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Stability of calcium silicate in basic solution ①

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Abstract: Mixture of CaO and SiO_2 was sintered at 1 200 or 1 400 ℃ according to the mole ratio of CaO/SiO_2 of 1 or 2, and then calcium silicate was leached in pure caustic or soda solution. The results indicated that calcium silicate exists much more stably in caustic solution than that in soda solution, and CaO·SiO_2 is more stable than β-2CaO·SiO_2 whether in caustic solution or in soda solution. The increase of sintering temperature favored the stability of calcium silicate in the leaching process. When β-2CaO·SiO_2 was leached in soda solution, the increase of leaching temperature and time resulted in decomposing of more calcium silicate. And when β-2CaO·SiO_2 was leached in caustic solution at high temperature, much 2CaO·SiO_2·H_2O but little CaO·SiO_2·H_2O appeared in slag.

Key words: calcium silicate; stability; caustic/soda solution
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1 INTRODUCTION

In alumina production by sintering process, the mole ratio of CaO/SiO_2 is about 2 in order to form β-2CaO·SiO_2. The β-2CaO·SiO_2 exists relatively stably in the leaching process, and then discharges together with the red mud. But some β-2CaO·SiO_2 is to be decomposed, and then converts into hydrate garnet or sodium hydrate alumino-silicate. This process is often called as the secondary reaction. There are two different opinions in the cause of decomposition of β-2CaO·SiO_2, the first is that β-2CaO·SiO_2 is decomposed into $SiO_2(OH)_2^{2-}$ and $Ca(OH)_2$ for OH^- anion in caustic solution, and then converts into CaO·SiO_2·H_2O which hinders the secondary reaction in turn. The second is that β-2CaO·SiO_2 is decomposed into $SiO_2(OH)_2^{2-}$ and $CaCO_3$ into CO_3^{2-} in the soda solution[1-5]. Lately, new technologies in sintering process have reported, that the composition of the sintering also changes, and the secondary reaction takes in different degrees[6-9].

This paper begin from using lime and quartz to produce calcium silicate according to the mole ratio of CaO/SiO_2 of 1 or 2, and then the calcium silicate is leached in caustic solution or soda solution to study the stability of calcium silicate.

2 EXPERIMENTAL

2.1 Preparation of calcium silicate

CaO was made from $Ca(OH)_2$(A. R.), calcined in a muffle at 850 ℃ for 2 h. SiO_2(A. R.) was dried at 110 ℃ for 2 h. SiO_2 and CaO were mixed according to the mole ratio of CaO/SiO_2 of 1 or 2, and then the mixture was placed in a corundum crucible, firstly pre-calcined at 850 ℃ for about 10 min, then calcined at 1 200 or 1 400 ℃ for 1h in another muffle, finally the sinter(calcium silicate) was placed in desiccator.

2.2 Leaching of calcium silicate

The caustic solution or soda solution was made from NaOH(A. R.) or Na_2CO_3(A. R.). In every experiment, 50 mL basic solution and 3 g calcium silicate were mixed in reactor, and leached for 30 min or 60 min, and then the concentration of SiO_2 in the filtrate was detected by spectrophotometer. The slag was washed with boiling water and dried, and then analyzed by using X-ray diffractometer(D/max-rA, Japan)

3 RESULTS AND DISCUSSION

3.1 Stability of calcium silicate in caustic solution

The thermodynamic calculation results[10] indicated that both 2CaO·SiO_2 and CaO·SiO_2 will form in the sintering process when mixture contained CaO and SiO_2, but the content of β-2CaO·SiO_2 or CaO·SiO_2 is different at different ratios of CaO/SiO_2. It is necessary to know the reaction activity of CaO·SiO_2 and the effect on sintering. Now the study on the stability of calcium silicate is in pure caustic solution or soda solution because the same product, hydrate garnet, can easily form in aluminate solution after β-2CaO·SiO_2 or CaO·SiO_2 is decomposed.

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Firstly different calcium silicates were calcined under different conditions, as listed in Table 1.

The results in Table 1 indicated that the effect of temperature on the sintering appearance is obvious, hard and dark color sinter might be resulted from CaO reacting with SiO_2 sufficiently at high temperature, but the incompact and pale color sinter at low temperature.

Secondly the leaching experiments were carried out in caustic solution(ρ_{Na_2O}= 101.21 g/L), the results were listed in Table 2.

