Behavior of calcium silicate hydrate in aluminate solution [①]

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Abstract: Using calcium hydroxide and sodium silicate as starting materials, two kinds of calcium silicate hydrates, $CaO \cdot SiO_2 \cdot H_2O$ and $2CaO \cdot SiO_2 \cdot 1.17H_2O$, were hydro-thermally synthesized at 120 ℃. The reaction rule of calcium silicate hydrate in aluminate solution was investigated. The result shows that $CaO \cdot SiO_2 \cdot H_2O$ is more stable than $2CaO \cdot SiO_2 \cdot 1.17H_2O$ in aluminate solution and its stability increases with the increase of reaction temperature but decreases with the increase of caustic concentration. The reaction between calcium silicate hydrate and aluminate solution is mainly through two routes. In the first case, Al replaces partial Si in calcium silicate hydrate, meanwhile $3CaO \cdot Al_2O_3 \cdot xSiO_2 \cdot (6-2x)H_2O$ (hydro-garnet) is formed and some SiO_2 enters the solution. In the second case, calcium silicate hydrate can react directly with aluminate solution, forming hydro-garnet and $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot nH_2O$ (DSP). The desilication reaction of aluminate solution containing silicate could contribute partially to forming DSP.

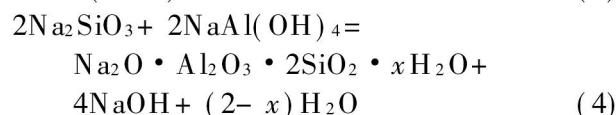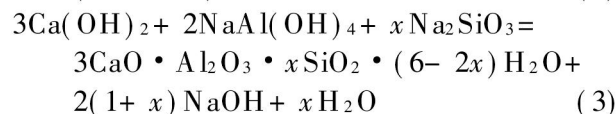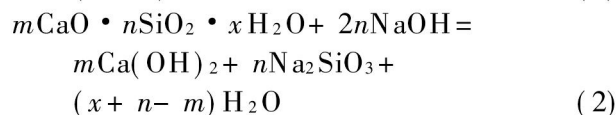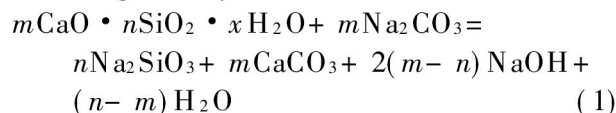**Key words:** calcium silicate hydrate; aluminate; caustic; reaction behavior

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1 INTRODUCTION

Calcium silicate hydrate ($mCaO \cdot nSiO_2 \cdot xH_2O$, C-S-H) is an important hydrate product of Portland cement. Because of its key rules in setting and hardening performance of cement[1], it has attracted a lot of interest of many researchers[2−4]. Calcium silicate hydrate is also a very important substance in alumina production, but its reaction behavior with aluminate solution has not been paid adequate emphases upon.

The key project in alumina production is the separation of aluminum and silicon. Calcium silicate hydrate is an important compound containing silicon in the process of alumina production. In order to separate aluminum and silicon, the silicate compounds without or with less alumina, such as C-S-H, are formed in high-pressure hydro-chemical process under very rigorous condition of high temperature and high caustic concentration[5, 6]. A method to obtain C-S-H from sodium alumino-silicate hydrate (DSP) under mild condition was put forward[7, 8]. Moreover, in sintering process of alumina production, the secondary loss of alumina and soda is actually caused by the reactions between calcium silicate hydrate and aluminate solution in the operation of leaching sinter[9]. Therefore it is of great importance for alumina production to know the reaction law between C-S-H and aluminate solution.

