Study on hydrothermal synthesis dynamics of xonotlite spherical particles

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Abstract. The xonotlite crystals were synthesized via the hydrothermal synthesis manner from CaO and SiO₂ as the raw materials with their Si/Ca molar ratio of 1.0. The products were characterized by XRD and SEM techniques to investigate their crystalline phases and morphologies. Hydrothermal synthesis dynamics of xonotlite spherical particles was explored by masterly measuring the pH and the calcium concentrations of product slurries synthesized at various reaction temperature in this paper. The results indicated that the calculated values of the products’ quality at various reaction temperatures were consistent with the measured values. Based on chemical reaction kinetic, using fourth-order Runge-Kutta method, spline interpolation and least-squares fitting method, the dynamic relationship of xonotlite spherical particles synthesized via hydrothermal synthesis process is of \[-\frac{dc_A}{dt} = kc_{A}^{0.9}\].

1. Introduction
Xonotlite crystal belongs to monoclinic system (a=1.67nm, b=0.73nm, c=0.695nm), and it is a mineral of calcium silicate hydrate with the lowest crystalline water content, the best heat resistance and thermal stability (decomposition temperature of 1050-1100 °C) [1-2]. Xonotlite has been widely utilized in the fields of thermal insulation, architecture and so on, for its distinct physical and chemical properties, such as thermal stability, biological activity and environmental friendliness [3-4]. In general, the xonotlite products used in industry were fabricated using dynamic process from CaO and SiO₂ as the raw materials with their Si/Ca molar ratio of 1.0 [5-17]. The previous researches revealed that raw materials posed a great impact on the growth of xonotlite crystals [14-18]. Due to the dissolution characteristics of siliceous material, the xonotlite crystals from H₂SiO₃ and K₂SiO₃ as siliceous materials could grow to form the various morphologies of spherical particles and spherical particles respectively [19]. Actually, it was difficult to synthesize xonotlite crystals because of the harsh conditions such as the high reaction temperature and pressure [14-17]. It can be confirmed by many scholars’ research that the synthesis of xonotlite crystals was feasible based on the hydrothermal synthesis thermodynamics [21-22]. But since the invisibility of the reaction and the harsh conditions of xonotlites’ formation, the dynamics data of xonotlite crystals was hardly possible to obtain so that few people took the hydrothermal synthesis dynamics into account [23-24]. In recent years, our group has completed the researches on the morphology and growth mechanism of xonotlite crystals.
[4,6,7,13,19,20]. Moreover, by masterly measuring the electrical conductivities and the calcium concentrations of product slurries, our group achieved the dynamic test of xonotlite fibers and pointed out that the dynamic relationship of xonotlite fibers synthesized via hydrothermal synthesis process was of \(-dc_A/dt = kc_A^{4.5}\). Therefore, based on the existing researches, hydrothermal synthesis dynamics of xonotlite spherical particles was explored by masterly measuring the pH and the calcium concentrations of product slurries in this paper, aiming to further reveal the dynamic relationship of xonotlite spherical particles.

2. Experiment

2.1. Materials and methods

The xonotlite spherical particles were synthesized via the dynamic hydrothermal synthesis method. \(\text{H}_2\text{SiO}_3\) solution and \(\text{Ca(OH)}_2\) suspension were used as siliceous material and calcareous material respectively. \(\text{Ca(OH)}_2\) suspension was prepared by mixing \(\text{CaCl}_2\) with KOH 100 g·L\(^{-1}\) at the molar ratio of 1:2. The calcareous material, distilled water, and siliceous material were homogeneously mixed, and then the mixture was transferred into a reaction chamber with a stirrer at a heating rate of 1.5 °C·min\(^{-1}\) and a stirring rate of 200 rpm. The hydrothermal treatment proceeded under the following conditions: the Ca/Si molar ratio of 1.0, the reaction temperature of 190 °C, 210 °C and 230 °C respectively. After the hydrothermal treatment, the suspensions were filtrated and washed three times by distilled water. The resultant powders were dried at 75 °C for 12 h. Technological flow diagram of hydrothermally synthesizing xonotlite spherical particles was shown in figure 1.