Table 1 Sintering conditions of calcium silicate

No.	Calcium silicate (expected)	Mole ratio of CaO/ SiO_2	Calcined temperature/ ℃	Time/ h	Appearance of sinter
1	$CaO·SiO_2$	1	1 400	1	Hard
2	$CaO·SiO_2$	1	1 200	1	Incompact
3	$2CaO·SiO_2$	2	1 400	1	Hard
4	$2CaO·SiO_2$	2	1 200	1	Incompact

Table 2 Results of calcium silicate leached in caustic solution

Kind of calcium silicate and sintering temperature	Leaching temperature/ ℃	Time/ min	ρ_{SiO_2}/ $g·L^{-1}$	η_{1SiO_2}/ %
$CaO·SiO_2$, 1 400 ℃	85	30	0.130	0.42
	85	60	0.156	0.50
	100	60	0.479	1.54
$CaO·SiO_2$, 1 200 ℃	85	30	0.200	0.64
	85	60	0.173	0.56
$2CaO·SiO_2$, 1 400 ℃	85	30	0.140	0.67
	85	60	0.173	0.83
	100	60	0.381	1.82
$2CaO·SiO_2$, 1 200 ℃	85	30	0.170	0.81
	85	60	0.342	1.63

It is indicated that all concentration of SiO_2 are less than 0.5 g/L, and η_{1SiO_2} (the rate of SiO_2 in caustic solution) is less than 2%, due to that little calcium silicate is leached out in caustic solution, which is consistent with the results from thermodynamic calculation, i. e. $CaO·SiO_2$ can't be reacted sufficiently with OH^- to form $CaO·SiO_2·H_2O$, but β-$2CaO·SiO_2$ can be reacted with OH^- to form $CaO·SiO_2·H_2O$ when temperature is more than 70 ℃[10]. Meanwhile, the results also indicated that the sintering temperature affects η_{1SiO_2} because η_{1SiO_2} of β-$2CaO·SiO_2$ sintered at 1 200 ℃ is large than that at 1 400 ℃.

Unexpectedly, a little white deposition appeared in the filtrate at the end of washing. It is necessary to know what it is. So the deposition was filtrated again, and the content of SiO_2 was less than 2.1% but the content of CaO was more than 50% in the white deposition. Based on this fact, the white deposition must be $Ca(OH)_2$. On the other hand, the phenomenon indicated indirectly that it is difficult for $CaO·SiO_2·H_2O$ to form in the leaching process because there are some $Ca(OH)_2$ in slag and $SiO_2(OH)_2^{2-}$ in solution.

3.2 Stability of calcium silicate in soda solution

The leaching experiment was conducted in soda solution(ρ_{Na_2O}= 101.21 g/L), the results were listed in Table 3.

Table 3 Results of calcium silicate leached in soda solution

Kind of calcium silicate and sintering temperature	Leaching temperature/ ℃	Time/ min	ρ_{SiO_2}/ $(g·L^{-1})$	η_{2SiO_2}/ %
$CaO·SiO_2$, 1 400 ℃	85	30	0.645	2.08
	85	60	0.685	2.21
	100	60	0.545	1.76
$CaO·SiO_2$, 1 200 ℃	85	30	3.420	11.02
	85	60	3.504	11.29
$2CaO·SiO_2$, 1 400 ℃	85	30	1.340	6.40
	85	60	1.902	9.09
	100	60	2.130	10.18
$2CaO·SiO_2$, 1 200 ℃	85	30	2.900	13.86
	85	60	3.092	14.77

Compared with the results in Table 2, η_{2SiO_2}(the rate of SiO_2 in soda solution) was much larger than η_{1SiO_2}, which showed that calcium silicate appears more stable in caustic solution than that in soda solution. The results(Table 3) indicated that the sintering temperature has fair effect on η_{2SiO_2}. For example, when $CaO·SiO_2$ was leached at 85 ℃ for 30 min in soda solution, η_{2SiO_2} for sintering at 1 400 ℃ and at 1 200 ℃ were 2.08% and 11.02%, respectively.

Simultaneously, $CaO·SiO_2$ and β-$2CaO·SiO_2$ showed different stability in soda solution, the leaching temperature and time have little effect on η_{2SiO_2} when $CaO·SiO_2$ (sintered at 1 400 ℃) is leached. However, the behavior of β-$2CaO·SiO_2$ was different. The increase of the sintering temperature favored the stability of β-$2CaO·SiO_2$. However, the increase of leaching temperature or time resulted in increasing of η_{2SiO_2}.