The reactions between C-S-H and aluminate solution are generally considered as follows[9]:

$$mCaO \cdot nSiO_2 \cdot xH_2O + mNa_2CO_3 = \\ nNa_2SiO_3 + mCaCO_3 + 2(m-n)NaOH + \\ (n-m)H_2O \quad (1)$$

$$mCaO \cdot nSiO_2 \cdot xH_2O + 2nNaOH = \\ mCa(OH)_2 + nNa_2SiO_3 + \\ (x+n-m)H_2O \quad (2)$$

$$3Ca(OH)_2 + 2NaAl(OH)_4 + xNa_2SiO_3 = \\ 3CaO \cdot Al_2O_3 \cdot xSiO_2 \cdot (6-2x)H_2O + \\ 2(1+x)NaOH + xH_2O \quad (3)$$

$$2Na_2SiO_3 + 2NaAl(OH)_4 = \\ Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot xH_2O + \\ 4NaOH + (2-x)H_2O \quad (4)$$

Conclusions can be drawn from the above reactions, i. e., the decomposition reactions of C-S-H with Na_2CO_3 and NaOH in aluminate solution (reactions (1) and (2)) are the basis of forming hydro-garnet and DSP (reactions (3) and (4)). The concentration of SiO_2 in the solution from leaching sinter can reach 4−6 g/L, which is generally considered the decomposition of C-S-H by Na_2CO_3 and especially by NaOH[9, 10]. However, Liu et al[11] experimentally studied the reaction behavior of C-S-H with Na_2CO_3 and NaOH and the results showed that the SiO_2 concentration in the obtained solution is only 0.1−0.5 g/L in both NaOH and Na_2CO_3 system with concentration of

100 g/L Na_2O. The SiO_2 concentration is much less than that in sinter leaching, indicating the limited reaction degree of C-S-H with Na_2CO_3 and NaOH. Therefore the reaction mechanism between C-S-H and aluminate solution is not clear and further investigation is necessary.
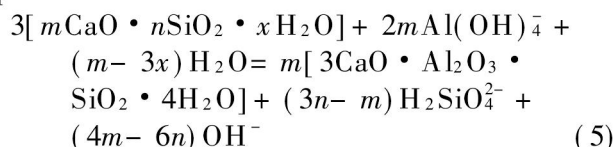
2   METHODOLOGY

Firstly, the possibility of the reaction between C-S-H and aluminate solution is analyzed thermodynamically, and then experiments are carried out to validate the thermodynamic conclusion. Calcium hydroxide and sodium silicate are used as starting materials to synthesize two kinds of calcium silicate hydrate at 120 ℃, respectively being $CaO \cdot SiO_2 \cdot H_2O$ (signed as CSH1) and $2CaO \cdot SiO_2 \cdot 1.17H_2O$ (signed as CSH2). The content of dissociated CaO in both $CaO \cdot SiO_2 \cdot H_2O$ and $2CaO \cdot SiO_2 \cdot 1.17H_2O$ are measured as respectively 0.3% and 0.7% by glycol-ethanol means[12]. The loss of alumina in solution, caused by the formation of $3CaO \cdot Al_2O_3 \cdot xSiO_2 \cdot (6-2x)H_2O$ due to the reactions of those CaO with aluminate, is not significant (respectively 0.018 g/L and 0.4 g/L) and can be ignored. The samples are then treated in aluminate solution with the caustic ratio α_k of 1.5(Na_2O/Al_2O_3, molar ratio) at L/S of 10 (mass ratio of liquid to solid), unless especially noted. The specimens are taken out and filtered at designed time to measure the concentration of SiO_2 and Al_2O_3 in filtrate and mineral phase in residue.
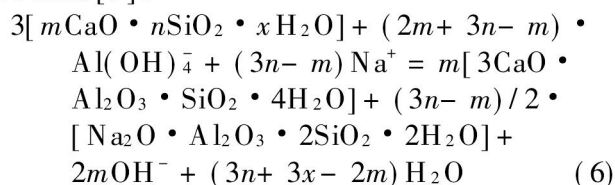
3   RESULTS AND DISCUSSION

3.1   Thermodynamic analysis

The high SiO_2 concentration in the solution after the reaction of C-S-H and aluminate solution means that the substitution reaction of Al for Si, only in bridging sites of the dreierkette[13], may happen as follows:

$$3[mCaO \cdot nSiO_2 \cdot xH_2O] + 2mAl(OH)_4^- + (m-3x)H_2O = m[3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O] + (3n-m)H_2SiO_4^{2-} + (4m-6n)OH^- \qquad (5)$$

