcium silicate is leached in soda solution

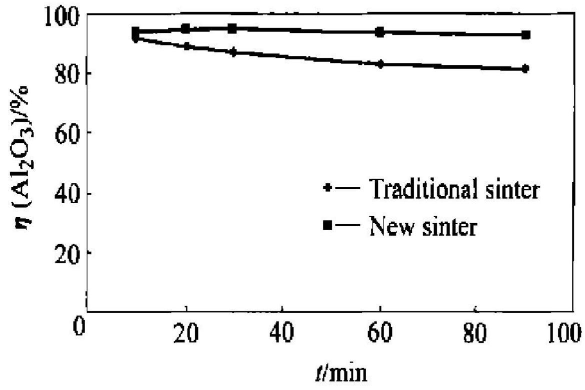

Fig. 5 Rate of alumina extraction with new sinter and conventional sinter leached in aluminate solution

(Solution: 59.96 g/L Na_2O_k, 23.12 g/L Na_2O_c, 60.11 g/L Al_2O_3, temperature 85 ℃)

SiO_2 and $CaO \cdot SiO_2$ are stable in caustic solution because the Gibbs free energy is positive when temperature is less than 80 ℃. But $CaO \cdot SiO_2$ appears more stable than β-$2CaO \cdot SiO_2$ in caustic solution as temperature increases because its reaction Gibbs free energy is more than 12 kJ/mol.

The result in Fig. 4 indicates that both β-$2CaO \cdot SiO_2$ and $CaO \cdot SiO_2$ are decomposed in soda solution. However, the reaction Gibbs free energy of β-$2CaO \cdot SiO_2$ is much less than that of $CaO \cdot SiO_2$, which means that $CaO \cdot SiO_2$ is more stable than β-$2CaO \cdot SiO_2$ in soda solution.

Results from Fig. 3 and Fig. 4 indicate that β-$2CaO \cdot SiO_2$ is decomposed more easily in soda solution than in caustic solution. Meanwhile, β-$2CaO \cdot SiO_2$ is more unstable than $CaO \cdot SiO_2$ either in caustic solution or in soda solution, so the content increase of $CaO \cdot SiO_2$ will benefit the rate of alumina extraction in the leaching process.

3 COMPARISON OF TWO KINDS OF SINTER IN LEACHING

In general, the solution with low mole ratio of Na_2O to Al_2O_3 (α_K) is used in the leaching process to prevent the secondary reaction because β-$2CaO \cdot SiO_2$ decomposes rapidly[9]. Based on the results above, the new sinter was made in laboratary with bauxite 2 according to the new burden of which the mole ratio of Na_2O to (Al_2O_3 + Fe_2O_3) was 1 and the mole ratio of CaO to SiO_2 was much less than 2. Both conventional sinter (from an alumina plant) and the new sinter were leached at 85 ℃, and results are given in Fig. 5.

The results indicated that the rate of alumina extraction ($\eta(Al_2O_3)/\%$) from the conventional sinter decreased obviously as leaching time passing by. It meant that the secondary reaction increased because of the following reaction:

$$3Ca(OH)_2 + xH_2SiO_4^{2-} + 2Al(OH)_4^- \longrightarrow 3CaO \cdot Al_2O_3 \cdot xSiO_2 \cdot (6-2x)H_2O + 2(1+x)OH^- + 2xH_2O \quad (8)$$

where $x = 0.1 - 0.2$

On the contrary, calcium silicate in the new sinter had better stability because the rate of alumina extraction was almost constant among 90 min, and little alumina was lost in the leaching. All might be attributed to the more content of $CaO \cdot SiO_2$ in sinter because $x(CaO)/x(SiO_2)$ was much less than 2.0.

4 COMPOSITION OF SINTER

Silica often converts into β-$2CaO \cdot SiO_2$ in conventional sintering process, and the content of $CaO \cdot SiO_2$, perhaps, is too little to discuss in literature. When the mole ratio of CaO to SiO_2 is less than 2.0, and the bauxite with high A/S is used, the mole ratio of $2CaO \cdot SiO_2$ to $CaO \cdot SiO_2$ in sinter becomes less according to thermodynamic calculation above, so the content of $CaO \cdot SiO_2$ is enriched. The XRD pattern of the new sinter was given in Fig. 6, and main composition was marked.

The results indicated that there were $Na_2O \cdot Al_2O_3$, $Na_2O \cdot Fe_2O_3$, $Na_2O \cdot SiO_2$, $CaO \cdot SiO_2$, β-$2CaO \cdot SiO_2$ in the new sinter, besides a little $CaO \cdot TiO_2$. It was consistent with the results from thermodynamic calculation.

The XRD pattern of the red mud after the new sinter being leached was also given in Fig. 7, and main composition was also marked.