![Technological flow diagram of hydrothermally synthesizing xonotlite spherical particles.](image)

In this paper, the accuracy of the dynamic equation of xonotlite spherical particles synthesized via the dynamic hydrothermal synthesis method was verified by two methods, one was comparing the production rate of the xonotlite products calculated by the dynamic equation with the experimental values, and the other was comparing the apparent activation energies calculated by the dynamic equation with that calculated by the Kondo model \((1-(1-\alpha)^{4/3})^4 = k(t-t_0)\).

2.2. The determination method of samples

The reaction equation for the formation of the xonotlite spherical particles could be simplified as equation (1).

\[
6\text{Ca(OH)}_2 + 6\text{H}_2\text{SiO}_3 + \text{H}_2\text{O} \rightarrow 6\text{CaO} \cdot 6\text{SiO}_3 \cdot \text{H}_2\text{O} + 12\text{H}_2\text{O}
\] (1)

The above equation (1) was only a simplified final reaction equation for the preparation of xonotlite spherical particles, but the whole reaction was actually made up of a series of complex chemical reaction steps. Due to the invisibility of the hydrothermal synthesis reaction, it was impossible to observe the reaction process directly. However, the above chemical reaction equation (1) was acid-base neutralization reaction, with increasing reaction time; the pH of the system would be
close to neutral. Therefore, the dynamic test of the hydrothermal synthesis process of the xonotlite spherical particles can be achieved by measuring the change of the pH during the reaction process.

The product slurries synthesized by hydrothermal synthesis process at various reaction temperatures and time were kept at 25 °C in thermostat water bath cauldron, and the pH of various slurries was measured using a PHS-3C precise pH meter. The EDTA titration method was used to determine the calcium concentrations of various product slurries formed by hydrothermal synthesis process under various reaction temperatures and time. The product slurries were accurately weighed by FA2004 electronic balance after drying. After the induction time (t₀), the qualities of the products obtained under various reaction times can be defined as m(Total)=m(HCl)+m(Ca(OH)₂)+m(C-S-H(1))+m(xonotlite).

The crystalline phase composition and microstructure characteristics of the samples were characterized by X-ray diffraction (XRD, Model D/max-2200, Japan). A scanning electron microscope (SEM, Model JSM-6490LV, operating at 25 KV, Japan) was used to observe the morphology of xonotlite crystals.

3. Results and discussion

Figure 2 shows the XRD patterns of the products synthesized hydrothermally at various temperatures. Clearly, the main crystalline phases prepared by hydrothermal synthesis method at 190 °C, 210 °C and 230 °C respectively were xonotlite (corresponding to Ca₆Si₆O₁₇(OH)₂, standard JCPDS card No. 23-0125). From the analysis result of XRD patterns, the existence of a series of strong diffraction peaks showed that the xonotlite crystals synthesized at various temperatures were well-crystallized and almost no impurity.

![X-ray diffraction patterns](image)

(a) 190°C; (b) 210°C; (c) 230°C

Figure 2. X-ray diffraction patterns of the products hydrothermally synthesized at various temperatures.

Figure 3 displays the SEM images of the products synthesized via the dynamic hydrothermal synthesis method at 190 °C, 210 °C and 230 °C respectively. The products obtained by hydrothermal synthesis were xonotlite spherical particles with diameters of 10-50 μm.

The pH and calcium concentrations of the system were respectively measured after various reaction time, shown in figure 4 and figure 5 respectively. It can be seen from figure 4, with prolonging reaction time, the pH of hydrothermally synthesized products at various temperatures decreased, and its descending trend can be divided into three stages. The descending trend of these three curves in the first stage was fastest, in the second stage was relatively slow, obviously, the slowest of the descending trend existed in the third stage. And in the third stage, the pH tended to a certain value. The descending trend of these three curves indicated that the reaction rate in the first stage was fastest, then it became slightly slow in the second stage, and the slowest reaction speed appeared in the third stage.
In the hydrothermal synthesis process of xonotlite spherical particles, the reaction process can be expressed by the following reaction steps:

$$\text{Ca(OH)}_2 + \text{H}_2\text{SiO}_3 + \text{H}_2\text{O} \rightarrow \text{C} - \text{S} - \text{H} \text{(gel)}$$  \hspace{1cm} (2)

$$\text{C} - \text{S} - \text{H} \text{(gel)} + \text{Ca(OH)}_2 + \text{H}_2\text{SiO}_3 + \text{H}_2\text{O} \rightarrow \text{C} - \text{S} - \text{H} \text{(II)}$$ \hspace{1cm} (3)