The XRD patterns reveal that DSP emerges at the beginning of the reaction of C-S-H and aluminate solution, which means that the formation of DSP may be not only caused by the reaction between $H_2SiO_4^{2-}$ from reaction (5) and $Al(OH)_4^-$ in solution, but also by the following reaction regarding to Ref.[9]:

$$3[mCaO \cdot nSiO_2 \cdot xH_2O] + (2m+3n-m) \cdot Al(OH)_4^- + (3n-m)Na^+ = m[3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O] + (3n-m)/2 \cdot [Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] + 2mOH^- + (3n+3x-2m)H_2O \qquad (6)$$

The calculation results of dependence of Gibbs free energy change on temperature for reactions (5) and (6) have been carried out with the Alumina Thermodynamic Database[14]. Fig.1 shows that it is possible for both $CaO \cdot SiO_2 \cdot H_2O$ and $2CaO \cdot SiO_2 \cdot 1.17H_2O$ to react with $Al(OH)_4^-$ according to reaction (5), but impossible for $6CaO \cdot 6SiO_2 \cdot H_2O$. Meanwhile, all the C-S-H are able to react with aluminate solution on the basis of reaction (6). Thermodynamically speaking, the stability sequence of the calcium silicate hydrates mentioned above is $6CaO \cdot 6SiO_2 \cdot H_2O > CaO \cdot SiO_2 \cdot H_2O > 2CaO \cdot SiO_2 \cdot 1.17H_2O$.
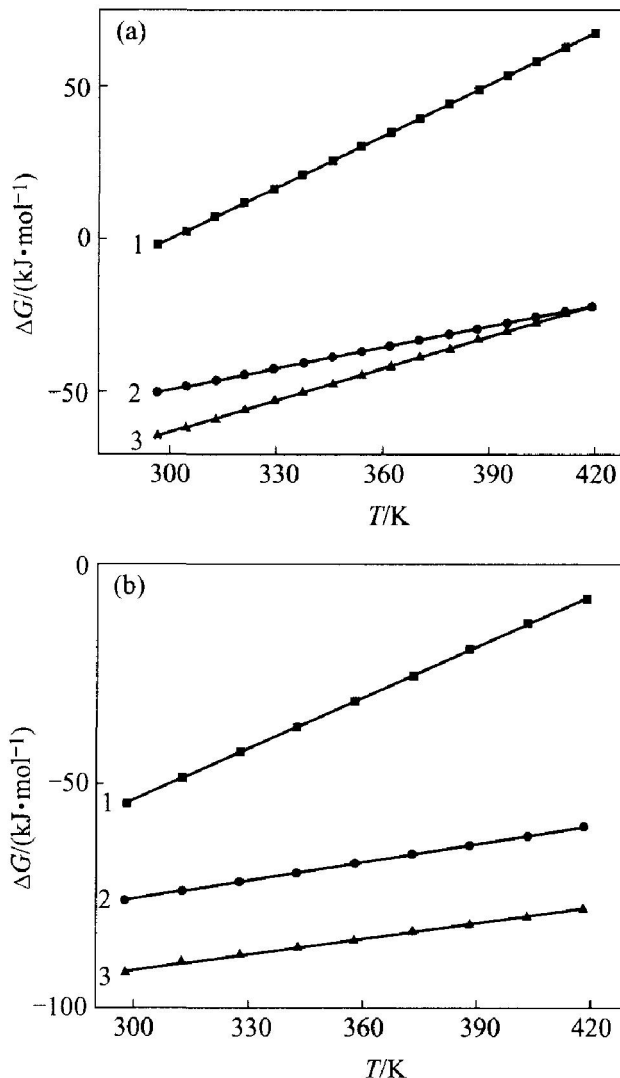
Fig. 1   Variation of ΔG versus temperature
(a) —Reaction (5); (b) —Reaction (6)
(1 —$6CaO \cdot 6SiO_2 \cdot H_2O$; 2 —$CaO \cdot SiO_2 \cdot H_2O$;
3 —$2CaO \cdot SiO_2 \cdot 1.17H_2O$)