Compared with the results in Tables 2 and 3, the decomposition of β-$2CaO·SiO_2$ was easier than that of $CaOSiO_2$, especially in soda solution, and the stability of $CaOSiO_2$ appeared better than that of β-$2CaOSiO_2$ whether in caustic solution or in soda solution. Furthermore, the secondary reaction might be attributed to the decomposition of β-$2CaOSiO_2$ in soda solution when conventional sintering is in the leaching process.

3.3 Analysis of component of solid[11, 12]

When the ratio of CaO/SiO_2 was 1, and sintering temperature was 1 400 ℃, there were much $CaO SiO_2$ and a little β-$2CaOSiO_2$ in sinters(Fig. 1(a)). After calcium silicate was leached in caustic solution (Fig. 1(b)), β-$2CaO·SiO_2$ disappeared, but some $Ca(OH)_2$ appeared for β-$2CaO·SiO_2$ decomposed into $SiO_2(OH)_2^{2-}$ and $Ca(OH)_2$. Based on the fact that the concentration of SiO_2 is little in caustic solution(Table 2), it can be summed up that the SiO_2 in solution mainly dates from the decomposition of β-$2CaO·SiO_2$, not from $CaO·SiO_2$. Furthermore, it is difficult to find $CaO·SiO_2·H_2O$ in slag.

When calcium silicate was leached in soda solution(Fig. 1(c)), the main components were $CaOSiO_2$ and $CaCO_3$ in the slag, and there wasn't β-$2CaOSiO_2$ either. And that SiO_2 in solution was high(Table 3), which might result from the decomposition of β-$2CaOSiO_2$ and $CaOSiO_2$.

Fig. 2 was XRD patterns of $CaOSiO_2$ sintered at 1 200 ℃. Compared with the results from Fig. 1(a), though there were $CaOSiO_2$ and β-$2CaO·SiO_2$, the intensity of characteristic peak of calcium silicate appeared infirmly, and more quartz and CaO were found (Fig. 2(a)). When the calcium silicate was leached at 85 ℃ in caustic solution(Fig. 2(b)), β-$2CaOSiO_2$ decomposed, so the main components were $CaOSiO_2$, $Ca(OH)_2$ and quartz in slag. All indicated that the high temperature favors the formation of $CaOSiO_2$ in the sintering process.

Fig. 3 was the XRD pattern of slag after β-$2CaO·SiO_2$ was leached in caustic solution. β-$2CaOSiO_2$, little quartz and $Ca(OH)_2$ were found in the slag. Furthermore, much $2CaOSiO_2H_2O$ but little CaO·

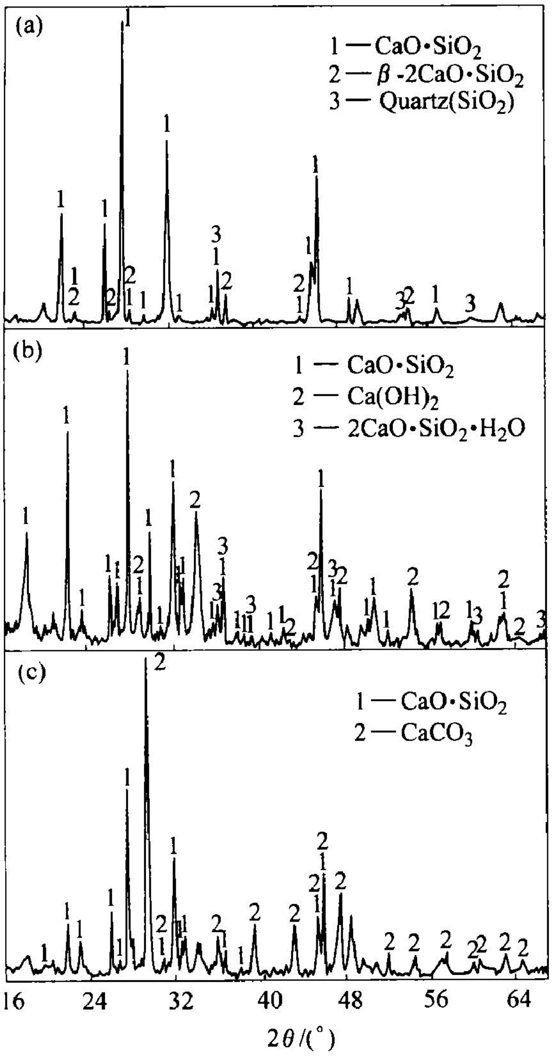

Fig. 1 XRD patterns of $CaOSiO_2$
(original $CaOSiO_2$ sintered at 1 400 ℃(a), solid from leaching in caustic solution (b) and solid from leaching in soda solution(c))
(a) —$CaOSiO_2$, $2CaOSiO_2$, quartz;
(b) —$CaOSiO_2$, $Ca(OH)_2$, and little $2CaOSiO_2H_2O$;
(c) —$CaOSiO_2$, $CaCO_3$