$$\text{C} - \text{S} - \text{H} \text{(II)} + \text{Ca(OH)}_2 + \text{H}_2\text{SiO}_3 + \text{H}_2\text{O} \rightarrow \text{C} - \text{S} - \text{H} \text{(I)(5CaO:6SiO}_2:5\text{H}_2\text{O)}$$  \hspace{1cm} (4)

$$\text{Ca(OH)}_2 + \text{C} - \text{S} - \text{H} \text{(I)(5CaO:6SiO}_2:5\text{H}_2\text{O)} \rightarrow 6\text{CaO:6SiO}_2:3\text{H}_2\text{O} + 5\text{H}_2\text{O}$$ \hspace{1cm} (5)

Equation (2) represented the formation of amorphous C-S-H gels in the initial stage of the reaction. With the progress of the reaction, as shown in equation (3), C-S-H gels were transformed into calcium-rich hydrated calcium silicate C-S-H (II). Then due to the silicon-rich state in the reaction system, as shown in equation (4), C-S-H (II) would be transformed into the silicon-rich C-S-H(I) which owned a structure that similar to the tobermorite (Ca$_{6}$SiO$_6$(OH)$_2$3H$_2$O). Finally, the silicon-rich C-S-H(I) directly transformed into the spherical xonotlite crystals, as shown in equation (5).
According to the reaction process of the xonotlite spherical particles and figure 4, it can be assumed that the above-mentioned chemical equation (2, 3 and 4) occurred in the first stage of figure 4 to form C-S-H. And there was no formation of the spherical xonotlite crystals in the first stage. Moreover, the reaction time of the first stage was assumed to be the induction time ($t_0$) required for the formation of spherical xonotlite crystals. Assuming that the chemical reaction of above equation (5) occurred in the second stage, at this moment, the nucleation and growth of xonotlite spherical particles took place on the surface of the C-S-H, and there was no C-S-H formation in this stage. As before, we also supposed that most of the xonotlite spherical particles had formed before the third stage. So in the third stage, the reaction rate decreased to the minimum, which led to the pH decreased slowly and tended to a certain value.

Based on the above assumptions and the data of calcium concentrations in figure 5, the qualities of the products under various reaction temperatures and time during the second stage can be calculated, as shown in tables 1, 2 and 3. According to the experimental method of 2.2, the quality-time values of the products at various reaction temperatures were measured, as shown in tables 4, 5 and 6. At the same reaction temperatures, the quality-time calculated values of the products were compared with the measured values, and the results were as shown in figure 6.

### Table 1. Calculated data of quality-time of products hydrothermally synthesized at 230 °C.

| $t$/[h] | m(HCl)/[g] | m(Ca(OH)$_2$)/[g] | m(C-S-H)/[g] | m(Xonotlite)/[g] | m(Total)/[g] |
|---------|-------------|---------------------|--------------|----------------|-------------|
| 1       | 7.4500      | 0.8806              | 6.0833       | 0.0000         | 14.4139     |
| 2       | 7.4500      | 0.5550              | 3.8343       | 2.1997         | 14.0391     |
| 4       | 7.4500      | 0.1654              | 1.1429       | 4.8321         | 13.5905     |
| 5       | 7.4500      | 0.0934              | 0.6452       | 5.3189         | 13.5075     |
| 7       | 7.4500      | 0.0454              | 0.3134       | 5.6435         | 13.4522     |
| 15      | 7.4500      | 0.0000              | 0.0000       | 5.9500         | 13.4000     |

### Table 2. Calculated data of quality-time of products hydrothermally synthesized at 210 °C.

| $t$/[h] | m(HCl)/[g] | m(Ca(OH)$_2$)/[g] | m(C-S-H)/[g] | m(Xonotlite)/[g] | m(Total)/[g] |
|---------|-------------|---------------------|--------------|----------------|-------------|
| 3       | 7.4500      | 0.8806              | 6.0833       | 0.0000         | 14.4139     |
| 4       | 7.4500      | 0.7896              | 5.4547       | 0.6148         | 14.3092     |
| 6       | 7.4500      | 0.4608              | 3.1836       | 2.8362         | 13.9306     |
| 8       | 7.4500      | 0.2583              | 1.7844       | 4.2047         | 13.6974     |
| 10      | 7.4500      | 0.1996              | 1.3789       | 4.6013         | 13.6298     |
| 14      | 7.4500      | 0.1350              | 0.9328       | 5.0377         | 13.5555     |
| 20      | 7.4500      | 0.0646              | 0.4461       | 5.5137         | 13.4744     |