3.2   Relationship between types of C-S-H and its stability

Fig.2 demonstrates the loss of alumina due to $SiO_2(m_{Al_2O_3})$ and the dissolution of $SiO_2(\eta_{SiO_2})$ versus time in the reaction of the two types of C-S-H with aluminate solution. Fig.2 indicates that the stability of the two types of C-S-H are quit differ-

ent in aluminate solution. The $m_{Al_2O_3}$ of CaO • SiO$_2$ • H$_2$O is obviously less than that of 2CaO • SiO$_2$ • 1.17H$_2$O and the η_{SiO_2} of the later is more than that of the former. Thus it can be concluded that CaO • SiO$_2$ • H$_2$O is more stable than 2CaO • SiO$_2$ • 1.17H$_2$O, being consistent with the thermodynamic calculation. This can be explained as that there are silicate anion chains in all C-S-H and these chains become progressively longer as the Ca/Si ratio decreases, which causes the enhancement of the aggregation degree of Si and thus the increment of stability of C-S-H[15].

3.3   Influence of temperature on stability of C-S-H

Fig. 3 indicates the effect of temperature on η_{SiO_2} in the case of the same aluminate solution and tells that the stability of C-S-H depends on temperature. The change of Gibbs free energy for the reactions increases with the elevation of temperature, resulting in the decrease of η_{SiO_2} and thus C-S-H becomes more stable in aluminate solution at higher temperature.
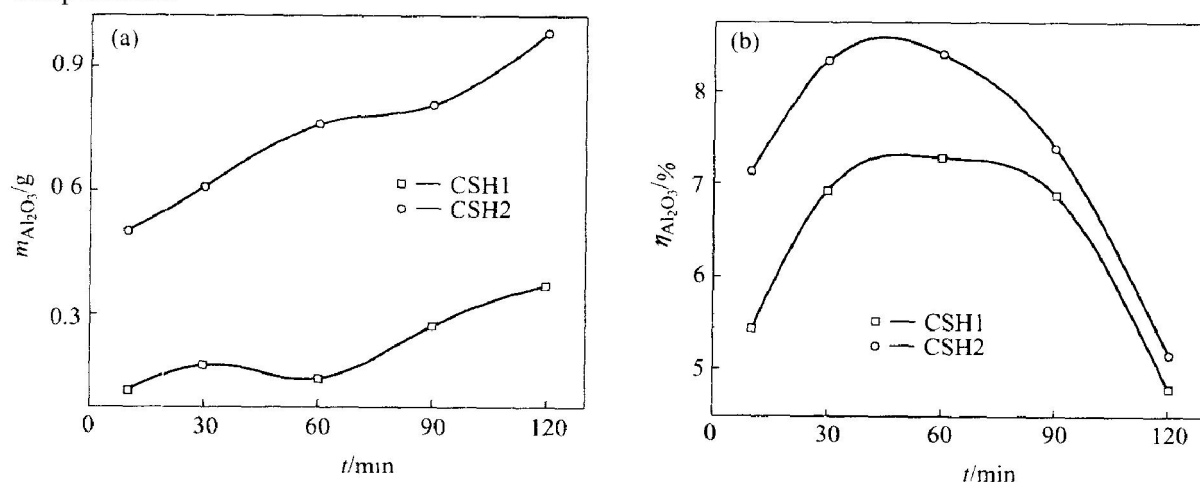
3.4   Influence of composition of aluminate solution on stability of C-S-H

3.4.1   Caustic(Na$_2$O$_k$) concentration

Fig. 4 depicts the results of the reaction between CaO • SiO$_2$ • H$_2$O and aluminate solution with different Na$_2$O$_k$ concentrations. The concentration of SiO$_2$ entering the solution remarkably increases with the augment of Na$_2$O$_k$ concentration and has a maximum value. The high Na$_2$O$_k$ concentration represents a high Al(OH)$_4^-$ concentration at a certain α_k which is beneficial to SiO$_2$ in C-S-H entering the solution according to reaction (5). Subsequently, after the SiO$_2$ exceeds its equilibrium, the concentration of SiO$_2$ in the solution will drop due to the formation of DSP produced by the reaction of H$_2$SiO$_4^{2-}$ and the components of solution. This process, together with reactions (5) and (6), will contribute to the loss of alumina, $m_{Al_2O_3}$. On the contrary, there is a low concentration of Al(OH)$_4^-$ in the system with low Na$_2$O$_k$ concentration (50 g/L) and thus a limited reaction degree, which results in a less and invariable SiO$_2$