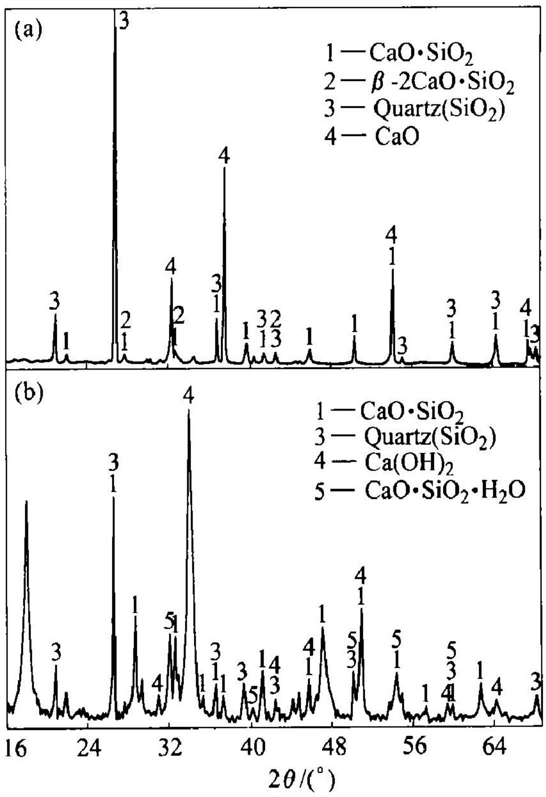

Fig. 2 XRD patterns of $CaOSiO_2$
(original $CaOSiO_2$ sintered at 1 200 ℃(a), solid from leaching in caustic solution(b))
(a) —$CaOSiO_2$, $2CaOSiO_2$, CaO, quartz;
(b) —$CaOSiO_2$, $Ca(OH)_2$, quartz, and little $CaOSiO_2H_2O$

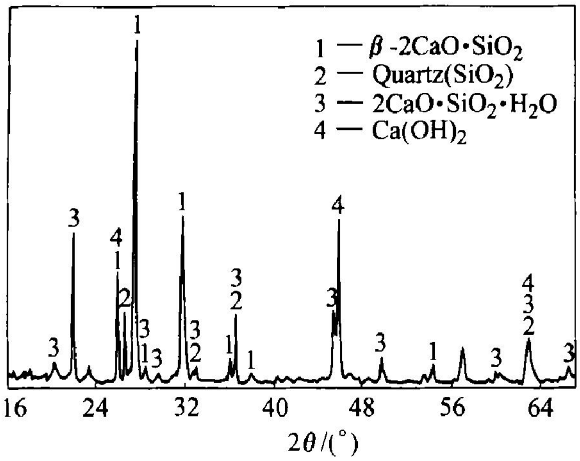

Fig. 3 XRD pattern of solid from leaching in caustic solution when β-2CaO·SiO2 sintered at 1 400 ℃

$SiO_2\cdot H_2O$ was also found in slag. The reason might be that the solubility of $CaO\cdot SiO_2\cdot H_2O$ was high. Perhaps, $CaO\cdot SiO_2\cdot H_2O$ might not be the key product of calcium hydrate silicate in leaching process.

4 CONCLUSIONS

1) There are $CaO\cdot SiO_2$ and β-$2CaO\cdot SiO_2$ in the sinters. Temperature affects the preparation of calcium silicate obviously, the ratio of CaO/SiO_2 only affects the content of $CaO\cdot SiO_2$ or β-$2CaO\cdot SiO_2$.

2) $CaO\cdot SiO_2$ and β-$2CaO\cdot SiO_2$ appear stablely in caustic solution but unstably in soda solution. $CaO\cdot SiO_2$ is more stable than β-$2CaO\cdot SiO_2$ is. The secondary reaction mainly accounts for the decomposition of calcium silicate in the soda solution.

3) To β-$2CaO\cdot SiO_2$, the increase of leaching temperature and time leads to more calcium silicate decomposing in soda solution, and the decomposition also occurs at high temperature in caustic solution.

4) After β-$2CaO\cdot SiO_2$ is leached in caustic solution, much $2CaO\cdot SiO_2\cdot H_2O$ but little $CaO\cdot SiO_2\cdot H_2O$ are found in slag.

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