### Table 3. Calculated data of quality-time of products hydrothermally synthesized at 190 °C.

| $t$/[h] | m(HCl)/[g] | m(Ca(OH)$_2$)/[g] | m(C-S-H)/[g] | m(Xonotlite)/[g] | m(Total)/[g] |
|---------|-------------|---------------------|--------------|----------------|-------------|
| 7       | 7.4500      | 0.8806              | 6.0833       | 0.0000         | 14.4139     |
| 8       | 7.4500      | 0.8003              | 5.5283       | 0.5429         | 14.3214     |
| 10      | 7.4500      | 0.6563              | 4.5958       | 1.4549         | 14.1660     |
| 12      | 7.4500      | 0.5785              | 3.9964       | 2.0412         | 14.0661     |
| 15      | 7.4500      | 0.4114              | 2.8418       | 3.1704         | 13.8737     |
| 20      | 7.4500      | 0.3182              | 2.1980       | 3.8002         | 13.7663     |
| 25      | 7.4500      | 0.2410              | 1.6651       | 4.3214         | 13.6775     |
| 27      | 7.4500      | 0.2185              | 1.5907       | 4.4734         | 13.6516     |
| 30      | 7.4500      | 0.1511              | 1.0435       | 4.9294         | 13.5739     |
Table 4. Experimental data of quality-time of products hydrothermally synthesized at 230°C.

| t/[h] | 0   | 1   | 2   | 4   | 5   | 7   | 15  |
|-------|-----|-----|-----|-----|-----|-----|-----|
| m(Total)/[g] | 15.05 | 14.42 | 14.05 | 13.58 | 13.50 | 13.45 | 13.41 |

Table 5. Experimental data of quality-time of products hydrothermally synthesized at 210°C.

| t/[h] | 0   | 1   | 2   | 3   | 4   | 6   | 8   | 10  | 14  | 20  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| m(Total)/[g] | 15.05 | 14.73 | 14.58 | 14.42 | 14.31 | 13.92 | 13.71 | 13.62 | 13.55 | 13.48 |

Table 6. Experimental data of quality-time of products hydrothermally synthesized at 190°C.

| t/[h] | 0   | 5   | 7   | 8   | 10  | 12  | 15  | 20  | 25  | 27  | 30  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| m(Total)/[g] | 15.05 | 14.69 | 14.42 | 14.32 | 14.17 | 14.05 | 13.88 | 13.76 | 13.68 | 13.65 | 13.57 |

(a) 230 °C  
(b) 210 °C  
(c) 190 °C

Figure 6. The experimental data comparison with calculated data of xonotlite spherical particles hydrothermally synthesized at various temperatures.
It can be seen from figure 6 that when the reaction temperature was 230, 210 and 190 °C respectively, the quality-time calculated values were consistent with the measured values after the reaction time of 1 h, 3 h and 7 h respectively. So the reaction time of 1 h, 3 h and 7 h can be defined as the induction time required for the formation of spherical xonotlite crystals at 230 °C, 210 °C and 190 °C respectively, as indicated by points A, B and C in figure 4. There was no formation of spherical xonotlite crystals before the induction time. At the same time, the above analysis also showed that the above hypotheses were confirmed, that was, the second stage, beginning with the induction time, was the stage of the formation of xonotlite spherical particles, and there was no C-S-H produced in this stage.

According to the above analytical results, the equation (5) can be simplified as the following chemical reaction:

$$ A + B \rightarrow C + 5D \quad (6) $$

In the equation:
- A — Ca(OH)$_2$
- B — C$-S-H$(1)(CaSiO$_4$(OH)•$4H_2O)$
- C — CaSiO$_4$(OH)$_2$
- D — $H_2O$

According to the equation (6), the rate equation usually has the following form:

$$ -\frac{dc_A}{dt} = k_A c_A^n c_B^m $$

Because $c_{A,0} = c_{B,0}$, that is, $c_A = c_B$. Thus, equation (7) can be simplified as:

$$ -\frac{dc_A}{dt} = k c_A^n $$

(8)

In the equation, $k = k_A$ was the total rate constant of the reaction, $n = n_A + n_B$ was the total order of reaction.