Fig. 2   Loss of alumina (a) and dissolution of SiO$_2$(b) versus time
(Concentration of Na$_2$O$_k$ in aluminate solution 110 g/L)

Fig. 3   Dissolution of SiO$_2$ versus time
(a) —CSH1; (b) —CSH2
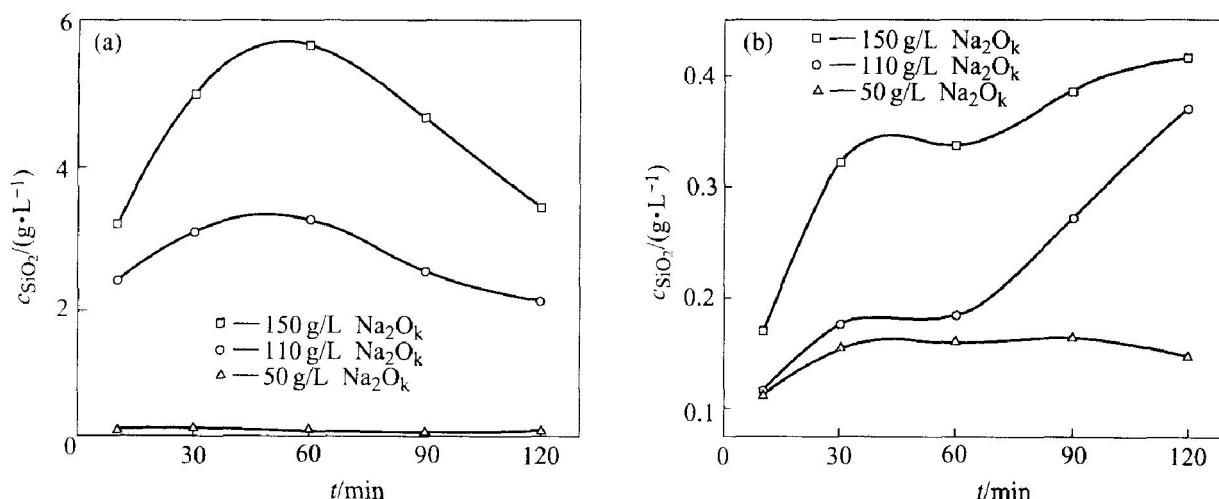(Aluminate solution c(Na$_2$O$_k$) = 50 g/L, α_k = 3)

Fig. 4　SiO₂ concentration in solution(a) and loss of alumina(b) versus time

concentration in the solution at any time.

3.4.2　Concentration of Na_2CO_3

Fig. 5 shows the result of the reaction of two kinds of C-S-H and aluminate solution in different Na_2CO_3 concentrations. We can conclude from the figure that the dependence of η_{SiO_2} on Na_2CO_3 concentration for C-S-H is not significant, indi-

cating a less effect of Na_2CO_3 concentration on the stability of C-S-H.