There were not only hydro-hematite, sodium hydro alumino-silicate, hydro garnet, but also $CaO \cdot SiO_2$, β-$2CaO \cdot SiO_2$ in red mud. The intensity of the $CaO \cdot SiO_2$ peak appeared stronger and its characteristic peak emerged more frequently. This was one of main reasons why the rate of alumina extraction of the new sinter was high and it showed good stability in the leaching process.

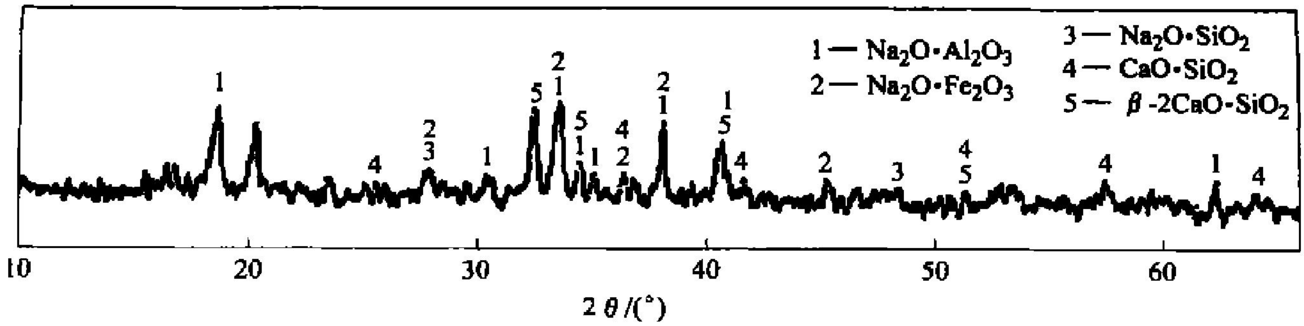

Fig. 6 XRD pattern of new sinter

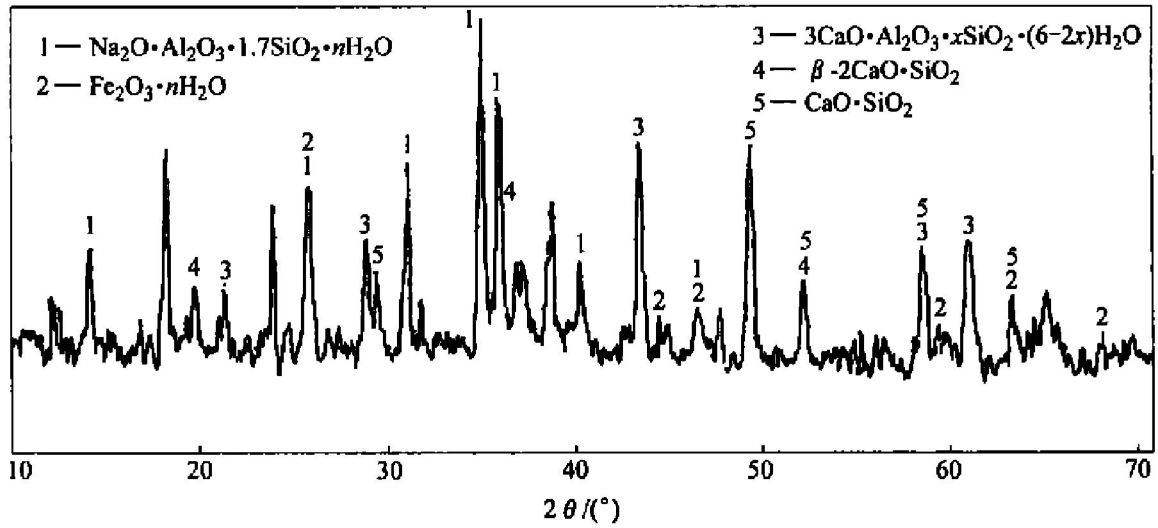

Fig. 7 XRD pattern of red mud after new sinter being leached

5 CONCLUSIONS

1) From thermodynamic calculation, both β-$2CaO·SiO_2$ and $CaO·SiO_2$ can be easily formed in the sinter. The mole ratio of CaO to SiO_2, temperature, A/S value of bauxite can affect the mole ratio of $2CaO·SiO_2$ to $CaO·SiO_2$. And $CaO·SiO_2$ appears more stable than β-$2CaO·SiO_2$ either in caustic solution or in soda solution.

2) The rate of alumina extraction of the new sinter is large and the secondary reaction is restricted mainly due to the more content of $Cao·SiO_2$.

3) The XRD patterns of the new sinter and the red mud indicate that there are β-$2CaO·SiO_2$ and $CaO·SiO_2$, meanwhile the intensity of $CaO·SiO_2$ peak appears stronger and its characteristic peak emerges more frequently in red mud.

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