In this equation, the kinetic parameters were only $k$ and $n$, therefore, the rate equation can be established by determining the two parameters. Since there was only one constant in the equation, the form of the rate equation only depended on $n$, so the key to determine the rate equation was to determine the reaction order. In order to determine the reaction order, it was necessary to know the concentrations of the reactants ($C_A$) at different times ($t$) at a definite temperature, that was, to know the relationship of $C_A - t$ in this chemical reaction.

In this paper, the internal performance function provided in Matlab were used. Then the reaction order ($n$) and the rate constant ($k$) were determined and calculated respectively by dealing with the dynamic data ($C_A - t$) corresponding to the various temperatures in figure 5 using the differential method. The values of $n$ and $k$ were used as the iterative initial values in the process of solving the fourth-order Runge-Kutta method, and the detailed solving process was shown in figure 7.

![Flow chart for program of kinetic parameters](image_url)
It should be noted that a series of \( (c_{\Delta t} \cdot \Delta t) \) values obtained by the fourth-order Runge-Kutta method may not have a corresponding value \( (c_{\Delta t} \cdot \Delta t) \). Therefore, it was necessary to use spline interpolation to solve the values of \( c_{\Delta t} \). Firstly, the values of \( c_{\Delta t} \) were calculated by using Matlab which completed the loop iteration of the fourth-order Runge-Kutta method and the spline interpolation. Then according to \( \min F = \sum (\Delta t \cdot c_{\Delta t})^2 \), the optimum solution of \( k \) were obtained by the least-squares fitting method.

\[
\begin{align*}
y_{n+1} &= y_n + \frac{h}{6} [k_1 + (2 - 2^1)k_2 + (2 + 2^1)k_3 + k_4] \\
k_1 &= f(t, y_n) \\
k_2 &= f(t + \frac{1}{2}h, y_n + \frac{1}{2}hk_1) \\
k_3 &= f(t + \frac{1}{2}h, y_n + \frac{2^1 - 1}{2}hk_1 + (1 - \frac{2^1}{2})hk_2) \\
k_4 &= f(t + h, y_n + \frac{2^1}{2}hk_2 + (1 + \frac{2^1}{2})hk_3)
\end{align*}
\]

According to the above-mentioned method, the initial values of kinetic parameters \( n \) and \( k \) at hydrothermal synthesis temperature of 230 °C were 0.8765 and 0.2808 (mol·m\(^{-3}\))\(^{1/5}\)·s\(^{-1}\) respectively. Since the errors of experimental measurement and the errors of calculation, \( n=0.9 \) and \( k=0.2808 \) (mol·m\(^{-3}\))\(^{1/5}\)·s\(^{-1}\) were taken as the iterative initial values after rounded the reaction order. Then according to \( \min F = \sum (\Delta t \cdot c_{\Delta t})^2 \), the value of \( k \) that obtained by a least-squares fitting method was of 0.3147 (mol·m\(^{-3}\))\(^{1/5}\)·s\(^{-1}\). Similarly, when the hydrothermal synthesis temperature was 210 °C or 190 °C respectively, according to \( \min F = \sum (\Delta t \cdot c_{\Delta t})^2 \), the values of \( k \) were 0.1330 (mol·m\(^{-3}\))\(^{1/5}\)·s\(^{-1}\) and 0.0549 (mol·m\(^{-3}\))\(^{1/5}\)·s\(^{-1}\) respectively. When the hydrothermal synthesis temperature was of 230 °C, 210 °C and 190 °C respectively, the value of \( n \) was of 0.9, and the values of \( k \) were of 0.3147 (mol·m\(^{-3}\))\(^{1/5}\)·s\(^{-1}\), 0.1330 (mol·m\(^{-3}\))\(^{1/5}\)·s\(^{-1}\) and 0.0549 (mol·m\(^{-3}\))\(^{1/5}\)·s\(^{-1}\) respectively. The fitting results of the fourth-order Runge-Kutta method were shown in figure 8.