3.4.3　Caustic ratio(α_k)

From Fig. 6 we can know that the higher the α_k of aluminate solution is, the more the SiO_2 in C-S-H dissolves. Obviously, the free NaOH concentration in the aluminate solution with $\alpha_k = 3.0$ is
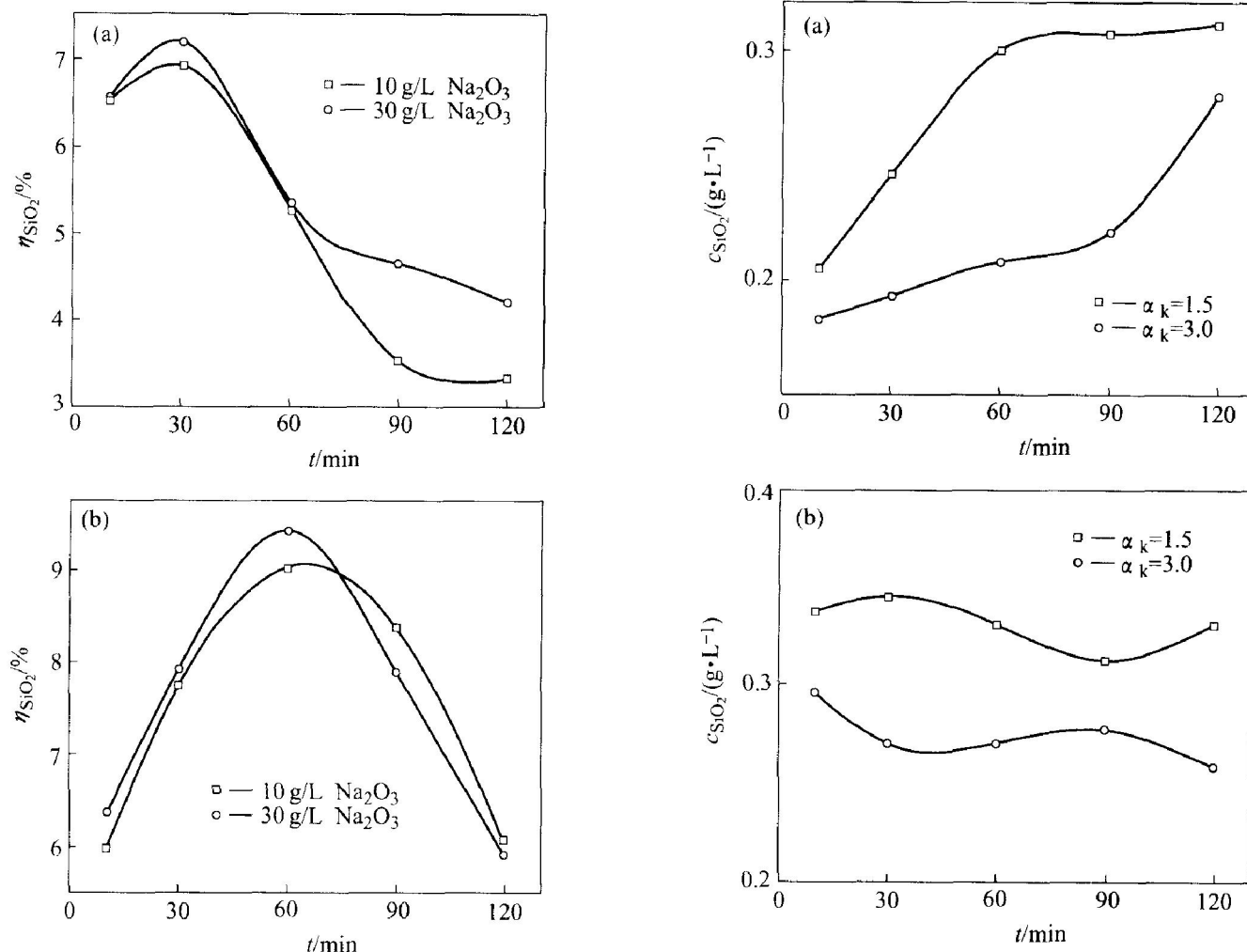

Fig. 5　Dissolution of SiO₂ versus time
(a) —CSH1;　(b) —CSH2
(Aluminate solution: $c(Na_2O_k) = 110$ g/L)

Fig. 6　SiO₂ concentration in solution versus time
(a) —CSH1;　(b) —CSH2
(Aluminate solution: $c(Na_2O_k) = 50$ g/L)

higher than that in the aluminate solution with α_k = 1. 5 in a certain caustic concentration. The concentration of SiO_2 entering the solution in the former solution should be more than that in the later, which is not identical with the fact, if the decomposition of C-S-H is mainly through reaction (2). Combining what mentioned above and Fig. 5, the conclusion that reactions (1) and (2) contribute less than reaction (5) to the higher SiO_2 concentration in the sinter leaching operation in the sintering process, can be drawn.