It can be seen from the figure 8 that the curves of reaction concentration-time fitted by fourth-order Runge-Kutta method at various temperatures were consistent with the experimental data. Obviously, the results showed that the values of \( n \) and \( k \) obtained by aforementioned computational method had a high accuracy. Therefore, the rate equation of xonotlite spherical particles hydrothermal reaction could be confirmed as \(-dc_A/dt = kc_A^{0.9}\).
4. Conclusions

(1) With $\text{H}_2\text{SiO}_3$ solution and $\text{Ca(OH)}_2$ suspension as siliceous material and calcareous material respectively, the dynamic test of the hydrothermal synthesis process of the xonotlite spherical particles can be achieved by measuring the change of the pH during the reaction process.

(2) By measuring the pH and the calcium concentrations of product slurries synthesized at various reaction temperatures, it can be assumed that the hydrothermal synthesis process of xonotlite spherical particles can be divided into three stages, that was, the stage forming amorphous C-S-H gels, the stage forming the most of spherical xonotlite crystals, the stage forming a little xonotlite spherical particles.

(3) According to the data of calcium concentrations, the calculated values of the products’ quality at various reaction temperatures were consistent with the measured values, showing that the hypotheses dividing the formation process of spherical xonotlite crystals into three stages were confirmed.

(4) Based on chemical reaction kinetic, using fourth-order Runge-Kutta method, spline interpolation and least-squares fitting method, the dynamic relationship of xonotlite spherical particles obtained by direct conversion of silica-rich C-S-H (I) is of $-dc_A / dt = k_{c_A}^{0.9}$.
Acknowledgments
We gratefully acknowledge the supports of this work by the National Natural Science Foundation of China (Grant No. 21666007), Science Technology Foundation of Guizhou (Grant No. 2014-2007) and Program for “Hundred” High-level Talents in Guizhou (Grant No. 2016-5655).

References
[1] Dachowskia R and Stępień A 2011 Procedia Engineering 21 1173-8
[2] Wei G S, Zhang X X and Yu F 2009 J. Therm. Sci 18 142-9
[3] Hsiang H, Wei S C and Wei C H 2016 Mater. Struct 49 905-15
[4] Liu F, Wang X D and Cao J X 2011 Adv. Mater. Res 382 384-8
[5] Zou J, Guo C, Jiang Y, Wei C and Li F 2016 Mater. Chem. Phys 172 121-8
[6] Liu F, Zhu B and Cao J X 2011 Adv. Mater. Res 148-149 1755-8
[7] Liu F, Wang X D and Cao J X 2013 Mater. Int. J. Miner. Metall. Mater 20 88-93
[8] Hartmann A, Schulenberg D and Buhl J C 2015 J. Mater. Sci. Chem. Eng 3 39-55
[9] Zou J J, Guo C B, Wei C D and Jiang Y S 2015 Res Chem Intermed 18 1-12
[10] Kurdowski W 2014 Cement and Concrete Chemistry (Dordrecht: Springer Netherlands) 205-77
[11] Shaw S, Clark S M and Henderson C M B 2000 Chem. Geol 167 129-40
[12] Milestone N B and Ahari G K 2007 Adv. Appl. Ceram 106 302-8
[13] Liu F, Chen S, Lin Q, Wang X D and Cao J X 2017 Optoelectron. Lett 13 81-3
[14] Spudulis E, Šavareika V and Špokauskas A 2013 Mater. Sci-medzg 19 190-6
[15] Guo X Y, Ma S H, Lü S Q, Zheng S L and Zou X 2015 Chin. J. Nonferrous. Metals 25 534-44
[16] Black L, Garbev K and Stumm A 2009 Adv. Appl. Ceram 108 137-44
[17] Liang H X and Li M Q 2002 J. Chin. Ceram. Soc 30 294-9
[18] Baltakys K and Prichockiene E 2010 Mater. Sci-Poland 28 295-304
[19] Liu F, Wang X D and Cao J X 2011 Adv. Mater. Res 382 379-83
[20] Liu F, Zeng L K, Cao J X and Li J 2010 J. Wuhan. Univ. Technol 25 295-7
[21] Clodic L and Meike A 1997 Thermodynamics of calcium silicate hydrates (California: Lawrence Livermore National Laboratory) 1-27
[22] Newman E S 1956 J. Res.Nat. Bur. Stand 57 27-30
[23] Li M Q and Liang H X 2004 China Part 2 124-7
[24] Moorehead D R and Mccartney E R 1965 J. Am. Ceram. Soc 48 565-9