4   CONCLUSIONS

1) Thermodynamically, $CaO \cdot SiO_2 \cdot H_2O$ is more stable than $2CaO \cdot SiO_2 \cdot 1.17H_2O$ in aluminate solution and the stability of C-S-H increases with the elevation of temperature, which has been verified by experiments.

2) The concentrations of Na_2CO_3 and $NaOH$ have less influence on the stability of calcium silicate hydrates; meanwhile the $Al(OH)_4^-$ concentration in aluminate solution affects those remarkably through the formation of hydro-garnet and sodium alumino-silicate hydrate.

3) $Al(OH)_4^-$ contributes more significantly than $NaOH$ and Na_2CO_3 on the high SiO_2 concentration in the solution after the reaction of calcium silicate hydrates with aluminate solution.

REFERENCES

[1] Garrault-Gauffinet S, Nonat A. Experimental investigation of calcium silicate hydrate(C-S-H) nucleation [J]. Journal of Crystal Growth, 1999, 200: 565 - 574.

[2] Viehland D, LI Jie-fang, YUAN Li-jian. Mesostructure of calcium silicate hydrate(C-S-H) gels in Portland cement paste: short-range ordering, nanocrystallinity, and local compositional order [J]. J Am Ceram Soc, 1996, 79(7): 1731 - 1744.

[3] CONG Xian-dong, James K R. ^{29}Si MAS NMR study of the structure of calcium silicate hydrate [J]. Advn Cem Bas Mat, 1996, 3: 144 - 156.

[4] Moropoulou A, Cakmak A, Labropoulos K C. Accelerated microstructural evolution of a calcium-silicate-hydrate(C-S-H) phase in pozzolanic pastes using fine siliceous sources: comparison with historic pozzolanic mortars [J]. Cement and Concrete Research, 2004, 34: 1 - 6.

[5] Sazhin V S. Advance of Hydrothermal Chemical Process for Alumino-silicate Mineral and Bauxite with much Silicon [M]. MOSKVA, Metallurgical, 1989. 63 - 100. (in Russian)

[6] SHAO Zhi-bo. The development way of Chinese alumina industry [J]. World Nonferrous Metals, 1999 (3): 8 - 12. (in Chinese)

[7] ZHANG Ya-li, LIU Xiang-min, PENG Zhi-hong. Study on the wet treatment hydrate alunino silicate — alkali recovery [J]. Mining and Metallurgical Engineering, 2003, 6(23): 56 - 58. (in Chinese)

[8] LIU Gui-hua, ZHANG Ya-li, PENG Zhi-hong. Alumina recovery from sodium hydrate alumino-silicate [J]. The Chinese Journal of Nonferrous Metals, 2004, 3(14): 499 - 503. (in Chinese)

[9] YANG Zhong-yu. The Technology of Alumina Production [M]. Beijing: Metallurgical Industry Press, 1982: 254 - 265. (in Chinese)

[10] YUAN Yi, XIANG Yang, HUANG Fang. An elementary analysis on the secondary of leaching sintering mixture of aluminum[J]. Light Metals, 1999, 12: 18 - 21. (in Chinese)

[11] LIU Gui-hua, LI Xiao-bin, PENG Zhi-hong. Exploration of reaction mechanism of calcium silicate hydrate in basic solution [J]. Journal of the Chinese Ceramic Society, 2004, 32(6): 777 - 780. (in Chinese)

[12] GONG Jin-sheng, DENG Zhao-ying. A method to measure the dissociated CaO in the sinter quickly: glycol-ethanol means [J]. Cement, 1987(8): 31 - 32. (in Chinese)

[13] Richardson G, Brough R, Brydson R. Location of aluminum in substituted calcium silicate hydrate(C-S-H) gels as determined by ^{29}Si and ^{27}Al NMR and EELS [J]. J Am Ceram Soc, 1993, 76(9): 2285 - 2288.

[14] LI Yong-fang. Thermodynamics Database for Alumina Production [D]. Changsha: Central South University, 2001. (in Chinese)

[15] Yoshihiko O. ^{29}Si NMR spectroscopy of silicate anions in hydro-thermally formed C-S-H [J]. J Am Ceram Soc, 1994, 77(3): 765 - 768.

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